Second International Symposium

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

Symposium Proceedings

SECOND INTERNATIONAL SYMPOSIUM

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

CO-SPONSORS

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Symposium Chairman - Llewellyn Williams, EPA/EMSL-Las Vegas, NV
Vice-Chairman - Eric Koglin, EPA/EMSL-Las Vegas, NV
Executive Secretary - John Koutsandreas, Florida State University

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coordinating this symposium:
Program Manager – Ms. Jo Ann Duchene
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Ms. Donna Studniarz
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FOREWORD

The role of and need for field screening methods for the identification and quantification of contaminants in environmental media is growing rapidly. This nation and its European neighbors are faced with the tremendous task of remediating thousands of hazardous waste sites -- the legacy of our much less environmentally aware predecessors. Field screening methods that generate real-time information on the nature and extent of contamination improve the cost-effectiveness of remediation. Many of these same methods can, and in some cases are already being used to improve our capability to measure exposure, at the point of exposure, thereby improving our ability to assess risks to human health and the environment.

The U.S. EPA is not the only viable user of field screening methods; that fact is reflected in the list of this Symposium's co-sponsors. Other agencies are discovering applications for these same technologies to address issues such as worker safety, drug interdiction, and chemical warfare defense. The research activities supported by these same agencies are advancing innovative technologies that may have application in environmental monitoring and field screening.

To present a global view of technological developments, this Symposium featured over 120 platform and poster presentations from the United States and around the world. The papers and discussions that follow represent three days of intense communication and cooperation among a variety of communities — regulatory, academic, industrial and users. It is my hope that the products of this Symposium will find many uses and will provide the impetus for new initiatives in field screening methods.

Llewellyn R. Williams
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada

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OPENING REMARKS

Welcome to the Second International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals.

Twenty-eight months ago, the first of these symposia was held here in Las Vegas, here at the Sahara, and the response to that Symposium clearly indicated that the time was right. There was really a need for a forum to exchange information about the emerging technologies that can be and have been applied to environmental monitoring in the field.

As you can see from the list of the Symposium sponsors, EPA is certainly not alone in its appreciation for these technologies and their potential for the future. I believe that we have assembled a powerful program for you this next two and a half days.

The team responsible for this program was made up of, Mr. John Koutsandreas, the Executive Secretary from Florida State University, Mr. Eric Koglin, the Matrix Manager here at EPA-Las Vegas for the Advanced Field Monitoring Methods Program and the coordinators at Life Systems, Inc. But for all of the efforts of the Symposium team, it's really the interest, the enthusiasm, and the participation, over the next couple of days, of all the attendees, that will really set this Symposium apart.

We are already planning for the Third International Symposium. We try to stagger them in such a way that enough time elapses -- that the papers aren't the same and the technologies have had an opportunity to advance. We're looking at just about two years from now.

We are very interested in getting your feedback on what you like and what you don't like about the way the Symposium goes this year, and any recommendations you can make to help us strengthen the next Symposium will be greatly appreciated.

This year, we have added a Scientific Awards Committee. Some of you have had an opportunity to see the certificates and a couple of dramatic eagle trophies as you came in.

We're privileged to have a number of leaders in the area of environmental measurement here at this Symposium. We'll share their views and the views of their organizations about current and future applications of field screening and field analytical technologies.

Someone once said, Llew, why don't you write a poem? It was a long time ago, but it was never quite forgotten, so if you'll bear with me:

The Second International has finally arrived.
Your program will suggest to you just how hard we have strived.
To bring to you the latest scoops and field technology
That's based on engineering, chemistry, biology.
Besides the platform papers that I know you'll want to hear.
The poster session entrees will just knock you on your ear.
And for the technophilic crowd, exhibitors galore
Will tell you all about their products, and a wee bit more.
We'll try to slake your appetite for the newest and the best.
And give you opportunities to mingle with the rest,
To share and learn, to see and show our efforts, may they yield
Accelerated products we can take into the field.
The future of our measurements, if any bets I'd hedge.
Resides in these technologies, we're on the leading edge.
So welcome to this overview of all those things to come.
And welcome to Las Vegas, where the Rebs are number one.

Llewellyn R. Williams
Symposium Chairperson

KEYNOTE ADDRESS
ANALYTICAL ISSUES IN THE U.S. EPA SUPERFUND PROGRAM

Larry Reed, U.S. Environmental Protection Agency, Director Hazardous Site Evaluation Division, Office of Emergency and Remedial Response

I am glad to be invited to this Field Screening Symposium because our Superfund office in EPA is such a primary user and booster of the technology. We want to get more and more use out of the technology and the field analytic methods. It's always good to be here and participate. We've been very strong participants and boosters of the EMSL-Las Vegas operation in field methods, and we'll continue to do so for years to come.

I wanted to begin by setting the backdrop of where we are in the Hazardous Waste Superfund Program, and then discuss the vital role that field methods plays in that program.

We now have a Superfund Program that encompasses a full pipeline: from discovery of sites (1,500) to two thousand new potential sites identified to us each year, to the listing of approximately about one hundred sites a year on the National Priorities List, through the remedial action and remedial design process. The whole pipeline is in complete use, and now more than ever, we're putting higher and higher emphasis on focusing on the worst sites first throughout the program. This obviously puts a premium on having the best and the quickest environmental data available to evaluate and clean up sites in the program.

The second aspect of where we are now in the Superfund Program that bears on this Symposium, is we have just, (in December) promulgated revisions to the Hazard Ranking System (HRS) which will become effective March 12, 1991. This will expand the types of sites that we will be looking at and screening. We have added new concerns, a greater emphasis on ecological concerns, incorporated direct exposure to soils and more emphasis on sediments. We are very proud of this rule, and we will be gathering a lot more information for screening sites for future National Priorities List updates.

Also, we have finalized the last of our proposed sites. In the Federal Register, we proposed ten sites under the old HRS. All sites have therefore been finalized. Eleven hundred and eighty-nine (1,189) final sites are now on the National Priorities List. We will be hitting the ground running, listing new sites as quickly as possible under the new Hazard Ranking System, for the rest of the Superfund Program.

The focus of our Superfund Program has been on enforcement first, integrating the use of the fund with the use of our enforcement authorities. This is focusing more and more on a consistent use of analytic methods, including both field methods and fixed lab methods, across the program, on appropriate QA procedures across all the different types of sites, regardless of whether they are enforcement lead, state lead or fund lead.

The final background point as far as field methods is concerned is our adoption and phased incorporation of the principles of Total Quality Management (TQM) into the Superfund Program. We began with pilot projects last year, designed to embrace the principles of TQM. The basic concepts of this program include:

- continual improvement in the process
- identifying our clients (ensuring that you know who they are, and since there are various levels of clients and different relationships with those clients)
- working with our clients
- identifying and addressing the worst problems first
- gathering data for informed decision making

These are the kinds of principles we're trying to address in all the aspects of our program. So more and more, we'll be working with you, and participating in this kind of audience where, at various times, either you're our clients or we're your clients. This type of gathering enforces that interaction among the various communities that deal with field screening.

I now want to discuss some specific points on field analysis.

Howard Fribush of my staff went out and visited all 10 of our regional offices to determine what is the state of the use of field screening in our very decentralized program. We found field screening has a lot of purposes including determining worker safety requirements, particularly for our removal program and for the site assessment program, which lists sites.

Field screening obviously provides immediate feedback to the site assessors, to the samplers and to our clean-up contractors. That, again, is a strong benefit that we see in encouraging the use of field methods to continually improve and streamline our Superfund process.

An important application of field screening methods is how they can be used to shorten the time that it takes to evaluate the risk posed at a site. This can also be used to generate data to determine the appropriate technologies to be used for clean-up and what levels of clean-up are appropriate. These applications are evident looking at Regional history — field screening technologies have been used in the Superfund Program, basically from its inception. We have seen advances in field instruments, and this is making on-site analysis at Superfund sites much more desirable.

As part of Howard's Regional visits, the different aspects of our Superfund program, were polled. The arms of the Program can be divided into three functional aspects 1) the Site Assessment Program, the front end of the Program that generates data needed to evaluate the site and whether it needs to be included on the National Priorities List, 2) the Remedial Program, where once a site is on National Priorities List the actual clean-up process is initiated, and 3) the Removal Program, which can be called out at any time to clean up immediate health threats at sites. We found a split among those different parts of the program. About ten percent of the data being gathered for the Site Assessment Program was from field screening. Similarly for the Remedial Program, about ten percent of the data gathered was with field screening methods, field analytic methods. The biggest user proportionally was our Removal Program, slightly over a third of the data gathered from the Removal Program is related to field screening methods. What we'd like to do is, working through symposia such as this, try to encourage and increase that use to even higher levels as appropriate.

The role that we play in the Office of Emergency and Remedial Response, and my division, the Hazardous Site Evaluation Division, is basically providing guidance for this on-site analysis. As I mentioned before, when you're dealing with a decentralized program, you always have to encourage consistency of methods among sites, but you also have to deal with the uniqueness of each site. We are bridging the gap by coming up with guidance to provide the Regional offices on the use of methods.

As follow-up to the Regional review we are evaluating the advantages of field analysis in the Superfund Program and building on that to expand its uses as appropriate in the future. Our future guidance documents will address evaluating when to use it and then how to use it. We are also trying to get consistent terminology in our guidance. Screening technology, portable methods, fieldable methods, mobile methods, all of these terms have been used. We've been trying in our field methods catalog to come up with some consistency so even those unfamiliar with these various technologies, can become familiar with the basic terminology.

Several major efforts are underway in the Superfund Program. Within the last year we established our first field methods management forum. The focus of that field methods management forum was to get managers involved, not just those that have to go out in the field and implement the technology, but the managers who would be the ones to determine what proportion of overall analytic support is necessary for field methods versus fixed labs. The first meeting of this group was in June, 1990. We had seven regions, headquarter offices, and the EMSL-Las Vegas group at this session. The objective of this effort was to get management involved and to focus on the blockages preventing us from getting field methods used to a greater extent. Future topics for meetings include: 1) regional administration of field screening (where does it go, who is in charge;) 2) collecting the method and instrument performance information, and 3) trying to get this data out to the field in the best usable form to those familiar with the technologies, their usage, their limitations and their strengths.

There's another effort underway — the Field Methods Work Group. This group contains the worker bees, the people that have to go out and get the job done. This group has been meeting since 1987. Their initial focus was looking at things at the very basic level of data quality objectives — how to define them in order to get them in a more useful format understood by both the chemists and the field engineers. In July, 1990, they met and focused on the catalog of field methods and the need for a new version. The Field Methods Screening Catalog User's Guide came out three or four years ago, and we realized the limitations of it. At the time we wanted to get information on some 30 different screening methods. Obviously the next stage is updating this, adding more methods and more data that will be useful to our field offices. We expect to release this update of the Field Methods Catalog some time this year. It will triple the number of methods that are contained in the original catalog to about 100.

We are obviously going to be looking at both QA and QC of field methods. The basic question is the need for Regional consistency. What is appropriate QA for a field lab? How can we get that guidance out? What are the appropriate QC requirements for field methods? We need to get that information out to the field again, by bringing in the user community.

Another issue obviously encouraging consistency and appropriate use of the technology is training. We have been working to come up with a training program on field methods with the regions and EMSL-Las Vegas. We've even gotten one of our regional offices to hopefully loan some of their field equipment in a true bureaucratic gesture to EMSL-Las Vegas to use as a basis for training programs. We hope to have this training program developed this year. Obviously the level we'll have to look at then is how much and what level of training do we need to provide out there? How much training should be done for the people using the field methods? At what levels should it be presented, and how much should be mandatory to ensure and promote consistency?

There are several basic field method issues that I haven't mentioned, but that I'd like to touch on before closing: how do we capture performance information on methods and the instruments? The state-of-the-art is obviously rapidly changing. How do we capture that information given, among other things, federal regulations about how much we can provide in working with industry. How do we capture that performance data and get it to the field for use in the most useable form? We have 100 methods that we have looked at for the upcoming catalog update. What type of data do the people want, and what type of format? How much? Do they want extensive data, shortened data or very abstract data. What type of data will encourage the use in the field?

The final point, and one that I know this Symposium will be working on, is introducing improved methods, particularly to the Superfund Program. How do we get the new methods out? What are the incentive systems? How do we call out and identify the best methods so that they are being selected for use in the field?

In closing, there are a lot of efforts we have underway to encourage a maximal, appropriate use of field screening methods. This symposium is a key one. I mentioned the Field Methods Management Forum and the Field Methods Work Group, two continuing efforts to provide direction and recommendations for additional guidance for consistency and use of technology in the field. Field screening methods is a big field. It is a continuing, emerging field that will continue to command national attention. We in the Superfund Program are great boosters and great users of it. I speak as both a provider, working with EMSL-Las Vegas and their services, and a user, working on risk assessments and the site assessment program. I encourage you in your pursuits to increase the use of field screening methods.

OVERVIEW OF DOE'S FIELD SCREENING TECHNOLOGY DEVELOPMENT ACTIVITIES

by

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ABSTRACT

The Department of Energy (DOE) has recently created the Office of Environmental Restoration and Waste Management, into which it consolidated those activities. Within this new organization, the Office of Technology Development (OTD) is responsible for research, development, demonstration, testing, and evaluation (RDDT&E) activities aimed at meeting DOE cleanup goals, while minimizing cost and risk. Site characterization using traditional drilling, sampling, and analytical methods comprises a significant part of the environmental restoration efforts in terms of both cost and time to accomplish. It can also be invasive and create additional pathways for spread of contaminants. Consequently, DOE is focusing on site characterization as one of the areas in which significant technological advances are possible which will decrease cost, reduce risk, and shorten schedules for achieving restoration goals. DOE is investing considerably in R&D and demonstration activities which will improve the abilities to screen chemical, radiological, and physical parameters in the field. This paper presents an overview of the program objectives and status and reviews some of the projects which are currently underway in the area.

INTRODUCTION

The Department of Energy (DOE) has recently consolidated its environmental restoration and waste management activities into the Office of Environmental Restoration and Waste Management, formed by Secretary James Watkins in early 1989. Within that

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new organization, the Office of Technology Development (OTD) oversees DOE's Technology Development Program, whose objective is to establish and maintain a national program for applied research, development, demonstration, testing, and evaluation (RDDT&E). These activities will pursue technologies that will enable DOE to meet its 30-year compliance and cleanup goals safely, efficiently, and effectively.[1]

The first step in environmental restoration is site and contaminant characterization. Characterization of the current distribution of contaminants and the geohydrological factors that promote and control their spread will provide the starting point for determining what must be remediated and for selecting and designing remediation methods.

STATUS OF OTD ACTIVITIES

A cross section of the technology development activities which have been or are being conducted are described below. Space limitations preclude describing all activities in this area. Some of these activities will be described in more detail by the principal investigators at this conference.

DUVAS Fiberscope for in Situ Groundwater Monitoring. Because of its proven ability to detect compounds such as benzene and its derivatives, which are common solvents and components of fuels, derivative ultraviolet absorption spectrometry (DUVAS) is being developed as a rapid and reliable method for in situ detection of aromatic pollutants. To date, a prototype DUVAS fiberscope has been constructed and tested for measuring spatial and temporal distribution of organics in groundwater. An important component of the fiberscope is a rugged, down-well probe with a unique "detector-in-head" design that increases the maximum depth of subsurface detection. Results comparable to those obtained with a conventional laboratory spectrometer have been achieved with optical fiber lengths up to 50 meters. The portable DUVAS fiberscope will provide faster, more reliable, and less expensive measurement of subsurface groundwater contamination. For further information, contact the Principal Investigators, J.W. Haas III and R.B. Gammage, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6113. Phone: (615) 574-5042 (Haas), (615) 574-6256 (Gammage).

Advances in Surface-Enhanced Raman Spectroscopy for Applications in Real-Time Subsurface Monitoring. Because of its excellent selectivity, surface-enhanced Raman scattering (SERS) has attracted considerable attention as a potentially powerful analytical tool for detecting and screening trace-level contaminants in groundwater. The narrow Raman bands hold promise for simplifying the identification of individual components in complex mixtures. An inexpensive computer-controlled portable spectrometer system coupled to a fiber-optic probe is being developed for rapid on-site and in situ determination of organic groundwater contamination. Critical issues pertaining to durability, repeatability, sensitivity, selectivity, and universality are being examined, while means for improvement in these areas are being tested. The feasibility of utilizing SERS under harsh conditions has been demonstrated. Substrates have been tailored for maximum efficiency at particular excitation wavelengths as a means for increasing the sensitivity of the technique. Ongoing efforts have refined the state-of-the-art Raman optrode design and have shown the feasibility of producing a simple, inexpensive instrument for field applications. As the technique approaches maturity, SERS will provide powerful screening capabilities for numerous organic and inorganic materials. It promises rapid, reproducible, quantitative detection of trace-level contaminants in aqueous solutions. For further information, contact the Principal Investigator, Eric A. Wachter, Oak Ridge National Laboratory, Health and Safety Research Division, P.O. Box 2008, Oak Ridge, TN 37831. Phone: (615) 574-6248 (FTS 624-6248).

Fiber Optic Raman Spectrograph for in Situ Environmental Monitoring. A small (suitcase-sized) surface-enhanced Raman spectrometer (SERS) is being developed to use in field screening for a wide variety of

organic and metallic pollutants in ground and surface waters. The focus of this contract is twofold: (1) to demonstrate a small spectrograph with high resolution ($<1cm^{-1}$) and wide spectral range ($>3500\ cm^{-1}$) and (2) to demonstrate a micro-optical SERS probe head with substrates engineered to detect certain critical pollutants at ppm to ppb levels. The spectrograph will have no moving parts and will employ fiber-optic sampling, an ultracompact solid-state diode laser for Raman excitation, a high-order diffraction grating, holographic optical filters, and a state-of-the-art charge-coupled device (CCD) detector. The probe head will be contained at the sampling end of a fiber-optic probe over 50 meters long inserted into a well less than 5 centimeters in diameter. The system will identify trace contaminants in groundwater in real time.

This technique will increase the efficiency of environmental characterization and mapping, reduce costs of field sampling and ex situ laboratory analysis, reduce personnel exposure, and provide site characterization information. For further information, contact the Principal Investigator, Michael Carraba, EIC Laboratories, Inc., 111 Downey St., Norwood, MA 02062, Phone: (617) 769-9540.

In Situ Detection of Organics. The long-term objective of this research is to develop a fiber-optic-based system for monitoring contaminant species in groundwater and to demonstrate it on contaminated groundwater at Lawrence Livermore National Laboratory (LLNL). These efforts require the development of optical indicator reagents that are compatible with fiber-optic chemical sensors (optrodes). Development of optrodes for ppb-level detection of trichlorethylene (TCE) and chloroform ($CHCl_3$) is complete and has moved into the demonstration phase. Carbon tetrachloride (CCl_4) and perchloroethylene (PCE) optrodes are currently being developed.

The fiber-optic approach has the potential of providing less expensive measurements of groundwater contaminants. Also, the reagent indicators and the chemistry developed in the process of developing the optrodes will "spin off" into other applications. For example, one chemistry that was developed serves as the basis for a proposed TCE remediation technique, the "TCE sponge". Finally, it should be pointed out that these simple indicators are new and could be used in other types of contaminant assays. For further information, contact the Principal Investigator, Mike Angel, Lawrence Livermore National Laboratory, Environmental Sciences Division, P.O. Box 808, L-524, Livermore, CA 94550. Phone: (415) 423-0375 (FTS 543-0375).

Optical Fiber Photothermal Spectroscopies for in Situ Monitoring and Characterization. Optical fiber sensors using thermal lens and photoacoustic spectroscopies for remote, on-site, real-time optical absorption measurements of chemical species in groundwater environments are being developed. Optical fiber sensors based on photothermal spectroscopies are ideal for ultrasensitive optical absorption measurements of actinides and other chemical species in aqueous environments. An optical absorption spectrum provides qualitative and quantitative analysis of the species present in the aqueous environment. The spectra can also provide complexation information for actinides, which is important for migration behavior. These photothermal sensors rely on tunable wavelength for selectivity and therefore do not require immobilized agents at the distal fiber end (in the sample area).

Research has demonstrated two optical fiber photothermal sensors with excellent sensitivity for rare earth and actinide ions in aqueous solutions. A remote photoacoustic sensor was demonstrated using a 100-meter fiber to deliver the tunable laser beam to a glove box located in a separate room from the laser. Acoustic signals were returned to the instrument lab via coaxial cables. An all-fiber thermal lens sensor was demonstrated using a fiber to deliver the laser light to a remote sample solution and a second fiber, with a photodiode attached to the distal end, to measure optical absorption; electrical cables were not required at the sample area. For further information, contact the Principal Investigators, Richard Russo, Lawrence

Berkeley Laboratory, Applied Science Division, M.S.90-2024, Berkeley, CA 94720, Phone: (415) 486-4258 (FTS 452-4258); and Robert Silva, Lawrence Livermore National Laboratory, Nuclear Chemistry Division, L-396, Livermore, CA 94550. Phone: (415) 423-9798 (FTS 543-9798).

Field Measurement of Groundwater Contamination by Ion Trap Mass Spectrometry. A transportable ion trap mass spectrometer for the in situ characterization of soil, air, or water at chemical waste sites is being developed and demonstrated. The instrument will have a turnkey operating system for use by minimally trained personnel. The approach uses modular design to produce an instrument that can be readily modified and repaired in the field. Specifically, this project will develop a daughter microprocessor system to control ancillary hardware for sampling and separation and will develop new software, write macros, and modify existing software for semi-automated computer control of the instrument.

The instrument consists of specialized sampling modules for air, soil, or water samples; a separations module containing sorbent traps and a megabore capillary chromatography column; and a detection module, the Finnigan Ion Trap Detector. Soil or water samples are purged with helium and the evolved organics are collected on sorbent traps. A sampling pump is incorporated for air samples. The full analysis sequence required 10 minutes. The Finnigan software was modified through the addition of macros and Forth routines. The analytical procedure can be selected from a menu from the instrument's data system. Sampling, calibration, analysis, and data reduction proceed under computer control.

The detection limit for TCE in water is approximately 20 picograms. Mass spectral identification of 50 picograms of TCE is possible by library comparison of spectra. A linear calibration curve can be obtained from 10 ppt to 10 ppm organics in water.

Although transportable mass spectrometers are commercially available for environmental analyses in the field, the transportable ion trap technology described here provides several additional benefits, including low cost. The instrument can be assembled for a parts cost of about $75K. For further information, contact the Principal Investigator, Philip H. Hemberger, Los Alamos National Laboratory, Analytical Chemistry Group, Mail Stop G740, Los Alamos, NM 87545. Phone: (505) 667-7736 (FTS 843-7236).

Direct Sampling Mass Spectrometry. Rapid analytical technology based upon direct sampling mass spectrometry is being developed to determine trace organic pollutants in the environment. This project is jointly sponsored by DOE, the Department of the Army, and EPA. Closely related work is sponsored by the National Cancer Institute (NCI) for analyses of physiological fluids. Oak Ridge National Laboratory (ORNL) has developed sampling, sample interface, and ionization chemistry techniques that are first being combined with commercial mass spectrometers to provide rapid laboratory-based methods. Knowledge gained is used to develop instrumentation optimized for on-site analysis. Field-sampling and field-sample-processing methods are being developed to support the mass spectrometric technologies. The general approach involves a systematic comparison of the developed methods using accepted EPA methods to analyze organics in water, soil, air, and waste. Ion trap mass spectrometry (ITMS) and glow discharge ionization quadrupole mass spectrometry (GDMS) are being investigated. Both GDMS and ITMS are applicable to the quantitative determination of ppb concentrations of organics in water and in soil with analysis times of five minutes or less. This is achieved by purging the water or soil-water slurry with air or helium and routing the purge stream directly into the mass spectrometer. Less volatile organics may be similarly determined by collection on a suitable solid sorbent followed by thermal desorption. The method has thus far been demonstrated for the quantitative determination of benzene, trichloroethylene, and tetrachloroethylene. Applicability to semivolatiles has been demonstrated by

the successful determination of nicotine and cotinine in urine for the NCI and for the determination of military chemical agents in air for the Army. A method is under development for the simultaneous collection of samples for subsequent confirmatory analysis in those cases where interferences cannot be distinguished by mass spectrometry or by mass spectrometry/mass spectrometry alone.

Successful development and validation can reduce costs and increase sample throughput by up to 90% as compared to current regulatory analytical methods. Field-versions of the technology will allow real-time monitoring of remedial action progress, monitoring of associated occupational exposure, and screening of samples prior to shipment to the laboratory for regulatory analyses. For further information, contact the Principal Investigators, M.B. Wise, M.R. Guerin, and M.V. Buchanan, Oak Ridge National Laboratory, P.O. Box 2008, Bldg. 4500-S, MS-6120, Oak Ridge, TN 37831-6120. Phone (615) 574-4862 (FTS 624-4862) (Mike Guerin).

Assessment of Subsurface Volatile Organic Compounds (VOCs) Using Chemical Microsensor Arrays. A new monitoring instrument that utilizes an array of coated surface-acoustic-wave (SAW) microsensors is being developed. Pattern recognition analysis of the multidimensional sensor output permits determination of the identity and quantity of target vapors from difference chemical classes typically found in contaminated soils and groundwater. The small size, low cost, low power requirements, high sensitivity, and large dynamic range of the instrument will facilitate its use in a variety of applications related to site assessment and process and control.

The project addresses some fundamental questions: (1) what is the performance of the SAW microsensor array instrument in applications relevant to site assessment and restoration, namely, monitoring volatile organic chemicals (VOCs) in high humidity environments, (2) how are the measurements provided by this instrument related to soil contaminant levels, and (3) how can they best be utilized in site assessment and restoration activities? A series of controlled laboratory experiments will be performed to address these questions.

The results of this research will demonstrate that microsensor array instruments can provide rapid and reliable compound-specific concentrations of volatile organics in soil vapor. The low projected cost of manufacture (less than $1000 in production quantities), the capabilities of continuous, unattended operation, and the ability to transmit data from remote locations make the SAW sensor-based monitors a cost-effective and desirable monitoring approach. For further information, contact the Principal Investigator, Stuart Batterman, University of Michigan, Department of Environment & Industrial Health, 2505 School of Public Health, Ann Arbor, MI 48109-2029. Phone: (313) 763-2417.

Thin-Layer Detectors: NO_2 Detection with Polystyrene Thin Layers. A solid-state sensor that can be used to detect NO_2 without interference by other species is being developed. The device incorporates an interdigitated electrode with a polystyrene thin layer and operates by simply monitoring the change in conductance of this thin film as a function of NO_2 exposure. Although the film is an insulator in the absence of NO_2 , showing conductance of less than 10^{-12} S, upon exposure to NO_2 gas, an increase in conductivity of this highly insulating material occurs over several orders of magnitude to 10^{-8}-10^{-9} S. No interference from ambient gases or water vapor has been observed, and the effect is very specific to NO_2. Upon elimination of the NO_2 gas, the device becomes completely insulating again, all effects occurring at ambient temperature and pressure.

The mechanism of the conduction within the film remains unclear, although the level of conductivity is related to the amount of residual benzene solvent within the film. Thus, as the benzene evaporates from the film, the change in conductivity of the film upon NO_2 exposure diminishes dramatically. This effect appears to be related to a stabilization of NO_2 dimer by benzene within the film. The increased conductivity of the film

in the presence of benzene is attributed to the well-known self-ionization of N_2O_4 to $NO^+ + NO_3^-$. For further information contact the Principal Investigator Stephen F. Agnew, Los Alamos National Laboratory, Los Alamos, NM 87545. Phone: (505) 665-1764 (FTS 843-1764).

Antibody-Based Fiberoptics Sensors For in Situ Monitoring. Sensitive and selective chemical sensors for in situ monitoring of hazardous compounds in complex samples are being developed. Special focus is on a unique fluoroimmuno-sensor (FIS) which derives its analytical selectivity through the specificity of antibody-antigen reactions. Antibodies are immobilized at the terminus of a fiberoptic within the FIS for use in in situ fluorescence assays under field conditions. High sensitivity is provided by laser excitation and optical detection techniques. The technique can detect femtomoles (10^{-15}M) of the carcinogen benzo(a)pyrene and other chemicals of environmental interest. For further information, contact the Principal Investigators, T. Vo-Dinh and G.D. Griffin, Oak Ridge National Laboratory, P.O. Box 1008, MS-6101, Oak Ridge, TN 37831-6101. Phone: (615) 574-6249 (Vo-Dinh) and (615) 576-2713 (Griffin).

Underground Imaging for Site Characterization and Clean Up Monitoring. State-of-the-art image reconstruction techniques (tomography) can be used to characterize the geology and hydrology of hazardous waste sites. These methods extend spatial information of geologic structure and hydrology between boreholes. Both two- and three-dimensional imaging can be done using these techniques. High-frequency electromagnetic (HFEM) tomography is a proven technology for imaging water content with high spatial resolution, (i.e., submeter scale for small geologic scale applications (ten meters). Electrical resistance tomography (ERT) is a newer technology which has been used in the field with moderate-scale resolution on larger scale images (meters on tens to hundreds of meters).

Characterization of the subsurface geology and hydrology is needed to select the most appropriate remediation alternative and to demonstrate regulatory compliance. Design of remedial actions must be based upon knowledge of the often anisotropic and heterogenous nature of the subsurface environment and the natural processes that act upon the waste, as well as upon protective barriers. Groundwater flow strongly influences contaminant mobilization and transport and geologic structure affects the flow of groundwater. Current subsurface characterization techniques for addressing these above problems depend heavily upon drilled boreholes. Drilling is expensive and time consuming and also creates conduits for contaminant spread. A special need exists for three-dimensional noninvasive subsurface characterization technologies. For more information, contact the Principal Investigator, William Daily, Lawrence Livermore National Laboratory, P.O. Box 808, L-156, Livermore, CA 94550. Phone: (415) 422-8623 (FTS 532-8623).

Development of the SEAMIST Concept for Site Characterization and Monitoring. This project is developing the Science and Engineering Associates' Membrane Instrumentation and Sampling Technique (SEAMIST). The technique permits rapid emplacement of instrumentation and sampling apparatus in a punched or drilled hole. The objective of the technique is to pneumatically emplace an impermeable membrane liner carrying many instruments into a hole to provide simultaneous access to the entire hole wall (e.g., many measurement horizons per hole), elimination of circulation of fluids within the hole, and isolation of instruments at discrete locations between the hole wall and the membrane. The membrane is emplaced by eversion--it is rolled inside out and then everted using air pressure. This causes minimal disturbance to the hole because the assembly does not slide down as with traditional rigid casings. Instruments such as fiber-optic sensors, thermocouple psychrometers, gas- and liquid-sampling systems, and other small instruments are easily attached to the membrane and carried into the hole with it.

Using this technique will save 50%-90% of the field costs, as compared to current monitoring well practices.

In addition, the technique is applicable to both vertical and horizontal wells. For further information, contact the Principal Investigator, Carl Keller, Science and Engineering Associates, 612 Old Santa Fe Trail, Sante Fe, NM 87501. Phone: (505) 646-5188.

Site Characterization and Analysis Penetrometer System (SCAPS). DOE is working with the Department of Defense on the further development and demonstration of the SCAPS for use on DOE facilities. The SCAPS, as developed by the Army Corps of Engineers Waterways Experiment Station for the Army Toxic and Hazardous Materials Agency, includes surface geophysical equipment, survey and mapping equipment, sensors for contaminant detection, and soil sampling equipment. Computer systems have been integrated with the SCAPS in order to provide data acquisition, data processing, and 3-D visualization of site conditions. The system is mounted on a uniquely-engineered truck that provides protective work spaces to minimize worker exposure to toxic chemicals. The truck also provides equipment to seal each penetrometer hole with grout.

Real-time sensors that are currently available for characterization work include those which can determine the strength, electrical resistivity, and spectral properties of soils. Two sensors successfully demonstrated to detect contaminant plumes at DOD facilities are the soil resistivity unit and a fiber optic contaminant sensor. The primary advantage of the fiber-optic sensor over resistivity measurements is based on laser-induced fluorescence, which presents a problem for contaminants such as TCE that do not fluoresce; however, colorimetry and absorption techniques such as the sensors which are being developed by Lawrence Livermore National Laboratory and by Fiberchem are tentatively planned to be demonstrated in conjunction with the penetrometer at the Savannah River integrated demonstration in FY-91. Additionally, samplers such as the "Terra Trog" developed by the Army Corps of Engineers may be tested in FY-91 at the Savannah River Site. For further information, contact the Principal Investigator, Stafford Cooper, Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39181-0631. Phone: 601-634-2477.

Design, Manufacture, and Evaluation of a Hydraulically Installed, Multi-Sampling Lysimeter. A new lysimeter sampling device design, approximately 1 inch in diameter, having multiple sampling zones and capable of being hydraulically installed at a desired depth in the vadose zone without drilling will be developed. This lysimeter will be readily retrievable for reuse and will provide an inexpensive monitoring technique in comparison to installation of lysimeters into predrilled holes. In this project, the hydraulically inserted lysimeter will be designed and constructed. The effect of hydraulic insertion on the operation of the lysimeter will be investigated by comparing hydraulic insertion with standard boring procedures. The lysimeter should be commercialized within three years. This new design is less disruptive to the subsurface, both during installation and after removal, requiring only a 1-inch-diameter hole vs. the 4-inch holes commonly drilled for monitoring wells. Costs are estimated to be under 50% of that to drill monitoring wells. This project is a collaborative effort among Bladon International, Inc., Institute for Gas Technology, and Timco Manufacturing. For further information contact the Principal Investigator, Joe Scroppo, Bladon International, Inc., 880 Lee Street, Des Plaines, IL 60018. Phone: (505) 883-3636.

Minimally Invasive Three-Dimensional Site Characterization. Hardware and software are being developed to permit data acquisition from three minimally invasive measurement techniques--cone penetrometer, synergistic electromagnetic mapping technology and reflection seismology. The software will permit rapid feedback, comparison, co-calibration, and data analysis from the combined technology. Simultaneous application of these three technologies permits physical and electrical property measurements to be used to cross-calibrate each data set. The early acquisition of preliminary data allows field personnel quickly to adapt their field study strategy to changes in the perceived site conditions or contamination distribution.

Costs will be saved by rapid feedback of the data to field personnel, the improved informational quality, and the lower cost of an integrated system. The minimally invasive system reduces environmental impact and reduces risk to field personnel. For further information contact Principal Investigator, John Gibbons, Applied Research Associates, Inc., 4300 San Mateo Blvd., N.E., Suite A220, Alburquerque, NM 87110. Phone: (505) 883-3636.

High Resolution Shear Wave Seismic Reflection Surveying for Hydrogeological Investigation. This technology will enhance the ability to directly determine aquifers in the characterization and sensing of geologic and hydrogeologic features. The project will extend the state-of-the-art of shallow subsurface hydrogeological characterizations by means of high resolution shear (S) wave seismic reflection profiling. High resolution seismic reflection profiling using conventional compressional (P) wave technology has evolved over the past ten years to the point where this technique has become a major component of numerous environmental investigations. Extension of the existing technology to include S-wave reflections has the potential for greatly enhancing the data which can be extracted from the subsurface. Unlike a P-wave, an S-wave will not travel through a purely liquid medium, hence its advantage over current P-wave techniques.

Conventional high-resolution seismic reflection profiling has proven cost-effective for environmental assessment by reducing the number of holes and the cost of boring. S-wave reflection technology will enhance the information content of the seismic reflection technique and improve the cost-effectiveness of the technique. For further information contact the Principal Investigator, William Johnson, Paul C. Rizzo Associates, Inc., 300 Oxford Dr., Monroeville, PA 15146. Phone: (412) 856-9700.

Field Measurements for the Hydrology and Radionuclide Migration Program (HRMP) at the Nevada Test Site. The HRMP was begun in 1974 for the purpose of determining the potential for migration of radionuclides from underground test areas. HRMP is a multi-agency research project and is coordinated by the Nevada Operations Office of DOE. The participants are Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Desert Research Institute, and the U.S. Geological Survey. The present goals of the program are to learn more about the groundwater rates and directions of flow on the Nevada test site (NTS), which is located approximately 80 miles northwest of Las Vegas, in regional and local systems, to develop mathematical models of the flow systems, to determine the effects of nuclear tests on the systems, and to measure the migration rates of selected radionuclides under various conditions.

Transport mechanisms for radionuclides from underground nuclear detonations are studied by sampling both the contaminated cavity water and groundwater pumped from the surrounding formation. Radioactivity in water greater than 9-cavity-radii distance from the detonation point has been measured without stressing or pumping the aquifer. A plume of radioactivity which is being rapidly transported by the local groundwater has been intercepted. Micro- and ultrafiltration studies on this groundwater have shown that radionuclides can be present and mobile in groundwater systems in colloidal form. Water pumped from a tritium contaminated satellite well over a 20-year period drains into a mile-long ditch and has created a secondary site emphasizing the unsaturated zone. Current studies along the discharge ditch are investigating the moisture and tritium front through shallow alluvium. This project is developing systems which can measure contaminants such as organics, tritium, and long-lived radionuclides in wells in depths from 1400 to 3300 feet. For further information, contact the Principal Investigator, Jo Ann Rego at Nuclear Chemistry Division, Lawrence Livermore National Laboratory, P.O. Box 808, L-234, Livermore, CA 94551. Phone: (415) 422-5516 (FTS 532-5516).

Depth Profiling in the Water Table Region of a Sandy Aquifer. The feasibility of using a new multilayered sampler to investigate organic contaminants in

groundwater is being explored. The device passively collects simultaneous groundwater samples from multiple levels in the subsurface. In addition, the project will develop a new device based on experience with existing sampler.

The sampler, developed at the Weizmann Institute of Sciences, Rehovot, Israel, was used to detect the presence of several inorganic and organic species at a contaminated Brookhaven site. The presence of microscale heterogeneities in concentration gradients over a vertical interval of 200 cm was observed for eight solutes, including metals, organics, and anions. A planned remediation was modified based on results of this short sampling event. It is believed that the new plan will be more cost effective than the original because the contamination was better defined in the vertical plane and because an oxygen-depleted zone was found where it was previously thought to be fully saturated. For further information, contact the Principal Investigator, Edward Kaplan, Brookhaven National Laboratory, Radiological Sciences Division, Building 703M, Upton, NY 11973-5000. Phone: (516) 282-2007 (FTS 666-2007).

Kr^{81} Counting for Nuclear Waste Sites. A new technology to date groundwater is being developed. By combining resonance ionization spectroscopy and mass spectroscopy, ultralow levels of Kr^{81} in groundwater can be detected. From the quantity of Kr^{81}, the age of the groundwater can be determined. This information helps find suitable locations to store nuclear wastes or highly toxic chemical wastes in groundwater. Several samples from Europe have been tested and the results are adequate to search for new waste sites. It is beneficial to the Department of Energy waste program to find a geologically safe place to store nuclear wastes and highly toxic chemical wastes. For further information, contact the Principal Investigators, C.H. Chen and M.G. Payne, Oak Ridge National Laboratory, Photophysics Group, Building 5500, MS-6378, P.O. Box 2008, Oak Ridge, TN 37831-6378. Phone: (615) 574-5895 (FTS 574-5895).

FUTURE TECHNOLOGY DEVELOPMENT NEEDS

The OTD activities described here address some, but by no means all, of the key needs which DOE foresees in the area of in situ monitoring.

Present site characterization methods are imprecise, costly, time-consuming, and overly invasive. Improved site characterization methods will require better technologies for accurately describing the subsurface geohydrologic features of a site. For example, more efficient nonintrusive sampling strategies and practical models are necessary for understanding and predicting subsurface transport. Also needed are more reliable procedures for interpreting characterization data, such as how clean is "clean".

Traditional hydrologic characterization of the subsurface environment is highly dependent on data from groundwater monitoring wells. A thorough understanding of the subsurface environment requires a series of hydraulic wells. Interpretation depends greatly on proficiency of the scientific staff, making subsurface characterization highly subjective and at times uncertain. Research is needed to make hydrologic characterization more precise and more cost effective.

Currently accepted analytical procedures such as those in the Environmental Protection Agency's (EPA's) SW-846 do not cover all materials that need to be measured at DOE sites. DOE is working with the EPA and others to alleviate such problems with sampling and analyses. Close coordination with EPA and other regulatory agencies is needed not only to identify, develop, and validate appropriate methods, but also to ensure the acceptance of data generated using these methods.

Intrusive exercises, such as sampling and excavation during remediation of a site, often involve immediate hazards to workers in the form of exposure to radioactive and/or toxic materials. Remote real-time analyses of ambient levels of potential hazards in the air, water, and soil during characterization, as well as in

the remedial action phase, would help ensure worker safety and allow continuous operation. Instrumentation capable of detecting broad classes of hazardous materials and specific compounds is needed to indicate cleanup status. Better characterization methods based on real-time analyses are especially important to confirm the most effective use of certain in situ remediation technologies. In the absence of real-time monitoring, excessive volumes of soil and water must be treated to guarantee compliance; otherwise, pockets of contamination may be missed.

Special characterization technologies are necessary for inactive facilities, underground storage tanks, and wastewater lagoons. These facilities often contain significant quantities of radioactive wastes, in certain cases mixed with heavy metals and/or hazardous organic compounds that make personnel entry unacceptable. Thus, the development of advanced robotic samplers, smart probes, mobile and in situ fiber-optic devices, and nonintrusive characterization instrumentation (based on electromagnetic, thermographic, and acoustic principles) is needed for sampling and chemically characterizing these sites. The development of such techniques will significantly reduce radiological exposure to workers and provide more assurance that the correct remedial technology has been selected.

Clearly, there are more technology development needs and more good ideas than there are resources to devote to these investigations. Priorities must be set to support those activities deemed most urgent.

OPPORTUNITIES FOR PARTICIPATION

OTD is interested in eliciting broad participation from qualified organizations who can contribute to its RDDT&E activities. We are becoming increasingly aware of the wealth of technological talent and good ideas in all sectors. OTD has initiated steps during the past year to increase participation of the private sector (academia and industry) through competitive solicitations and through funding of unsolicited proposals. We have also worked to increase participation by academia through interagency agreements for cooperative funding of research and through establishment of DOE educational consortia. Several significant technology development activities are being conducted at DOE sites such as national laboratories. DOE is funding technology development activities beyond the United States through direct contracts, international agreements, and other mechanisms.

DOE plans to continue this type of support for technology development in the coming years. Organizations interested in responding to solicitations should contact John Beller (for Innovative Technology) at Innovative Technology Program Coordination Office, EG&G Idaho, P.O. Box 1625, Idaho Falls, ID 83405-6902. Dr. Erickson (for applied R&D) at the above address or Mr. Snipes (for DT&E) at the above address to be placed on distribution lists. Organizations wishing to submit unsolicited proposals should contact Larry Harmon, Director, Division of Program Support (EM-53), Department of Energy, 12800 Middlebrook Road, Trevion II Building, Germantown, MD 20874, for information on submission format and procedures prior to preparation of a proposal.

REFERENCES

1. United States Department of Energy Environmental Restoration and Waste Management, Five-Year Plan, Fiscal Years 1992-1996, June 1990, DOE/S-0078P.

DEPARTMENT OF DEFENSE FIELD SCREENING METHODS REQUIREMENTS IN THE INSTALLATION RESTORATION PROGRAM

Mr. Dennis J. Wynne
U.S. Army Toxic and Hazardous Materials Agency

The Superfund Amendments and Reauthorization Act (SARA) and the implementing executive orders under this legislation require that contamination resulting from Department of Defense (DOD) past operations be remediated. In response to this legislation, the DOD has undertaken a comprehensive program to comply with these mandates. Over the years this program has expanded from a $150 millon effort in FY 1984 to a $1 billion effort in FY 1991. Some 17000 sites have been identified at 1808 DOD Installations. Ninety DOD Installations have been identified on the National Priorities list by the Environmental Protection Agency. The detection and remediation of contamination is a long term and resource intensive effort. Research that allows us to proceed more quickly in locating contaminants and in pin pointing key soil and water samples for analysis, assessment, and remediation purposes can provide a tremendous resource savings to the ITR Program and, ultimately, the taxpayer. It is noted that over 30% of the budget is estimated to be totally dedicated to drilling, sampling and sample testing. Any improvement in Field Sampling and Analysis will quickly repay the cost of its associated research and development.

DOD Field Sampling and Analysis accomplishments include the fielding of a truck-mounted cone penetrometer for more efficient contaminant plume identification, tracking and reducing well drilling requirements. Also completed was the development of a field Analytical Method for the explosives TNT and RDX in soil and water. Current program efforts include the development of various contaminant sensors to be employed in the cone penetrometer system to define concentrations of contaminants in soil and groundwater as the penetrometer is advanced through the soil. Future plans include the concept of placing sampling devices into the ground with the penetrometer which can be sampled and analyzed with field instrumentation at regular intervals thereafter. All these efforts have significant cost reduction implications and have the interest and funding support of not only DOD but also DOE.

AN OVERVIEW OF ARMY SENSOR TECHNOLOGY APPLICABLE TO FIELD SCREENING OF ENVIRONMENTAL POLLUTANTS

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ABSTRACT

The Army has under development a number of technologies directed toward the field detection and identification of chemical and biological (CB) agents. This includes not only specific sensors, but the technology required to integrate these sensors into effective field detection systems. Much of this technology can be adapted to materials of environmental concern. In particular, there are technologies in various stages of development which are applicable to vapor and aerosol clouds, as well as to contaminated surface water and terrain. These include both point sampling and monitoring systems, as well as remote sensing systems capable of providing rapid wide area coverage. This paper will provide an overview of Army programs applicable to field screening methods, with particular emphasis on mass spectrometric, infra red, and aerosol sampling technologies.

INTRODUCTION

Technologies which can be utilized for the detection of chemical warfare agents in the field may also be applicable to the field detection, classification and identification of various substances of environmental interest. Although Army detection programs, particularly those in the early stages of development, focus on biological as well as chemical detection, and much of the technology is applicable to both. In this paper, the emphasis will be on chemicals in the form of vapors or aerosols. The two main areas which will be covered are standoff detection and point detection. Standoff detection has sometimes been referred to as remote detection. However, remote detection is defined here as the use of point detectors which are located at the site to be monitored, which may be of some distance from the main monitoring station or base, and connected to it by hard wire or telemetry. Standoff detection refers to the use of equipment located at the monitoring base which can sense chemicals at a distant location. The point detection technology to be discussed in this paper is pyrolysis-mass spectrometry. There will also be some discussion of aerosol sampling, since this is pertinent to point detection of aerosolized particulates, liquid or solid. It is not the aim of this paper to present detailed experimental results but rather to provide an overview of the technology and its range of applicability.

DISCUSSION

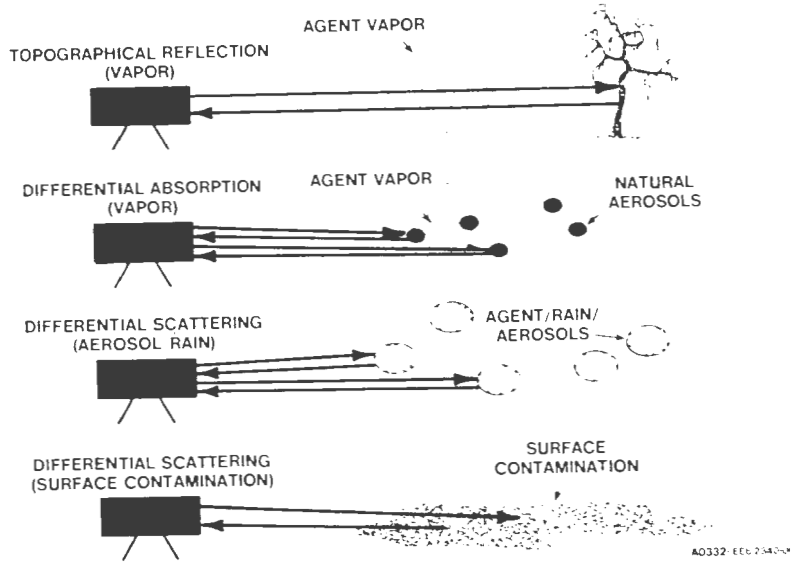
STANDOFF DETECTION: The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) is currently engaged in an extensive multi-year exploratory development program to exploit laser radar for Chemical Biological (CB) Standoff Detection. At present, the only near term capability for the detection of chemical agents at a distance is the use of passive infrared sensors. These sensors can detect only chemical vapors. Active (laser) infrared

(IR) systems employing Differential Scattering and Absorption Lidar (DISC/DIAL) are being developed for the detection of chemical agents in all physical forms: vapors, aerosols, and rains, as well as liquid surface contamination. In addition, an ultraviolet (UV) system employing laser-induced fluorescence is being developed for the detection of biological clouds consisting of organisms, toxins and related materials. The principles of operation of these systems and the background of their development will be briefly discussed. The IR and UV breadboard systems have recently been used in an extensive field test employing various non-toxic chemicals and interferents with excellent results. These data will be discussed along with the necessary development efforts required to adapt the DISC/DIAL technology to practical field use.

The Army is making a significant investment in standoff technology because it is the only technology known that can provide rapid wide area surveillance capability while simultaneously reducing the total number of detectors required. At CRDEC there are three phases to the Standoff Detection program; the XM21 Passive Remote Sensing Chemical Agent Alarm, along with technology upgrades; the Laser Radar (LIDAR) CB Standoff Detection System; and, for the future, combining these technologies with other electro-optic systems in integrated sensor suites.

First to be discussed is chemical detection portion of laser radar project called IR DISC/DIAL. The objective is to provide chemical laser Standoff detection systems for CB defense applications. The planned systems capabilities are to scan surrounding atmosphere and terrain, operate in fixed or mobile mode, detect chemical contamination in all its physical forms, and range resolve, quantify and map data. The purposes of the current program are to demonstrate concept feasibility, establish capabilities and limits, complete science base, determine effectiveness in field situations and establish basis for rapid transition to mature development. The IR DISC/DIAL system can develop data in four ways (as shown in Figure 1):

FIGURE 1



Topographic reflection DIAL: By transmitting different IR frequencies and detecting their topographic return, chemical vapor clouds can be identified by their selective absorption of some of the IR frequencies. This measurement detects the presence of the cloud and its total concentration times path length (CL); however, it does not tell how far away the cloud is or its density (concentration).

Aerosol backscatter DIAL: By the same technique, but with higher laser power, the normally occurring atmospheric aerosol begins to reflection IR energy back to the detector. This distributed reflector can be "range resolved" by gate timing the returning signal just as radar systems do. In this way, average concentrations and ranges can be developed for many cells (range lines) down the LIDAR path. By scanning the system spatially, a map can then be made of vapor chemical agents.

Agent backscatter DISC: In the same manner, chemical agent aerosols and agent rains can be detected by the selective frequencies that they directly backscatter to the detector.

Surface reflection: The fourth mode of detection is the detection of selective IR frequencies backscattered from agents on surfaces. This measurement is dependent on the amount of material located on the surface of dirt, grass, trees or equipment.

Figure 2 shows that, for each of the detection modes, the return signals are different so that all measurements can be made simultaneously. This is important because there are no significant hardware design constraints to add aerosol rain and surface detection to an aerosol backscatter DIAL system. The first objective of the DISC/DIAL project was to build a Ground Mobile Breadboard (GMB) system to demonstrate the feasibility of DISC/DIAL chemical detection. The system was mounted in a van and tested. Based on these tests, the GMB was upgraded. The current specifications of the Ground Mobile Breadboard Upgrade (GMBU) are given in table 1.

The GMBU along with other devices was then exposed to extensive U.S. Army Dugway Proving Ground (DPG) field testing. The goals of these tests were:

(1) Investigate effects of reducing system size, weight and power on detection performances. This was because the Army's near term use was a ground mobile vehicle application for reconnaissance.

(2) Obtain quantifiable data on vapors, aerosols, and liquid detection and on interferences to prove feasibility.

(3) Use more realistic field scenarios to develop workable use concepts.

FIGURE 2

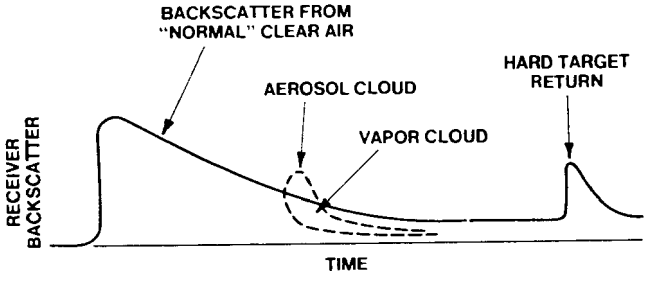


TABLE I. DISC/DIAL Specifications

Transmitter	
Lasers	Four CO_2 TEA Laser
Tunability	Line-Tunable by Grating
Wavelengths	9.2 to 10.8 Microns
Energy (on 10P20)	2.0 J/Pulse
Pulse-to-Pulse Power Stability	± 3 Percent
Pulsewidth (3dB)	90 ns
Repetition Rate	20 Hz
Beam Divergence	3.5x4.0 MRAD
Mode	Multimode or TEMoo
Timing Jitter	2 NS Pulse-to-Pulse
Receiver	
Telescope Diameter	16 Inches
Detector	HgCdTe Quadrant
Size	1x1 mm Per Element
Detectivity	4x10 $cm/Hz^{1/2}w$
Field of View	8 MRAD
Overall Electronic Bandwidth	10 Hz to 7 MHz

These tests involved large scale simulant clouds created by a special 100 meter long spray system as well as aircraft spray. Also, aerosols were generated by spray from a high ranger boom, and surfaces (such as dirt, grass, concrete, trees, or vehicles) were coated with simulants. The many accomplishments of these large scale tests were:

- Demonstrated feasibility of ISC/DIAL technology
- Demonstrated high sensitivity
- Demonstrated operation in motion, scanning and mapping
- Detected cloud through a cloud
- Detected collocated DMMP and SF_6
- Detected DMMP (dimethyl methylphosphorate)
  - up to 5 Km (range resolved)
  - up to 10 Km (column-content)
  - in presence of all interferents (fog, rain, dust and military smokes)
  - on ground by secondary vapor
  - at night and in reduced visibility
  - in calibrated chamber
- Detected SF96 - as an aerosol
  - as ground contamination on six surfaces
- Detected other volatile and non-volatile simulants
- Validate emulation and simulation models

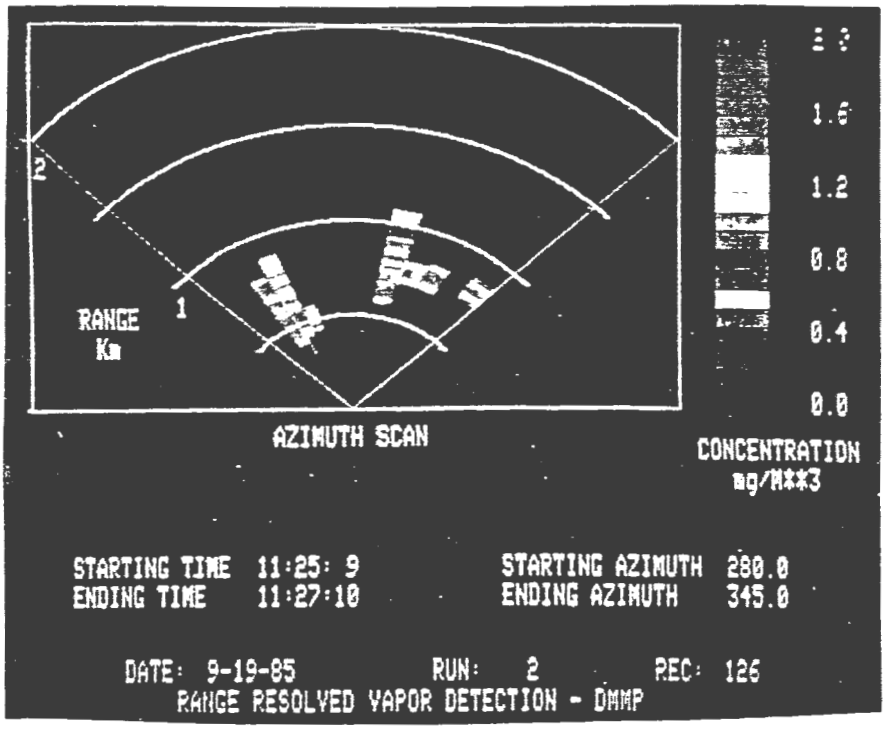
Figure 3 shows a typical GMBU map of a simulant vapor cloud. Although not evident in this black and white illustration, the range cells are colored to show the average concentration from 0.1 to 2.0 mg/m^3.

Additionally, this field work was backed up with an extensive emulation and simulation program which was able to show excellent correlation between predicted and actual performance. For example, the DMMP and SF_6 1 Km range resolved predicted and measured values are identical. Using this excellent agreement, one can infer the following sensitivities to chemical vapors with strong absorptions in the 9-10 micron region of the infrared.

Column Content		Range Resolved
2 Km	10 Km	1 Km
10 mg/m^2	12 mg/m^2	0.5 mg/m^3

The minimum detectable concentration of liquid simulants on the ground were measured at 0.5-5.0 g/m^2 depending on the porosity of the surface. Also very encouraging is the

FIGURE 3 GMBU MAP



fact that one four wavelength set (1/20 sec data) can provide a high amount of information about the situation. An example:

Accuracy of Prediction (Range Over All Data)	Information
97.2-100 percent	1 simulant on any 1 of 5 surfaces
87.4-87.8 percent	1 simulant on any 5 of 5 surfaces
66.2-74.1 percent	3 simulants on any 6 of 6 surfaces

This demonstrates that a real time surface detection algorithm can be developed.

The UV LIF based laser radar was also successfully tested at DPG for detection of biolcgical and toxin materials. While not nearly as far along in development as the IR system, this system demonstrated significant detections at ranges up to 1.2 Km. The system, which measures the laser induced fluorescence of tryptophane, a compound occurring in all living material, can sense the presence of biological/toxin clouds but cannot as yet uniquely identify the material. Relative optical discrimination between biological simulants and interferents/backgrounds of UV/LIF are below:

	Scattering Signal Level 248 nm	Fluorescence Signal Level 280-410 nm
Tryptophane	None	Strong
BG	None	Strong
Egg Albumen	None	Strong
Diesel Exhaust	Small	Strong
Auto Exhaust	Small	Weak
Road Dust	Strong	None
Trees	Strong	Strong

Other optical concepts based on Mueller Matrix scattering are currently being investigated to add additional identification capabilities to UV/LIF system.

Passive IR. The standoff detection and identification of chemical vapor clouds is currently achieved by recording the IR spectrum in the 8-12 micron wavelength region by means of an interferometer. This is the XM21 Remote Chemical Agent Sensing Alarm. It is a tripod-mounted device weighing approximately 55 pounds, exclusive of the source power. It scans a 1.5^{o} field of view (FOV) for 2 seconds, co-adding eight scans. If the cloud fills the entire FOV, the sensitivity is on the order of a concentration-path length product of 150 mg/m^2, the precise value depending upon the strength of the absorption bands. The interferogram, taken in the time domain, is converted to a frequency domain spectrum in the microprocessor by means of a fast Fourier transform. A background spectrum of the FOV must be obtained and stored, and then subtracted from the sample scan prior to further signal processing. Because of the relatively slow scan speed, and the requirement of the current algorithm for a background subtract, it cannot be operated from a moving platform.

A lightweight (20 lbs), fast scan interferometer is under development. In addition, recent developments in direct signal processing in the time domain have both reduced demands on the microprocessor and relieved the requirement for a background scan. Since results equivalent to those on the XM21 can be achieved in a single scan without a pre-determined background spectrum, this device can be operated from a moving platform such as a ground vehicle or airframe. Thus, if only vapor detection is required, passive technology represents an attractive method for rapid survey of an area, particularly by air.

In summary, CRDEC has demonstrated the feasibility of IR DISC/DIAL technology for the detection of chemical agents in all forms, as well as passive IR for chemical vapor detection. Prototypes for ground mobile, fixed site and test facility application are beginning to be developed. The potential exists for modifying these systems to mount on helicopters, RPVs, and even satellites, and to add the capability of detecting biologicals and toxins, as well as chemicals.

POINT DETECTION: There are two specific technologies which form the basis of recently fielded and developmental Army point detectors; namely, ion mobility and mass spectrometery.

Ion Mobility Spectrometry. This is a technology which operates at atmospheric pressure. The air sample containing the vapor(s) to be detected are drawn through a permselective membrane into an ionization region where reagent gas ions react with the (polar) compounds to be detected and form cluster ion species. These are gated into a drift tube where the ions migrate under an applied electric field, and are separated according to their mobility as measured by their time of arrival at the collection at the end of the drift tube. These may be operated in both a positive and negative mode. The U.S. Army currently has fielded a hand-held monitor, the Chemical Agent Monitor (CAM), and has a point alarm system (XM22) under development. These relative low weight, man portable, field hardened devices are quite sensitive and should be quite useful for field screening and monitoring of a wide variety of environmentally hazardous vapors. Since this technology and its applications will be discussed extensively in the symposium, it will not be considered further here.

Mass Spectrometry. A mass spectrometer system which can provide sensitive, effectively real time detection and identification of chemicals in the form of vapors, aerosols, and ground surface contamination, is currently under development by CRDEC. Since this system also has the potential to detect materials of biological origin, it is referred to as the Chemical Biological Mass Spectrometer (CBMS).

The CBMS consists of two major components, the biological probe and the mass analyzer chassis. An artist's concept is shown in figure 4. The biological sampling probe contains the virtual impactor and infrared pyrolyzer. The mass analyzer chassis contains the mass analyzer, instrument computer, data processing computer and display, alarm and communication modules.

The virtual impactor block of the biological sampling probe consists of a 1000 l/min pump and a four stage virtual impacter concentrator. This device separates the aerosol particles from the air by virtue of their inertia and directs them onto a quartz wool matrix. The quartz wool is mounted inside of the infrared pyrolyzer assembly. Periodically this assembly is heated to

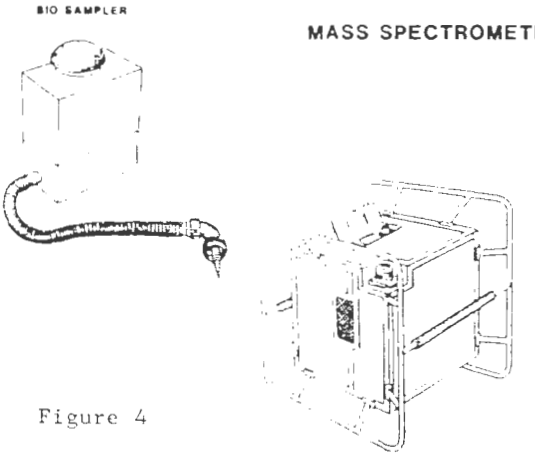


Figure 4

temperatures near 600 C. As a result, any biological material collected on the quartz wool is pyrolyzed. Although the focus is on biological aerosols, any aerosol particle in the applicable size range will also be collected and analyzed in the same way. This includes liquid or solid chemical aerosols, or chemicals adsorbed on or attached to other aerosol particles of network or anthromorphic origin. These pyrolysis products are then drawn into a heated 3 meter long, 1mm O.D. capillary column and pulled to the mass analyzer chassis. Any chemical vapors in the air are also drawn into this capillary and pulled to the mass analyzer.

The pyrolysis products and/or chemical vapors enter the mass analyzer by permeating through a silicone membrane. This membrane separated the high vacuum mass analyzer from the ambient pressure sample. After the sample enters the mass analyzer, it is ionized using an electron gun and the mass spectra taken of the ionized components.

The instrument control computer controls the mass analyzer, the pyrolysis event, and all other instrument related functions including temperature settings, electron gun current, and rf/dc voltages and frequencies. The data processing computer interprets the mass spectra and generates the necessary system responses. The display, alarm and communications modules are the primary interfaces to the operator. A block diagram is shown in figure 5.

A QUISTOR (Quadrupole Ion Storage Device) mass analyzer is used in the CBMS. (Figure 6) This mass analyzer consists of two end caps and a ring electrode. An ion getter pump or molecular drag pump can be used to produce the required vacuum. An electron gun is mounted on the sample inlet side. Selected masses are either trapped within the QUISTOR or expelled out through the end caps depending on the voltages and frequencies applied to the caps and ring. The masses of the ions that are expelled are directly correlated to the voltages and frequencies applied to the rings and caps.

In principle, a mass analysis is made as follows. First a vapor sample enters the QUISTOR. This sample is then ionized using the electron gun. The voltages and frequencies applied to the rings and end caps cause these ions to become trapped within the QUISTOR's internal electric fields. The dc voltage applied to the QUISTOR is then changed at a controlled rate. At specific voltages, certain masses become unstable and are expelled from the QUISTOR and are detected at the electron multiplier. A plot is made of the signal from the electron multiplier as a function of the applied voltage. This voltage is increased until all ions are expelled. The final mass record is then obtained by correlating the applied and plotted voltage to the corresponding masses that should be expelled.

Figure 5

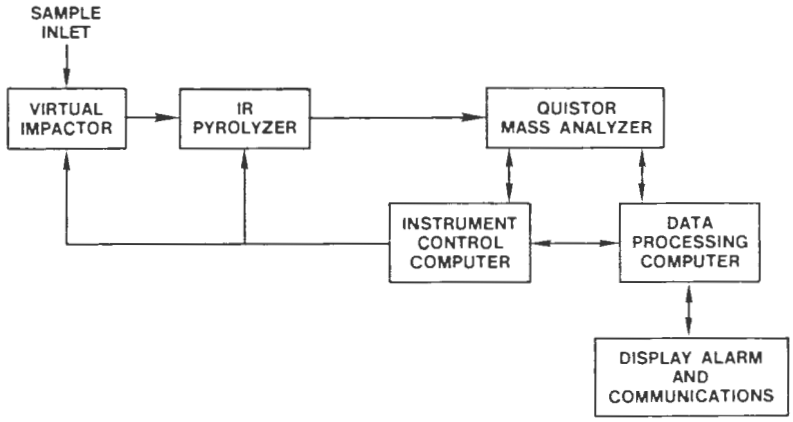
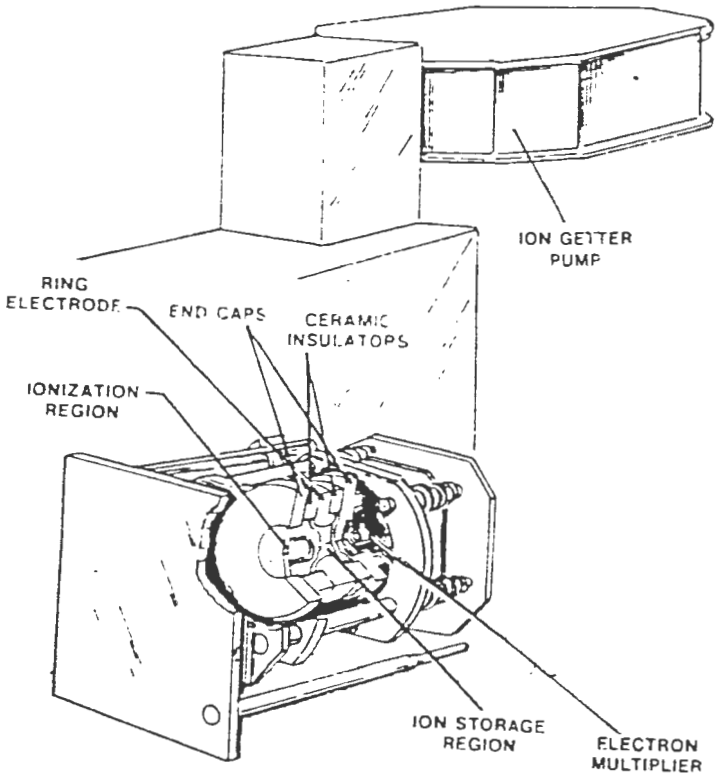


Figure 6. QUISTOR Schematic



FIELD ANALYTICAL METHODS FOR SUPERFUND

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Abstract

The Analytical Operations Branch (AOB) of the U.S. EPA is responsible for coordinating field analytical methods information transfer for Superfund. With the assistance of the Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV), AOB has initiated a series of projects designed to facilitate the appropriate use of field analytical methods throughout Superfund. This paper will summarize the use of field analytical methods in the various phases of Superfund activities, and will describe AOB efforts in coordinating field analytical methods information transfer throughout EPA. In addition, this paper will summarize the field analytical methods currently used throughout EPA's Superfund program and describe the development of comprehensive document that will compile field analytical methods and provide guidance to the use of field analytical methods for environmental samples.

Introduction

Field analytical methods have been widely used for the past eight-to-ten years by EPA organizations under various Superfund contracts, such as Field Investigation Teams (FIT), Technical Assistance Teams (TAT), Emergency Response Cleanup Services (ERCS), and Remedial Engineering Management (REM) contracts. As efforts to streamline the Superfund site assessment, site characterization, and site clean-up processes have developed, the need to assess field analytical technologies for their appropriate use in Superfund decision-making have increased. The Analytical Operations Branch (AOB) of the Hazardous Site Evaluation Division (HSED) has been involved in coordinating information on field analytical methods used in support of Superfund. The AOB's first efforts at coordinating field analytical methods resulted in a paper entitled 'Field Monitoring Methods in Use for Superfund Analyses' (1) and the Field Screening Methods Catalog (2).

Field analytical methods are used throughout the Superfund process. In EPA's Site Assessment, or Pre-remedial Program, FIT teams under the direction of EPA Site Assessment Managers (SAMs) analyze samples in the field for Site Inspections (SI). The results of the SI determine whether a site should be added to the National Priorities List (NPL) of Superfund hazardous waste sites. In EPA's Removal Program, a TAT team, under the direction of an EPA On-Scene Coordinator (OSC), will conduct a Removal

Assessment, often using field analytical methods, to determine if an emergency response (a removal action) is necessary. When a Removal Action is initiated, an ERCS cleanup contractor, under the direction of the OSC, may be dispatched to the site for further analysis and cleanup. The result of the removal action is typically a short-term stabilization of a site, and field analytical methods are often used to monitor the extent of the cleanup and determine when to stop the removal action. In EPA's Remedial Program, REM contractors, under the direction of Remedial Project Managers (RPMs), have conducted field analyses to characterize the extent of contamination at a site (the Remedial Investigation), to test remedial treatment technologies (the Remedial Design), and for site cleanup activities (Remedial Actions). In all of these programs, field analytical methods are often used to identify critical samples for CLP confirmatory analyses.

Field analytical methods are typically not as rigorous as chemical analyses conducted in a "fixed" laboratory - a laboratory in a permanent location. Field methods are often used for screening sites to determine if contamination is present, and to obtain a general idea of the extent of contamination. Further, field analytical methods are most useful when the contaminants of concern have already been identified, so that the appropriate methods, dilutions, calibration ranges, etc., can be employed. In addition, field analytical methods are usually designed to identify only a limited number of analytes. Recently, however, more sophisticated and more rugged instrumentation have allowed for more rigorous analyses in the field; consequently, field analytical chemistry does not have to be limited to screening. Even so, it is generally believed that field analyses provide less precision and accuracy than analyses conducted in fixed laboratories. (It should be noted, however, that despite this perception, a focused gas chromatographic analysis is likely to be better than a heavily quality-controlled GC/MS screen.) In all of the Superfund activities described in the previous paragraph, field analyses are used for the rapid turnaround of sample results. These results are, in turn, used to expedite site assessments for NPL listings or for emergency removal actions, site characterizations, and ultimate cleanup. Data quality is not compromised, since field analyses are usually conducted in conjunction with confirmatory analyses, such as GC/MS or ICP/MS analyses using EPA Contract Laboratory Program (CLP) protocols. Consequently, field analyses are often used to identify samples for more rigorous, CLP-type analyses.

Site Assessment Program

As part of determining whether a site should be added to the NPL, the Site Inspection (SI) attempts to make a determination of "observed release". This determination indicates that the site is discharging contaminants into the environment.

The Site Assessment Program conducts up to ten percent of its analyses in the field, and about 75 percent of the samples are sent to the CLP for full scan analysis. In the Site Assessment Program, very little is usually known about the site and its contaminants; consequently, it is more cost effective to use the CLP as a screen rather than conduct extensive field analyses designed for analyzing a limited number of target compounds. Nevertheless, FIT, the Site Assessment Program's primary contractors, conduct a limited number of field analyses to obtain real-time data to determine worker safety requirements, the extent of contamination, the presence or absence of contamination, for the placement of monitoring wells, and to select samples for subsequent CLP confirmatory analysis.

To accomplish these analyses, EPA's Site Assessment Branch has developed the Field Analytical Support Project (FASP). This project has, at this writing, developed 31 field analytical methods, called FASP Standard Operating Guidelines (SOGs), and are designed to be modified as needed to meet site-specific conditions (3). These rapid turnaround, FASP SOGs have been developed by FIT for water, soil, or oil analyses for volatiles, polynuclear aromatic hydrocarbons, pesticides, PCBs, and metals.

Some EPA Regions have used FASP to perform preliminary evaluations of new instrumentation. For example, two Regions are evaluating Long Path Fourier Transform Infrared (FTIR) Spectroscopy

for the analysis of air samples remote from a site, and one Region has evaluated the Thermal Chromatography/Mass Spectrometry (TC/MS) system for the analysis of solid samples. According to these latter studies, TC/MS shows promise as a rapid screen for solid samples since there is minimal sample preparation.

Remedial Program

The purpose of the Remedial Program is to clean, or remediate, a site. This process can be rather complex, and usually consists of a Remedial Investigation (RI) phase, a Feasibility Study (FS), a Record of Decision (ROD), a treatability study, a Remedial Design (RD) phase, and a Remedial Action (RA) phase. The RI consists of data collection activities undertaken to determine the degree and extent of contamination within all media. The RI supports the FS, which determines the risk that the site poses to human health and the environment, and identifies the most appropriate remedial alternatives that can be used to remediate the site. The ROD is issued by EPA as the final remedial action plan for a site. If necessary, a treatability study is performed to determine the most appropriate conditions for treatment, the remedy is then designed (RD), and the site is cleaned (RA).

During all of these phases, the potential exists for the use of field analyses. For example, during the three-dimensional characterization of the extent of contamination (the RI), rapid turnaround of sample results may be necessary to focus subsequent analyses to the determination of the extent of contamination. Here, the analyses may be used to optimize sampling grids for three-dimensional site characterizations, to determine the location of monitoring wells and well screen depths, or to determine the direction and speed of groundwater plumes. During treatability studies, rapid turnaround of data may be necessary to avoid shutting down a treatment operation to wait for sample results. In the Remedial Design phase of the remediation, rapid turnaround of sample results may be necessary to evaluate the efficiency of a design. These data may then be used to make improvements on the design, the net result being more rapid development of remedial designs. In removal and remedial actions, rapid turnaround of data may be required to determine cleanup levels and to minimize the costs associated with using expensive cleanup equipment such as bulldozers. When the field analyses suggest that a regulatory level has been reached, CLP confirmatory analyses can then be performed to confirm the cleanup level reached.

To accomplish these analyses, EPA's Hazardous Site Control Division developed the Close Support Laboratory (CSL) Program. Because site remediations are often very complex and typically take several years to complete, the REM contractors found it more convenient to construct temporary, "close-support" laboratories at the site rather than use mobile laboratories or portable instruments for the analytical investigations. This program has resulted in the development of 15 field analytical methods for metals, volatiles, semivolatiles, and polynuclear aromatic hydrocarbons in water and soil matrices (4). In addition, the CSL program has developed 16 field protocols for the determination of physical measurements to be used during treatability studies.

The Remedial Program conducts about ten percent of its analyses in the field. Once EPA has placed the site on the NPL, Potentially Responsible Parties (PRPs) are finding that it is more cost-effective to assume the costs of site characterizations. Consequently, there are a growing number of these "PRP-Lead" sites, requiring fewer analyses by the EPA. As a result, in many Regions the Remedial Program is placing increasingly more resources on overseeing the analytical activities of the PRPs. This shifting of focus from "Superfund-Lead" sites to PRP oversight has also coincided with the phasing out of the REM contracts and phasing in of the new Alternative Remedial Contracts Strategy (ARCS) contracts. Nevertheless, there are still many Superfund-Lead remediations in progress, and the Remedial Program is planning to use ARCS contractors to perform analyses in the field.

Removal Program

In addition to the long-term remedial actions, Superfund legislation provides for short-term, removal actions. Removals are performed in emergency-type situations on unstable sites. A removal is the cleanup or removal of released hazardous substances which may present an

imminent and substantial danger. Consequently, removals may be necessary in the event of a release of hazardous substances, or to monitor, assess, and evaluate the threat of release of hazardous substances to prevent, minimize, or mitigate damage to human health or the environment.

Due to the nature of these activities, removals often require a rapid turnaround of analytical data; consequently, field analyses are used quite often. The Removal Program conducts about 30 percent of its analyses in the field. Under the direction of the OSC, TAT - the Removal Program's primary technical contractor - may use field analytical methods for purposes similar to those of the FIT teams. If a more in-depth study is required, the OSC may require the use of field analytical methods to determine an estimated extent of contamination. If drums are present and the contents within the drums are unknown, TAT may use a Hazard Categorization field kit to categorize the potential hazard associated with the contents of the drums. TAT uses this field kit to perform simple qualitative tests to determine gross characteristics of the waste - the compound class, flash point and other properties, and consequently, determine the disposal options for the waste.

The Removal Program uses field analyses for Classic Emergencies (for example, for fires, spills, train derailments, and explosions), to determine worker safety requirements, for designing sampling grids, to estimate exposure, for monitoring well placement, and to determine cleanup levels. Across all programs, the reasons for using field analyses are for time savings, cost savings, and to identify critical samples for confirmatory analyses. Other reasons include being able to take more samples, ease of acquisition, and minimal paperwork requirements.

To accomplish these analyses, the Removal Program established the Environmental Response Team (ERT). The ERT provides expertise to the OSCs in the area of performing field analyses and field analytical methods development. The ERT has developed a number of field analytical methods, including portable gas chromatography methods, X-ray fluorescence methods for metals, and methods for the screening and analysis of air samples (5).

EMSL-LV

The Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV) supports the Superfund field analytical programs through both research and development and through technical support to the EPA regions. In the Advanced Field Monitoring Methods Program (AFMMP), EMSL-LV is developing and validating field analytical methods. In its Technical Support Program, EMSL-LV dispatches field analytical teams to hazardous waste sites for characterization studies.

EMSL-LV is working under its Advanced Field Monitoring Methods Program (AFMMP) in coordination with the Analytical Operations Branch (AOB) to identify, develop, and validate new and existing field analytical methods and instrumentation. In addition, the objectives of AFMMP include the transfer to and exchange of information with the EPA regions. EMSL-LV has performed studies involving immunochemical methods, soil gas techniques, portable gas chromatographs and associated analytical methods, X-ray fluorescence, and fiber optic sensors. In addition, EMSL-LV has identified a number of new techniques for study, including Fourier Transform Infra-Red (FT-IR), portable supercritical fluid extractor and solid phase extraction, field test kits, portable GC/MS, ion mobility spectrometers, and luminescence methods.

Development of a Superfund Field Analytical Methods Catalog

The Analytical Operations Branch (AOB) is the focal point for coordinating field analytical method information transfer for Superfund. In 1988, the AOB coordinated an effort to compile some of the field analytical methods used in Superfund into a document entitled "Field Screening Methods Catalog".

The AOB is currently designing and developing a comprehensive compendium that will contain many of the field analytical methods described in this paper for use by all persons involved with Superfund field analyses. This compendium will contain developed field analytical methods, it will contain instrumentation requirements, requirements for quality assurance and quality control, analytical method

performance, guidelines for effective communication, health and safety guidelines, and evidentiary guidelines. This compendium is being prepared with the assistance of the Field Analytical Methods Workgroup, which had its first meeting on July 19-20, 1990 and the Field Analytical Methods Management Forum. The forum is a group of EPA Headquarters and Regional management representatives who met on June 27-28 to determine Superfund policies regarding field analyses in Superfund.

The field analytical methods that will be a part of the catalog will come from the sources described in this paper. The methods will be presented in chapters structured by fraction, analyte group, and media. In addition, the methods will be restyled into SW-846 format for consistency, ease of reading, and to allow for variations. Instrumentation requirements will be provided for each type of method based on available information and research by EMSL-LV. Quality Assurance and quality control information will be designed to facilitate a rapid turnaround of data appropriate for the generation of field analytical data, and will be tiered to allow a variation of requirements for quality. The compendium will contain a user's guide and will stress "interactive management" - the communication between the site manager, the field analyst, and the sampler. In addition, an electronic bulletin board will be established to house the methods for downloading, facilitate the quick transfer of technology, information, and ideas. Health and safety guidelines will be established based on recent OSHA regulations, and evidence guidelines for samples and analyses will also be addressed.

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FIELD DELINEATION OF SOILS CONTAMINATION ON HAZARDOUS WASTE SITES REGULATED UNDER NEW JERSEY'S HAZARDOUS WASTE PROGRAM

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ABSTRACT

The New Jersey Hazardous Waste Management Program (HWMP) recognizes the potential for field analysis techniques to expedite site delineation while decreasing site characterization costs. Although, field analysis methods produce accurate, real-time data at a low cost per sample, the absence of standardized data quality objectives and method specific quality assurance and quality control (QA/QC) requirements has prevented widespread use of these technologies. The HWMP has defined data quality objectives for each phase of site investigation, and outlined QA/QC procedures for several widely available field analysis methods, including field x-ray fluorescence spectrometry, field gas chromatography, colormetric analysis, and photoionization surveying. The development of these method-specific and use-specific procedures has allowed the HWMP to routinely recommend the use of field analysis methods to expedite site evaluation.

INTRODUCTION

The New Jersey Environmental Cleanup Responsibility Act (ECRA) program requires industrial facilities that handle hazardous materials to conduct a site evaluation and develop a site remediation plan (if necessary) prior to any real estate transfer or cessation of industrial operations. Given the real estate and stock market activity of recent years it is not surprising that ECRA subject sites are often operational facilities. Since ECRA's enactment in 1984, thousands of sites have been processed by ECRA. For larger industrial facilities, site evaluation has proven to be costly and time consuming, frequently taking several years to complete.

Site characterization efforts typically involve a historical site survey, site screening, and several phases of site delineation (1). Although, initial site screening is usually conducted using survey instruments, the remaining delineation phases generally involve collecting a limited number of samples for laboratory analysis and evaluating the lab results to determine the need for additional sampling phases. This typical investigation scheme is time consuming, requiring months between phases to allow for sample collection, data analysis, delineation plan development, and regulatory review and interface; however, the phased approach is necessary to limit analytical costs. The unfortunate result of phased investigation is that remedial investigations frequently last years and cost hundreds of thousands of dollars.

These delays in site remediation may not only render industrial operations or property transfers difficult or impossible to conduct, but also may cause unnecessary contaminant migration and exposure to

human or environmental receptors. In these situations it is desirable to implement analytical methods that can provide the necessary data in a timely and cost-effective manner. Field analysis is ideally suited for rapid, cost-effective site characterization as it can provide real-time data which is reliable and inexpensive on a per sample basis.

FIELD SCREENING AND ANALYSIS METHODS

To develop the standard operating procedures (SOPs) included in this paper, efforts were initially directed at determining the minimum data quality necessary to make appropriate technical and regulatory decisions (this is described in further detail below). Subsequently, a literature search was used to identify reliable methods from the vast number of commercially available technologies. Using this information, method specific SOPs were developed to detail the minimum requirements a field delineation plan must meet to receive agency approval. These SOPs are designed to encourage the generation of consistent and reliable data from user to user and site to site. The quality assurance and quality control (QA/QC) requirements in each SOP were formulated in consistency with the reliability, accuracy, and limitations of each method (particularly when considering field use), while considering the ultimate use of the resulting data.

Several instruments and methods have been evaluated and determined effective (or potentially effective) at detecting site contamination at milligram per kilogram (mg/kg) concentrations. Although, a single instrument or method may only be useful for analyzing one or two classes of compounds, the use of several field analysis procedures in tandem enables site investigation teams to detect most priority pollutant compounds at or near background concentrations. For example, ambient temperature headspace analysis is extremely effective in analyzing volatile organic compounds, but not polyaromatic hydrocarbons (PAHs) or metals. Colormetric tests, on the other hand, are effective at analyzing aromatic compounds (including the PAHs), and a field XRF will detect PCBs and most metals at concentrations as low as 20-100 milligrams per kilogram. Thus, by using several field instruments or methods in tandem a broader suite of contaminant compounds may be field analyzed. It should be noted that the methods cited in this paper are by no means a comprehensive list of suitable or potentially suitable field methodologies. Initial selection for these SOPs was based on instrument availability, amenability to field use, and in-house experience.

DATA QUALITY OBJECTIVES

The New Jersey Hazardous Waste Management program (HWMP) data quality designations are based on those developed by the EPA (2-3). The EPA has established five levels of data quality objectives (DQOs). Two of these, Level 1 (Field Survey Instruments) and Level 2 (Field Portable Instruments), generate real-time, field data. Level 3 and 4 are laboratory methods with differing QA/QC requirements, and level 5 is laboratory special services. The EPA has clearly stated the minimum data quality level required for each stage of site investigation. Additional explanation of these data quality levels may be found in any of the EPA's Data Quality Objectives manuals, cited above.

The HWMP data quality standards have been developed to encourage the use of real-time analysis methods during site characterization (4). The HWMP field data DQOs are: Level 1 (Field Survey Instruments), Level 1A (Field Analytical Methods), and Level 2 (Field Portable Instruments). However, unlike the EPA designations, minimum QA/QC and support documentation (deliverables) requirements are defined to assure that the data generated by these methods can be validated based on technical criteria. A detailed description of all DQO levels is provided below.

Data Quality Level 1 instrumentation are intended primarily for health and safety or initial site screening. Quality control and deliverable requirements are limited to a continuing calibration for site-specific compounds and the reporting of values on field/boring logs. Level one (1) methods are real-time and at times, erratic. These methods can be described as pseudo-qualitative and pseudo-

quantitative as the end user can easily be led to believe that these instruments are reporting "true values" or providing selectivity, when indeed they are not. For example, the photoionization detector (PID) survey instrument is commonly thought to be selective and not sensitive to species whose ionization potentials (IPs) are higher than that of the internal ionization lamp. In practice, however, species with IPs above the lamp energy are routinely detected by PID survey instruments. With respect to quantitation, a PID survey instrument reports a value often expressed in mg/kg; however, since detector response is highly variable among chemical species this reported value may not represent site conditions or correlate with other site data. For these reasons level 1 data should generally be used to indicate contaminant presence or absence, rather than compound identity or total concentration. The application of level 1 data should therefore be limited to health and safety screening or to guide the placement of samples being analyzed by higher DQO methods. Level 1 instruments include field x-ray fluorescence spectrometers (XRF) with a remote probe and PID survey instruments.

Data Quality Level 1A methods produce fairly precise data; however, a reduced quality control program is employed to allow high frequency, low-cost sampling. Level 1A methods are suitable for site screening and site delineation when proper QA/QC practices are employed. When delineating using level 1A methods, minimum deliverable requirements typically include: calibration data for site-specific compounds, check standards data, a non-conformance summary, a certification statement signed by the analyst, sample calculations, isopleth maps, tables indicating results (raw and "corrected" based on lab confirmation data), and chain-of-custody documentation. In addition, lab confirmation data (10-30% of all samples collected) must provide "calibration" throughout the entire analysis range and confirmation of the "clean" zone. Level 1A methods include headspace analysis of volatile compounds and analysis using colormetric techniques.

Data Quality Level 2 methods produce precise data when required QA/QC procedures are employed. Quality assurance and quality control requirements are sufficient to allow rigorous data interpretation, while providing reasonable field operation requirements. Level 2 methods are ideally suited for low-cost, one phase delineation. Minimum deliverables requirements will include: an instrument log, calibration data for site specific compounds, standards data, split sample data, raw sample data, blank data, a certification statement signed by the analyst, a non-conformance summary, sample calculations, isopleth maps, tables indicating results (raw and "corrected" based on lab confirmation data), and custody documentation. Lab confirmation data (5-15% of all samples collected) must provide "calibration" throughout the entire analysis range and confirmation of the "clean" zone. Level 2 methods include field gas chromatography (GC) and field XRF analysis using a silicon-lithium detector.

Data Quality Levels 3 and 4 are "Standard Lab Methods" with varying deliverable requirements. Methods which provide these data qualities may be used for conventional site characterization activities or to confirm field instrument results obtained during site delineation activities. It should be noted that the specific QA/QC procedures required will be dictated by the applicable regulatory program. Data quality level 3 methodologies include SW-846 (5) methods and NJ ECRA Deliverables (1). Data quality level 4 methods include CLP methods and Scope of Work (SOW) requirements (6).

Data Quality Level 5 methods are generally state-of-the-art or non-approved methods chosen specifically for a particular site. Level 5 methods are required when "Standards Lab Methods" are either unavailable or impractical. Level 5 data may be accepted to confirm field results or define a "clean zone".

The goal of any site investigation is to assure that the information obtained is sufficient to select and design an appropriate remedial technology. Ideally, site characterization will provide complete definition of contamination with respect to both concentration trends and actual contaminant load. The advantages of levels 1, 1A, and 2

analysis are rapid site delineation and low per sample costs allowing high frequency sampling and a rapid estimation of concentration gradients; however, the concentration results must be assumed to have up to a 150% error. Level 3 and 4 analysis methods are not real-time and are more expensive, limiting sampling frequency, but reported results can be assumed to be quite accurate and a good indicator of actual contamination present. In summary, the trade-off is rapid, less expensive site characterization verses data quality and accuracy.

At first glance it may appear as if HWMP has chosen to expedite site characterization at the expense of data quality by encouraging the use of level 1A and level 2 methods. Upon closer examination, it can be seen that although the raw data obtained by field instruments are less accurate and less precise, the data set is highly consistent within itself, clearly indicating trends and contamination zones. Also, since field analysis costs are generally per diem rather than per sample, field samples may be collected at a greater frequency, providing the project team with better site definition and fewer data gaps. Lastly, all field data are supported by an independent calibration or correction factor provided by the required lab confirmation samples, discussed above. Thus, the end product generated is actually a hybrid of field analysis data and lab data which, when combined, may not only be equivalent in data quality to that obtained by standard methods, but may actually provide a more reliable and complete characterization of site conditions.

SITE INVESTIGATION STRATEGY

The newly developed HWMP DQOs use a combination of high and low quality data to produce a data set which is moderate in both quality and quantity. These DQOs rely on the ability of users to calibrate field analysis data to laboratory confirmation samples, providing superior site characterization at a reduced cost. The net effect is that most site investigations may be completed in a maximum of 1-2 phases or less than one (1) year. To accomplish this, the following site investigatory procedure is recommended (where site contamination is known, step 1A may not be required).

1. Obtain historical information (i.e. past or present site activities).

1A. If the contamination source is unknown, a sampling program incorporating site screening tools (level 1) and laboratory sample analysis (level 3/4) should be implemented. The goal of this effort is to identify all contaminants present by documenting worst-case site conditions.

2. The information above should then be used to develop an open ended, contaminant delineation plan, including the use of real-time (Level 1A/2 quality data) methods. The plan should incorporate sampling contingencies to assure site delineation is completed during this sampling phase. To provide additional data reliability, field instruments should be calibrated to site-specific compounds of interest as defined by previously obtained information.

3. Upon receipt of the laboratory confirmation data, the need for a revised delineation plan should be assessed. If required, a phase II delineation plan should incorporate field analysis methods to complete site delineation.

4. The complete database should then be used to develop a site remediation plan. If in situ remedial measures are to be used and system design limits are being approached, an increased percentage of laboratory data may be required.

DEVELOPMENT OF FIELD SOPS

The development of field SOPs is considered the most efficient means of assuring that data collected from site to site is consistent. These SOPs were developed by consulting the literature, instrument manufacturers, and personnel with extensive field

and/or instrumental experience. Each SOP has 5 technical sections, i.e. method overview, method requirements (including QA/QC requirements), interferences and limitations, data interpretation and reporting requirements, and health and safety considerations.

The method overview or general guidance section is intended to provide the reader with a basic understanding of the method. This section details method applications, including applicable matrices, detectable compounds, and minimum detection limits (MDLs). Additional information is provided for use by the project manager, including estimated cost per sample, level of training required to effectively use the method, lab method equivalent, and theory of operation. The theory section contains instrumental and/or chemical details aimed at familiarizing the reader with the actual science of operation. The last section of each SOP also provides a list of references directing interested readers to a more detailed explanation of instrumental theory and use.

The method requirements section provides four types of information: sampling considerations, sampling requirements, field operation requirements, and QA/QC requirements. Sampling considerations include general information applicable when a sampling program is being developed. This section provides guidance with respect to sample frequency, selection of lab confirmation samples, and any other useful information gained through field experience. As would be expected, this section is continually evolving as the experience base grows. The sampling requirements section details proper sample collection procedures when standard field sampling methods (7) are inappropriate. This section also includes sample handling requirements when past experience has shown sample preparation to significantly impact final results, as is the case with XRF analysis. The field operation section contains actual method guidance intended to supplement or replace manufacturer's recommendations. This guidance customizes method procedures in an effort to meet the goals of the HWMP regulatory program. The last section, QA/QC, states all quality assurance recommendations and requirements. The requirements include analyst "competence" tests, submission of all raw data, and support documentation.

The interferences and limitations section discusses problems which may be encountered during field use. These comments are intended to supplement manufacturer's recommendations by highlighting problems encountered during previous site operations. It is likely that this section will be in constant transition until a comprehensive database has been established.

The data interpretation and submission requirements section details data manipulation procedures and regulatory submission requirements. Data interpretation requirements vary by method and DQO level; however, all SOPs require the calculation of "corrected" results, accounting for discrepancies between laboratory and field data. Reporting requirements are standardized for all field methods and include: scaled site maps with plotted data, summary tables indicating all field results (raw and corrected) and lab reported values, a calibration plot of lab split sample data verses field data, and quality assurance and quality control documentation (consistent with the QA/QC requirements stated above). These requirements are intended to expedite the required review time by standardizing report contents and format, while facilitating validation of both lab and field data.

CURRENT AND PENDING SOPs

Standard operating procedures have been completed for four field instruments and two field analysis methodologies. Additionally, several other SOPs are under development. A listing of all SOPs is provided below.

<u>Level 1 Data Quality</u>

Field Screening Using a Photoionization Survey Instrument.
Field Screening Using an X-ray Fluorescence Spectrometer Equipped with a Remote Probe.
*Field Screening Using a Flame Ionization Survey Instrument.
*Field Screening Using a Portable Infrared Instrument.

Level 1A Data Quality

Field Delineation Using a Colormetric Test Kit.
Field Delineation Using Ambient Temperature Headspace Analysis.
*Field Delineation Using a Portable Infrared Instrument.
*Field Delineation Using a Portable Ultraviolet Spectrometer.

Level 2 Data Quality

Field Delineation Using X-ray Fluorescence.
Field Analysis Using a Field Gas Chromatograph.
Attachments:
1. PID Detector.
2. FID Detector.
3. AID Detector.
4. ECD Detector.
*5. Analyzing Extractables (BNs/PCBs).
*6. Analyzing Water Samples.
*7. Analyzing Air or Headspace Samples.

* - under development

FUTURE DIRECTIONS

Currently, the field SOPs described above are in widespread use throughout the HWMP program. Since these instruments and methods are a small subset of all currently available field analysis methods, similar SOPs will be developed for several additional methods, including FID survey instruments, several spectrometers, and additional field gas chromatography applications.

The performance of each of these methods (on NJ regulated sites) will be monitored using an in-house database. Upon collection of sufficient data, the SOPs will be revised as appropriate. It is expected that additional field experience and the associated understanding of method limitations and accuracy will lead to wider use of field analysis methods, making site evaluation a much less time-consuming and costly process.

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TABLE I. NJDEP/HWMP DATA QUALITY CLASSIFICATIONS

DATA QUALITY LEVEL	PURPOSE OF SAMPLE	EXAMPLE METHODS OR INSTRUMENTS
1	Health & Safety Site Screening Field Use when excavating.	Portable PID (HNU). Colormetric Analysis. Portable FID (OVA). XRF with a remote probe (X-met).
1A	Site Screening. Field Use when excavating. Site Delineation.	ATH Analysis. Colormetric Analysis.
2	Field use when excavating. Site Delineation.	Portable GC. Portable XRF with SiLi detector. Mobile Lab (limited QA/QC).
3	Site Delineation. Lab Confirmation of field delineation samples. Traditional Site Characterization.	Laboratory Analyzed Samples, without QA/QC documentation, i.e. 600 Series. Mobile Lab.
4	Traditional Site Characterization. Lab Confirmation of field delineation samples.	Laboratory Analyzed Samples, with full QA/QC documentation, i.e. CLP-IFB.
5	Traditional Site Characterization. Lab Confirmation of field delineation samples.	Laboratory Special Services. Mobile Lab.

PLENARY SESSION DISCUSSION

LLEWELLYN WILLIAMS: There was a reference in the first or second paper to our concern about the acceptance of field screening and field analytical data by a regulatory group. How do we deal with, or how do we encourage the acceptance of field screening and field analytical method data in the regulatory arena?

DENNIS WYNNE: Part of it, I think, is encouraging the risk-taking among our managers. What we have dealt with in the past is a tendency to rely almost exclusively on the tried and true methods of the contract lab program (CLP). What we are trying to do in the Superfund Program is to wean people off inordinate use of the CLP by saying that that is for a specific intended purpose. It's not intended for all uses. If you focus on the data quality objectives approach, there's not a need to over rely on the CLP, because you often have for some uses a gold plated version that isn't needed for some of the basic uses. The field screening methods would be more appropriate. Some of the ways to do that is by the work group approach and trying things to encourage managers to use it. We're trying to focus on things like streamlining the remedial investigations and feasibility studies, and you really can't tell what you find if you're using fixed labs exclusively. There's downtime while the data are being sent out, analyzed and reviewed. In some cases I think what we're trying to do is look where the time being spent on the program. Trying to shorten those times where we can, trying to encourage the user community to come together in work groups, being able to provide guidance through training programs are ways we can get more people familiar with field screening and thereby limiting some of the conservativism that we deal with in some of the managers who tend to rely on contract lab programs.

Another part of it, I think, would be to emphasize that some of the field analytic methods can provide you with as much accuracy as you get through fixed labs. We need to emphasize those points, so people aren't always assuming field methods are sort of the poor cousin of the fixed labs.

I guess from a PRP perspective, which the Army is, our approach has been to use field screening as a powerful tool to guide the traditional quality control in lab data. We've been forced that way because of our negotiations with the regions, because of the requirement for a lot of this data to eventually stand up in court. So we see it as minimizing the requirement for that extreme case of chain of custody and total reliability of the data because of extreme quality control. We'll minimize the number of samples we really have to take, because of this powerful tool, the field screen.

HOWARD FRIBUSH: I think that your continued use of field analytical methods and analyses is going to force it to be accepted, for one thing. Another thing, the acceptance seems to be more fragmented. That is, it seems to be more accepted to say in the Removal Program, and less accepted but somewhat accepted in other programs. I think that without field analytical methods and analyses, we're really sampling blind, and there is no reason what 90% of the samples that get sent to the CLP should be nonhits, when 90% could be hits.

Another way is to document all this just like we're trying to do with the catalog and the user's guides. I think it will be accepted much more than it is now.

NABIL YACOUB: My question has two parts: 1) would that manual encompass methods developed by the Army and other entities? 2) would the methods include those for matrices other than water, because in the real world, you have a problem with soils and sludges and such.

HOWARD FRIBUSH: Yes, it will include other matrices. As long as the methods have been used for Superfund activities, and they have been shown to work, and they've been field tested, there is no reason why they can't be included. That's why channeling performance information one of these methods, back to EMSL-Las Vegas for an ongoing evaluation is so important. In the future updates, we can either delete some of the methods, or it might help us to combine some of the methods. And as far as your first question: I would say that we're definitely open to including methods developed by the Army, especially if they're users in Superfund activities, for example in the Federal Facilities Program. If there is performance information, we would like to know that.

MICHAEL CARRABBA: I have more of a comment or a suggestion directed at both the Environmental Protection Agency, as well as the Department of Energy.

If you look at the Chemical Sensors session, there are six talks: two representatives from the Federal Government, and four representatives from small business. My comment is that the Environmental Protection Agency, as well the Department of Energy, is grossly underutilizing the small business innovative research program to bring forth some of these field screening technologies, such as in the area of chemical sensors or optical spectroscopy. If you look at the current solicitations for 1991 for the Department of Energy, we've been hearing about this great problem in environmental restoration and field screening. There are no topics in there for small business, and a lot of the innovation that we're going to need in the future, particularly for the DOE and EPA, is going to come from small business with new and innovative ideas. This is not the case for the Department of Defense, who is actually doing a pretty good job in using the SBIR program to fulfill these needs.

EDGAR SHULMAN: I noticed in the user's guide that is presently out, that there is a heavy emphasis on fieldable methods, and very little on the man-portable type of instruments or methodology. Could you comment on what the future direction is relative to the man-portable type of instruments for field screening? And also perhaps to other panelists in terms of their judgment as to the value of smaller devices for field screening?

HOWARD FRIBUSH: I think that the catalog in the user's guide is intended to be comprehensive, and there is no reason that the smaller survey instruments, such as organic vapor analyzers, or portable radionuclide analyzers couldn't be included. In fact, since they are used a lot, especially in the Site Assessment Program, and the Removal Program, they should be included and will be included.

Up a stage to the man portable instruments, we now have portable GC/MS. Those certainly will be included. I think the short answer to your question is that we want everything that is used in Superfund typically to be included into the catalog and user's guide.

EDGAR SHULMAN: I guess I was looking toward your judgment in terms of the value of small devices. Would the priority in the future be toward encouraging people to actually get much smaller devices? I know you are talking about man-portable GC/MS, but they really are not man portable right now. They're fieldable, you still need a truck or something similar.

HOWARD FRIBUSH: Are you talking about field kits, or are you talking about survey instruments?

EDGAR SHULMAN: I'm talking about survey instruments, trying to encourage their research and development community, in terms of an agenda for research. Maybe that's what I'm looking for. Where should the priorities be put, from the R&D community, relative to the kinds of methods that are envisioned for the future.

LARRY REED: You've made a good point, I think looking at the present catalog we have out. There is a bias that was introduced when we were gathering existing information, a large pile which was available as part of the Field Analytical Support Program. This program was developed in part for field investigation teams, and the Site Assessment Program nationwide. There had been a focus to look at the bigger equipment and the more refined type of equipment. I think that was done just to get the catalog out, what information is in use — was available and useful. I think what we are going to try and do is balance it now by more of the technologies, try to focus more on portable kinds of instruments, also. I know

DISCUSSION

in particular when I'm looking at the future of the Site Assessment Program, as the field investigation team contracts start to expire this year, we're going to be looking at two phases of the shifting of the equipment, the larger field analytic support equipment, and then the portable equipment. We want to make sure that that equipment will be transferred to the people who are going to be doing the Site Assessment work and in looking at the next generation of it. That's a good point you make. I think we'll try to balance it out.

HOWARD FRIBUSH: I just wanted to say that the survey instruments have a definite use in Superfund. They are used quite often to determine the health and safety requirements for workers, and also to identify hot spots. So since they have a definite use in Superfund, they will be included in the next update.

LLEWELLYN WILLIAMS: I was just reminded that the EPA is not 100% Superfund. There are a fair number of other programs out there for which field screening technologies will have a place, and in many of those applications, I think some truly portable measurement instruments are going to be very, very important.

CHRIS LIEBMAN: I though that the key to the compendium and the success of the compendium was really dependent on people submitting their methods to the working group, so that we can see that they are included in the compendium. I think it's important to point out that if survey instruments are not currently in the compendium, that largely reflects the fact that people had not submitted methods. I think if you are unhappy with what is in the compendium, to change that, make your submissions.

DOUG PEERY: In putting the catalog together, of course you're addressing purely programs that the EPA is addressing, in dealing with private clients who rely on these things for their own information, you get locked in. We also have to respond to that. Is there going to be a flexibility in this catalog whereby we, as the person developing the procedure, can go through steps and prove that the procedures are applicable and usable, and not be locked in or having to reply. Maybe taking the USATHAMA Procedure and Methodology Proof Program, making it simpler, and integrating the two, so that it can be done very quickly and easily and economically would be one way. Is there a procedure or a thought to adding something along that line?

HOWARD FRIBUSH: I think that is a really good idea, and a really good statement. This is something that the work group has not yet addressed. I think that is a good topic for a future item at our next work group. Originally, we had talked about EMSL-Las Vegas doing some of that validation. When we look at all the methods that we have, I think it might be more appropriate to have EMSL-Las Vegas look at the performance information. But for new methods, I think that that is an area for future consideration and I appreciate the comment.

COLLEEN PETULLO: I notice that DOD, DOE and EPA are all developing innovative technologies, or supporting innovative technologies to be developed. We all march to a different drummer in terms of QA. How is that all being coordinated?

LLEWELLYN WILLIAMS: There are a number of ways in which attempts are being made to harmonize Quality Assurance, not the least of which is the interagency ad hoc committee on QA for environmental measurements that's just been established. We are looking very hard at both QC and QA requirements, both from a process standpoint and from an operations standpoint, to see if we can get more uniform application of QA/QC procedures, agency wide, as well as across the agencies. We're well aware that there have been concerns in the past with respect to dealing with each of our individual Regions, as separate autonomies, and that a DOE or a DOD may have a difficult time in getting the same kind of response to the same situation going from Region to Region. This is part of what we're hoping can come out of the interagency work is to get more uniform application and uses.

COLLEEN PETULLO: Is there one form of QA program plan that you're kind of leaning to at this point?

LLEWELLYN WILLIAMS: When you say a form of QA program plan, I'm not quite sure what you mean.

COLLEEN PETULLO: EPA tends to be more a laboratory type QA versus field operational, and DOE tends to be more field operational, and I'm just curious as to how you're going to get all this all melted together.

LLEWELLYN WILLIAMS: I think there is much we can learn from the approaches of other agencies. We will attempt to accommodate and utilize the best that the other agencies can offer, and provide a focused program that everyone can buy in on and live with.

A FiberOptic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons

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Abstract

We have developed a fiber optic chemical sensor for use in groundwater and vadose zone monitoring. The sensor is a result of modification of previous work in which we demonstrated a fluorescence based sensor for the non-specific determination of various volatile hydrocarbons. The principle of detection is a quantitative, irreversible chemical reaction that forms visible light absorbing products. Modifications in the measurement scheme have lowered the detection limits significantly for several priority pollutants. The sensor has been evaluated against gas chromatographic standard measurements and has demonstrated accuracy and sensitivity sufficient for the environmental monitoring of trace levels of the contaminants trichloroethylene (TCE) and chloroform.

In this paper we describe the principles of the existing single measurement sensor technology and show field test results. We also present the design of a sensor which is intended for continuous, sustained measurements and give preliminary results of this sensor in laboratory experiments.

Background

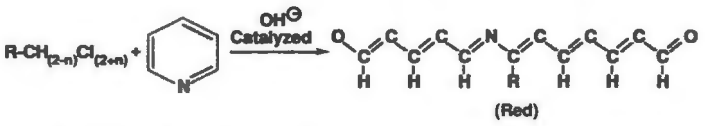
This sensor technology is an outgrowth of research initially sponsored by the U.S. Environmental Protection Agency. Here, a fluorescence based probe for the remote detection of chloroform was conceived, developed and demonstrated in the mid-1980's.[1] The sensitivity and accuracy of the probe proved insufficient for many monitoring applications and research was discontinued. However, in DOE sponsored research one of us (SMA) invented a new concept sensor that has demonstrated significantly improved sensitivity and accuracy for both TCE and chloroform.[2] This sensor is currently under evaluation in monitoring well and vadose zone applications.

Principles of Operation

The basic components of the sensor technology are the chemical reagent, electro-optic measurement device, and the sensors. For the latter, we have developed two versions, one for single and one for continuous measurements. A brief desrciption of the components follows.

Chemistry. The chemical basis of this technology is the irreversible development of color in specific reagents upon their exposure to various target molecules. The primary reagent is an outgrowth of the work of Fujiwara[3] who first demonstrated that basic pyridine,when exposed to certain chlorinated compounds, developed an intense red color. This red color is due to the formation of highly conjugated molecules as shown below. We and others have since demon-

strated that this and closely related reactions can be used to detect trace amounts of these same compounds.[4]



Sensors The single measurement sensor (Fig 1) is comprised of the terminus of two optical fibers and an aliquot (20 µl) of reagent in a small capillary tube. The fibers are sealed into one end of the capillary tube and reagent is placed into this capillary to a length of approximately 5 mm. A porous teflon membrane is placed over the open end of the capillary to prevent loss of the reagent. Target molecules, TCE for example, readily pass through the membrane and produce color in the reagent. This color results in decreased transmission of light at 540 nm. The measurement of the time history of the color development provides a quantitative measure of the target molecule concentration. Since the reaction is non-reversible, the reagent must be replenished for every measurement. This is readily accomplished through the use of easily replaceable, disposable capillaries.

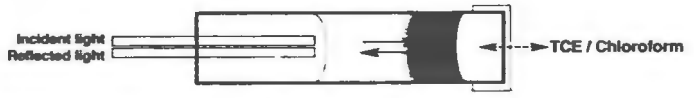


Figure 1. Schematic of the single-measurement sensor

Figure 2 shows a sensor that has been designed for continuous operation.[5] It is essentially identical to the single measurement version with the exception of the addition of two micro-capillary tubes. These are used to supply new reagent to the sensor either continuously or on demand.

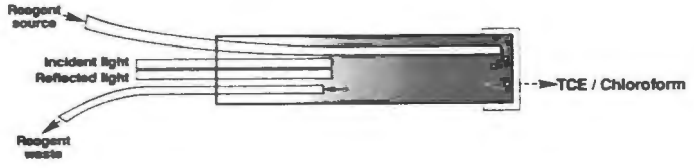


Figure 2. Schematic of the continuous-measurement sensor

Electro-optics. The readout device is shown highly schematically in Fig 3. Here the emission of a miniature tungsten-halogen lamp is collected by suitable optics, chopped with a tuning fork and directed into an optical fiber. The fiber transmits this light with high efficiency to the sensor where it passes through the chemical reagent, reflects off the teflon membrane, and is collected by a second optical fiber. This latter fiber transmits the reflected light to an optical block where it is divided into two beams by a long pass dichroic mirror. These resulting beams are optically filtered at 540 nm and 640 nm, respectively, and their intensity is ultimately measured with silicon photodiodes using phase sensitive detection techniques.

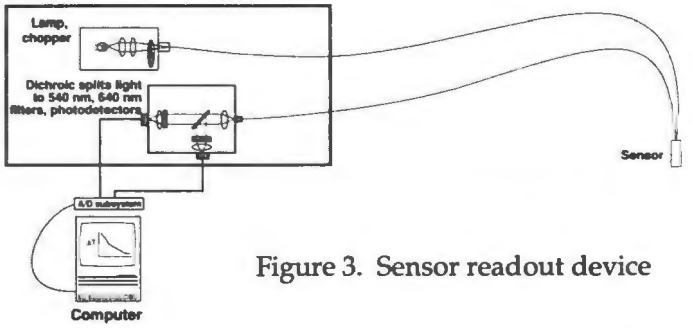


Figure 3. Sensor readout device

Since the colored product absorbs strongly at 540 nm and is virtually transparent at 640 nm, the ratio of 540 to 640 gives a nearly drift free measure of 540 nm absorption. The sensors are calibrated in two ways (1) in the headspace above standard TCE solutions of known w/w concentration or (2) in vapor phase using calibrated dilutions (v/v) of dry TCE vapor. Figure 4 shows the time dependent transmission of sensors exposed to TCE standard solutions and a resulting calibration curve.

Results and Discussion

Groundwater monitoring. The sensor has been evaluated against contractor sample and analysis of 40 monitoring wells located within the boundary of LLNL. These wells are sampled quarterly with subsequent chemical analysis performed by EPA standard 624 purge and trap gas chromatography (GC). We obtained concurrent samples during the quarterly contractor sampling and used our fiber sensor to make

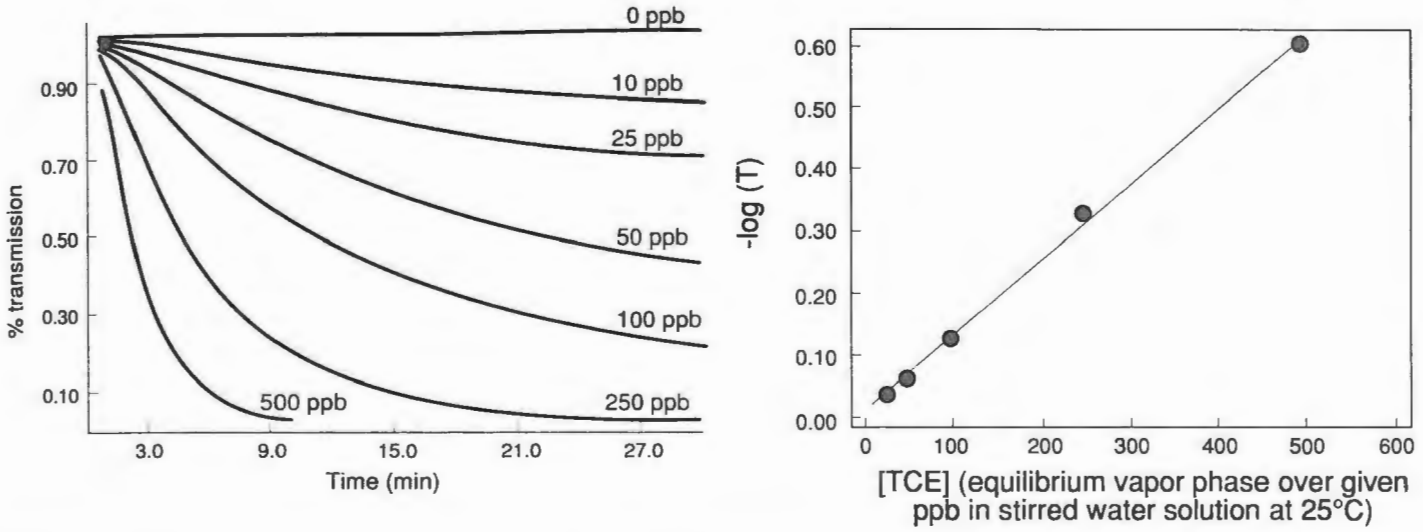


Figure 4. Sample transmission ratio curve, and working standard curve for dual-wavelength absorption sensor. Standard curve obtained from % transmission at a fixed time following iniation of exposure

duplicate TCE concentration determinations. Figure 5 shows a diagram of the laboratory measurement apparatus. Samples were sequestered with no head space into 250 ml Pyrex bottles. These were immediately returned to the laboratory and divided in half. The fiber sensor was then introduced into the resulting headspace through a gas tight valve and a measurement was initiated after stiring the sample for 5 minutes.

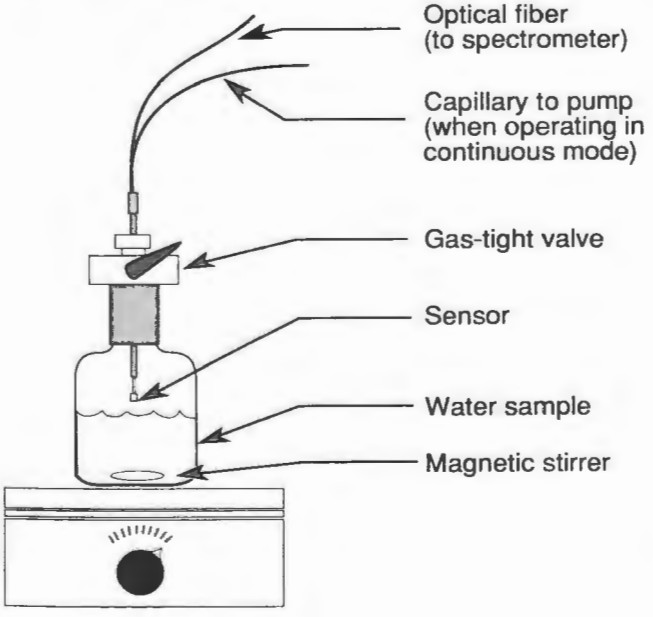


Figure 5. Schematic of vessel used for laboratory headspace measurements

Table 1 below shows the comparison of some of the contractor measurements with the fiber sensor. All fiber sensor values are the average of the duplicate samples. There is excellent agreement between the GC and fiber sensor determinations with nearly all values within the variance of the GC.

Vadose zone monitoring. LLNL site 300 was chosen as the location for initial vadose zone evaluation of the fiber sensor. The vadose zone was accesssed at several locations through existing dedicated soil vapor monitoring points. The samples were drawn at nominally 450 cc/min through copper tubing to a remote mobile laboratory. The lab contained both the fiber sensor apparatus and a portable GC. The instruments were connected to the sample stream in series as depicted in Fig 6 below. Both devices were calibrated for TCE

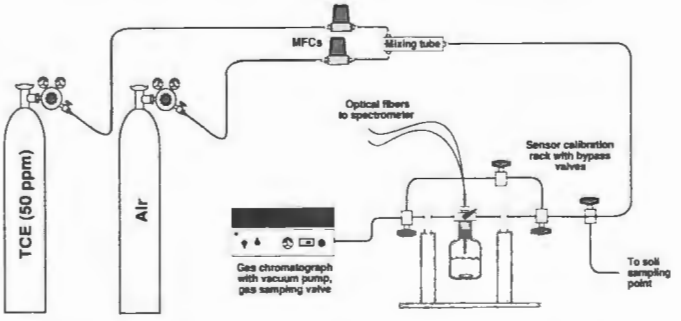
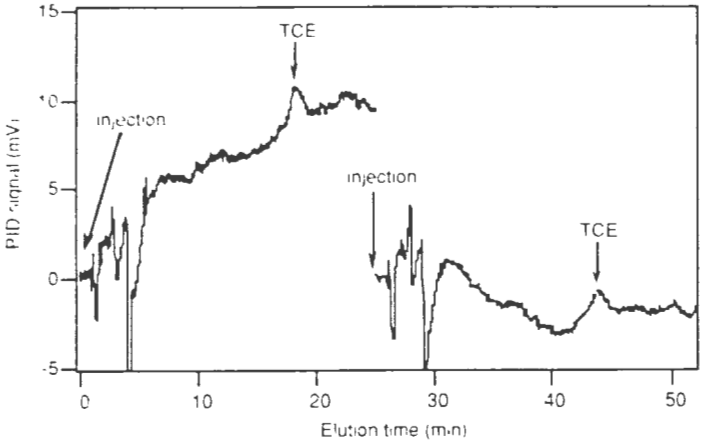


Figure 6. Schematic of vadose zone sampling and calibration apparatus. Sample air is drawn with a pump on board the GC

Table 1. Representative data from field calibration study, compiled from TCE measurements from monitoring wells and piezometers at LLNL.

		[TCE](ppb)				[TCE](ppb)	
Well	Date	Fiber	GC	Well	Date	Fiber	GC
MW352	2/13/90	44	58	MW357	2/13/90	78	84
P418	2/13/90	54	72	P419	2/13/90	61	66
MW271	3/7/90	86	160	MW364	3/7/90	59	74
MW217	3/5/90	106	86	MW458	3/6/90	33	20
MW365	3/6/90	27	22	MW142	3/6/90	94	140



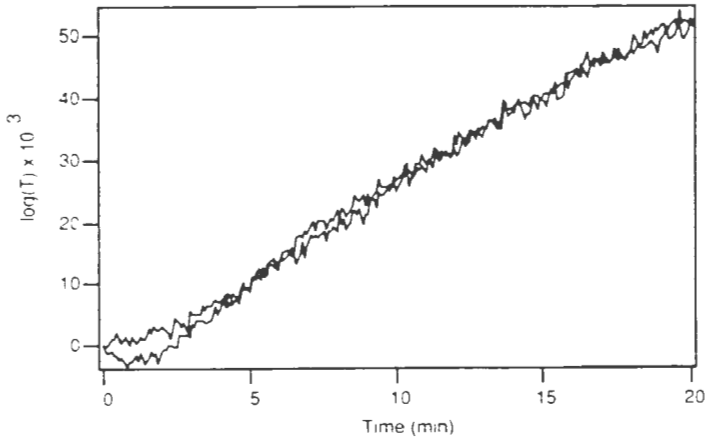


Figure 7. Results of (above) GC (SRI Instruments 8610, PID detector, 6' x 1/8" silica gel column), and (below) fiber sensor measurement of extremely low TCE levels in soil gas (estimated to be ~150 ppb$_{v}$, i.e.: 150 µmoles TCE per mole air).

measurements with precision gas mixtures prior to sampling. The fiber sensor tracked the GC very well through a wide range of concentrations. Figure 7 is a particularly interesting result. Here both instruments were compared in a nearly contamination free location. It is clear that the GC was at its limit of detection, whereas the fiber sensor readily made a successful measurement. Estimates of TCE concentration for this location was <10 ppb.

Continuous measuring sensor. The above described sensor has demonstrated adequate sensitivity and accuracy to represent a viable new environmental monitoring technology. However, the current design,

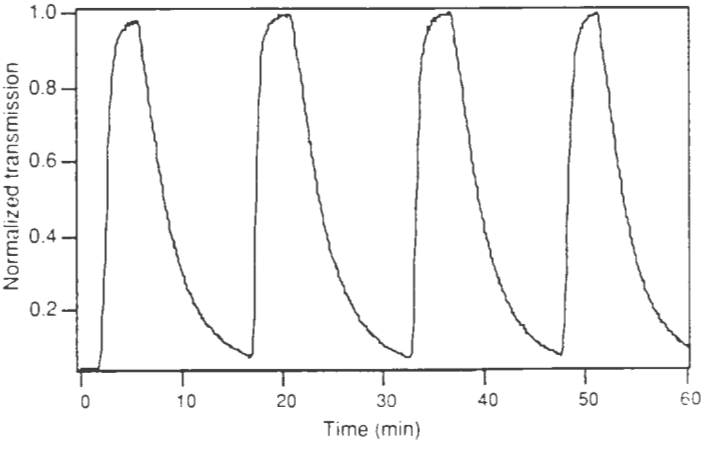


Figure 8. On-demand measurement of 10 ppm TCE (i.e.: headspace measurement over water containing 10 ppm TCE) with continuous sensor system

which incorporates an irreversible chemical reaction, requires the sensor to be refurbished subsequent to each measurement. This liability limits its application somewhat in environmental monitoring.

The sensor shown in figure 2 represents the lowest risk mitigation of this liability. Preliminary reslts with prototypes of this sensor are very promising. Figure 8 shows typical on-demand measurements obtained with this sensor in laboratory testing. We anticipate that this sensor will become an integral component in a down-well monitoring instrument currently being developed at LLNL.

Acknowledgements

This work is supported by the DOE Office of Technology Development (OTD) and performed under the auspices of DOE contract W-7405-Eng-48 and the Center for Process Analytical Chemistry. The authors are indebted to Dr. Lloyd Burgess and the Center for Process Analytical Chemistry, Univ of Washington for collaboration that led to the design and demonstration of the continuous sensor. The authors also wish to thank Dr. F. Hoffman of LLNL for many helpful discussions.

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Chemical Sensors for Hazardous Waste Monitoring

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ABSTRACT:

A family of novel fiber optic sensors is being developed for on-line monitoring of chemical species in gases and liquids. The sensors utilize porous polymer or glass optical fibers in which selective chemical reagents have been immobilized. These reagents react with the analyte of interest resulting in a change in the optical properties of the sensor (absorption, transmission, fluorescence). Using this approach, low parts per billion level detection of the aromatic fuel vapors, benzene, toluene and xylene, and hydrazines has been demonstrated, as have sensors for ethylene vapor. Also relevant to groundwater monitoring is the development of a pH Optrode System for the pH range 4-8, with additional optrodes for lower pH ranges.

INTRODUCTION

The functional operation of optical fiber chemical sensors involves the interaction of light which propagates through the fiber, with a reagent that in turn selectively interacts with the environment to be sensed. Typical optical properties including evanescent absorption and fluorescence, and chemiluminescence can be exploited in these sensors. The reagents are normally immobilized into a membrane or porous polymer matrix and then coated either on the tip or side of the fiber.

One of the problems encountered with fiber optic chemical sensors based on evanescent absorption is their characteristic low sensitivity. This results from the limited depth of penetration of the evanescent field of the light into the reagent cladding as well as the effect of internal reflections [1-4].

Figure 1 illustrates the principle of detection used in fiber optic chemical sensors. In the figure, porous glass and porous polymer approaches are compared to conventional evanescent chemical sensors. In the porous fiber, the analyte penetrates into the pores and interacts with the reagent which is previously cast (immobilized) into the pores. The porous fiber has a large interactive surface area (due to the large surface area provided by the pores), resulting in dramatically enhanced sensitivity in the optrode. Another advantage of a porous glass fiber is the small sensing region (about 0.5 cm in length and 250 microns in diameter). Additionally the sensor is an integral part of the fiber waveguide. This latter feature minimizes the complications associated with the physical and optical coupling of the sensor probe to data transmission fibers. In addition, multiple fiber sensors can be deployed using a single analytical interface unit. These sensors are expected to be less expensive than conventional fiber optic chemical sensors based on materials cost and ease of fabrication. Porous

fiber sensors for the measurement of humidity, pH, ammonia, ethylene, CO, hydrazines, and the aromatic fuel constituents benzene, xylene and toluene have been successfully demonstrated by GEO-CENTERS, and by Rutgers University [5-12].

Fabrication of Porous Glass Optical Fiber

Porous glass optical fibers are fabricated by the Fiber Optic Materials Research Program at Rutgers University, using the methodology described below [5].

The material used in the fiber is an alkali borosilicate glass with the components SiO_2, B_2O_3 and alkali oxides. This type of glass is a well characterized system, producible at a low cost. Most importantly it exhibits the phenomenon of liquid/liquid immiscibility within a certain temperature range. The above composition is melted in an electrical furnace at 1400°C and cast into rods with a 20 mm diameter and 0.5 m in length. The rods are drawn into fibers at about 700°C by a draw tower equipped with an electrical furnace. Fibers with a 250-300 micron diameter with a 5-10 cm length are then heat treated in a tube furnace at 600°C for about 3 hours. The heat treated glass becomes phase separated, with one phase silica rich and the other boron rich. The boron rich phase is leached out of the glass by placing the fiber in a bath of hydrochloric acid. The fibers are subsequently washed with distilled water and rinsed with alcohol. Figure 2 illustrates the processing steps for fabricating porous fibers.

Subsequent to fiber preparation, the porous segment is cast with the sensing reagent (indicator). This is done by dissolving the reagent in a solvent at a predetermined concentration and soaking the porous fiber in the solution. The reagent is then dried into the pores by air drying or in a low temperature oven. Alternatively, the glass surface can be treated with a silanizing reagent to facilitate chemical coupling to the sensing reagent.

Fabrication of Porous Polymer Optical Fiber

As an alternative to chemical immobilization or physical adsorption in porous glass, porous polymer optial fibers can also be used to create fiber optic chemical sensors. Sensors using these fibers have been demonstrated for ethylene, CO, NH_3, pH, and humidity detection. The principle of porous polymer fiber sensors has the same basis as porous glass sensors. Consequently high sensitivity is achieved. In this approach the indicator is dissolved directly into the monomer solution before forming the polymer fiber; therefore, the indicator is strongly bonded to the polymer network. In fact, the porous polymer approach provides the advantage of both chemical bonding and physical entrapping of the indicator. Also, the pore size and the amount of indicator can be precisely controlled by changing the composition of the monomer solution, resulting in very good sensor-to-sensor reproducibility. This fabrication process is additionally quite suitable for mass production. This reduces the cost of optrodes.

The porous polymer fibers are prepared by a heterogeneous copolymerization technique. The basic principle behind this technique is the polymerization of a mixture of monomers which can be crosslinked in the presence of an inert and soluble component solvent. Subsequent to polymerization, the inert solvent which is not chemically bound to a polymer network, is easily removed from the polymer leaving an interconnected porous structure.

Monomer starting solutions are prepared which contain the crosslinker, initiator, inert solvent and chemical indicator. The mixture, including the indicator, is injected into a length of glass capillary, (typically 500 microns in diameter). The filled glass capillaries are sealed such that they are virtually free of air, and polymerization is initiated and completed in a low temperature oven. After polymerization, the uniform and transparent polymer fibers are pulled out of the capillaries. Finally, the fibers

are washed in an organic solution to remove any remaining inert solvent.

A combination of parameters determines the final physical properties of the cross-linked polymer network. These include the solvent properties, amount and type of inert solvent, as well as the quantity of cross-linking agent employed.

Results and Discussion

Porous glass and porous polymer optrodes have been designed and demonstrated for aromatic fuel vapors (benzene, toluene, xylene), hypergol vapors (hydrazine and UDMH), for NH_3, CO and ethylene. Similarly, optrodes have been demonstrated for the chemical parameters pH, humidity and moisture content.

A pH Optrode System is currently under development which is applicable to a variety of field screening and contamination monitoring tasks. Porous glass pH optrodes have been fabricated which are operational in the pH 4-8 range. A unique co-immobilization technique was developed to tailor the sensor pH sensing range to a specific application. Optrodes are fabricated by first silanizing the porous fiber surface to facilitate the attachment of the sensitive indicator material. Spectral transmission scans are conducted in order to identify the wavelength region of maximum sensitivity to pH. The sensor interrogation wavelength is selected based on these spectral scans.

Optical intensity versus time measurements as a function of pH, have been made for each optrode at the interrogation wavelength. The sensitivity and linearity is determined by plotting optical intensity at equilibrium, versus pH. Figure 3 shows the response of the optrode with an immobilized indicator. The sensor is operational between pH 4 and pH 6.5, with greatest sensitivity and linearity between pH 4.5 and pH 6. Saturation of the sensor response occurs at pH values above 7 and less than 4.

A second indicator, which is structurally very similar to the first indicator, has been tested with the intent of increasing sensitivity at higher pH values. The response of this indicator is presented in Figure 4. The data indicates good linearity and sensitivity above pH 7.

A mixture of the two indicators was immobilized in a porous glass fiber. The results with this sensor are shown in Figure 5. The data indicates both excellent sensitivity and linearity across a pH range extending from 4 to 8. The co-immobilization of these two indicators represents a unique approach to sensor design and demonstrates that sensing range can be tailored to meet specific requirements.

The reversibility of these sensors has been evaluated. This is accomplished by cycling a test solution, into which the pH optrodes have been immersed, between pH values of 4.5 and 7.

Figure 6 depicts the variation in optical transmission of the pH optrode as a function of time. The data indicate that the sensor is fully reversible and peak to peak reproducibility is better than 90%. The spikes in the response curves are artifacts associated with the test setup. Similar results have been obtained using porous polymer optical fiber.

Fuel Vapor Optrodes

GEO-CENTERS, INC. has designed, fabricated and evaluated porous fiber optrodes for detection of aromatic fuel constituent vapors. A xylene optrode with sensitivity <50 ppb has been demonstrated. Response time, reproducibility, linearity, and selectivity have been determined. Benzene and toluene optrodes have also been demonstrated. Laboratory results indicate that there are highly sensitive optrodes, with near real time response. They are additionally capable of selective detection of target species.

With these optrodes (as well as the hypergol, ethylene, and CO optrodes) the rate of change of the optical transmission is directly proportional to analyte concentration. An example of xylene optrode response to different xylene concentrations is presented in Figure 7. Each curve corresponds to a different xylene concentration. A plot of the slopes of the data in Figure 7 versus xylene concentration is shown in Figure 8. This data demonstrates good sensor linearity from low part per billion to low part per million concentrations.

Hypergolic fuel optrodes have been developed to detect vapors for NASA and U.S. Air Force operation applications.

The principle of operation and sensor response is similar to that of the xylene optrodes. The hypergolic fuel optrodes can be configured as personal dosimeters for industrial hygiene applications or as portable detection instruments. Figure 9 shows a typical optrode response as a function of time for different concentrations of hydrazine. The slope of the optical intensity versus time curve may be correlated to the hydrazine vapor concentration.

Conclusions

Sensors utilizing optical waveguides offer many advantages for hazardous waste monitoring applications including size, near real time response, and low manning and expertise requirements. Additionally, porous glass and polymer optical fibers offer significant advantages in these applications because their large interactive surface area dramatically improves sensitivity. They also provide a continuous optical path. This minimizes mechanical and optical coupling losses. Additionally, sensor interfaces can be developed that allow multi-sensor operation. These chemical optrodes can be applied in a variety of environmental monitoring scenarios, as well as to developmental bioreactors, control of process streams, and industrial hygiene. A family of fiber optic optrodes offers the possibility of effectively having a wet chemistry laboratory that can be brought to the field.

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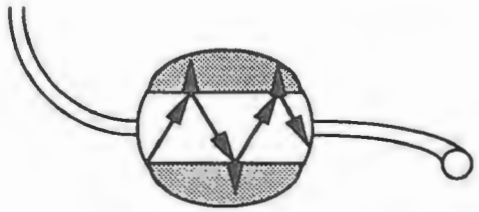
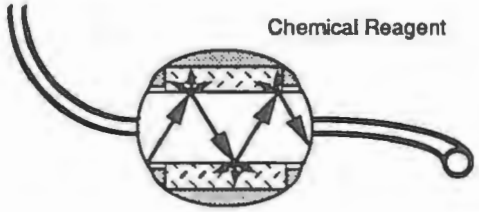
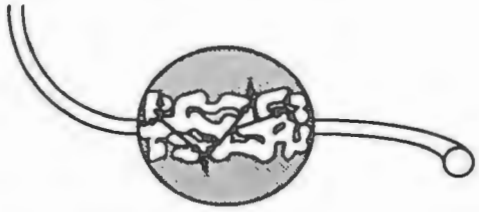


a) Evanescent (Internal Reflection), RFS



b) Evanescent (Internal Reflection), Side Coated FOCS



c) Porous Fiber (In-Line Absorption or Luminescence)

Figure 1.
Schematic Diagram Comparing Basic Sensor Designs

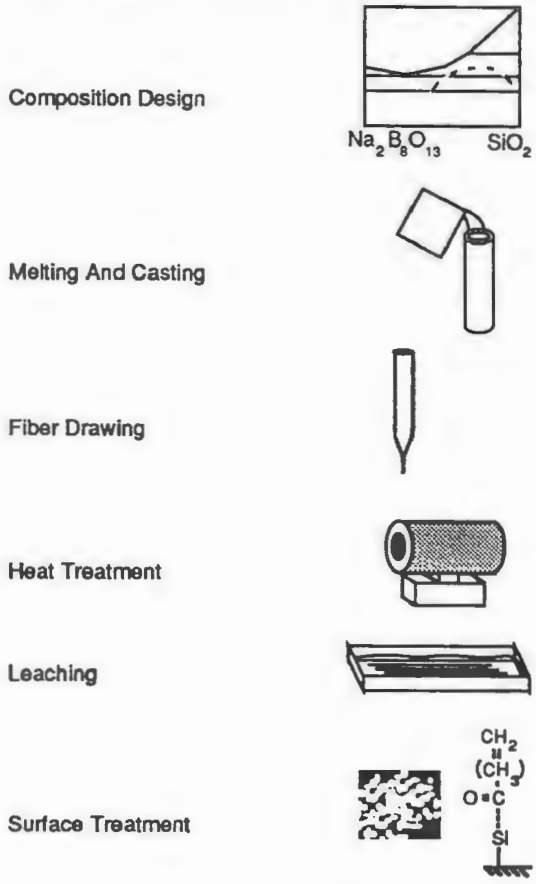


Figure 2.
Processing Steps For Producing Porous Glass Fibers

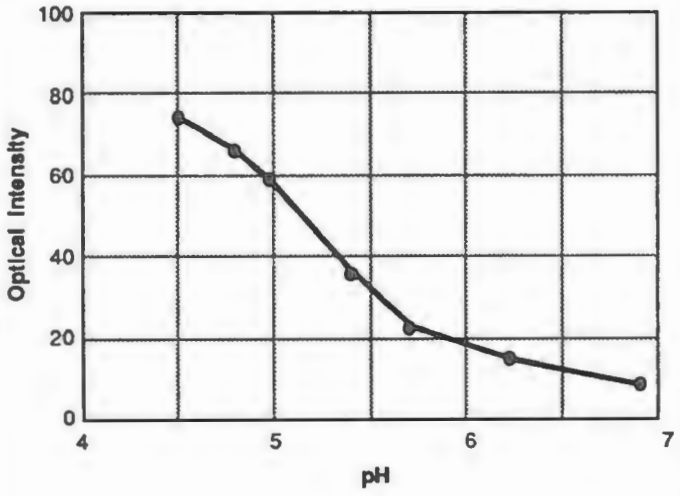


Figure 3.
Sensor Response With Bromocresol Green Indicator As A Function Of pH

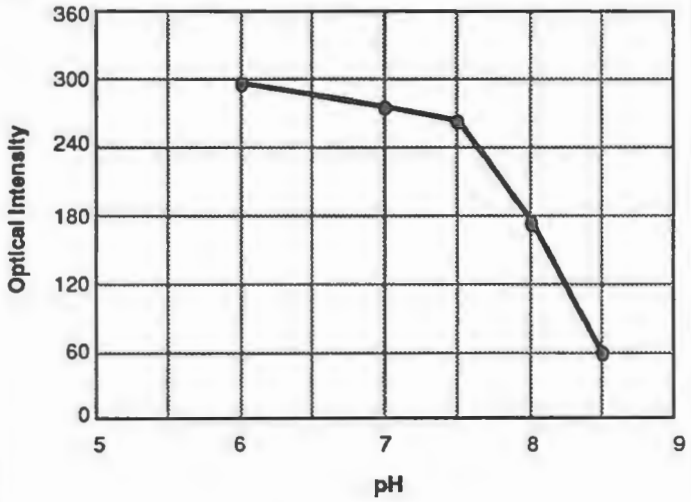


Figure 4.
Sensor Response With Bromocresol Purple Indicator As A Function Of pH

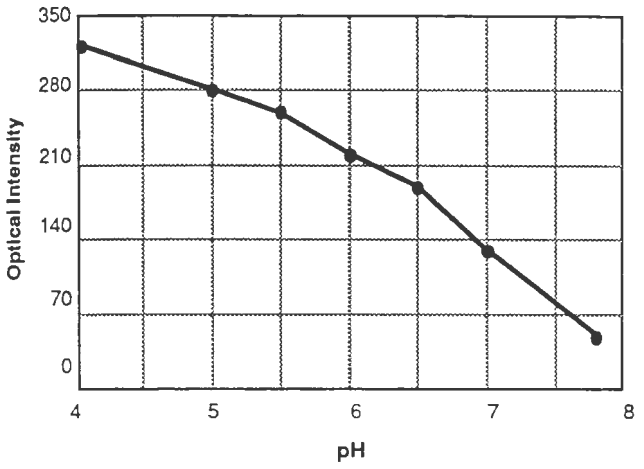


Figure 5.
Sensor Response With Co-immobilized Indicators As A Function Of pH

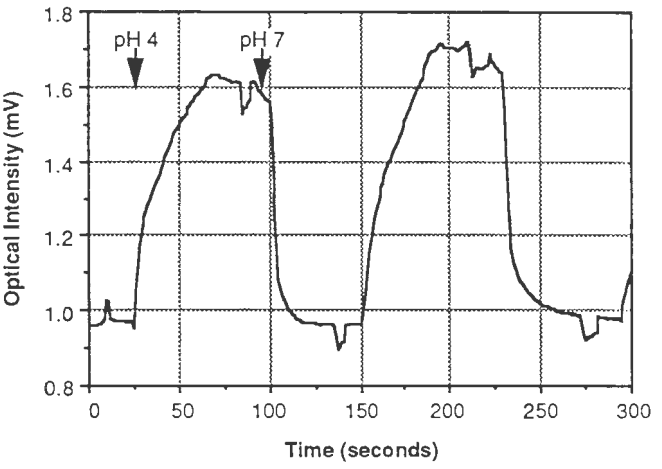


Figure 6.
Optrode response time as a function of pH

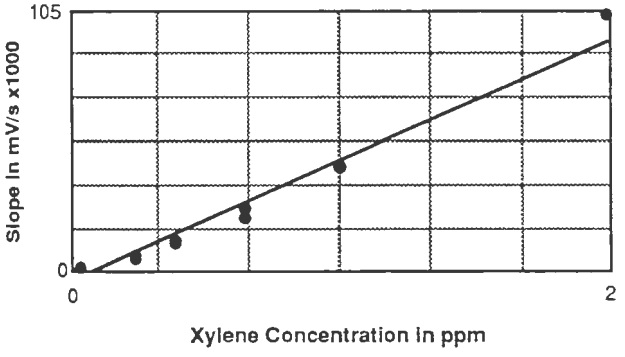


Figure 8.
Calibration Curve for Xylene Optrode Based onPorous Glass Fiber

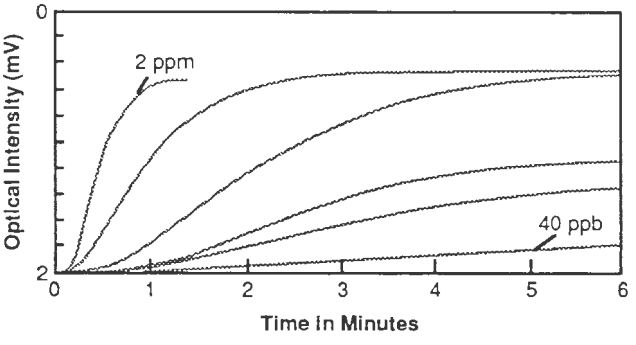


Figure 7.
Response Curves for Porous Glass Xylene Sensor. Xylene Concentrations Range from 2 ppm to ~40 ppb

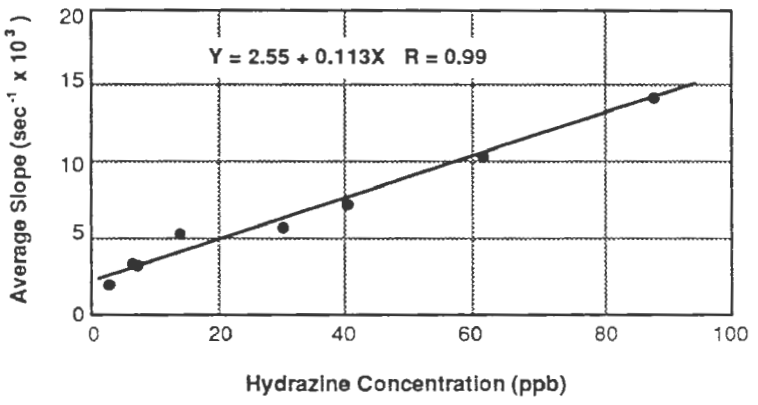


Figure 9.
Optrode Response to Hydrazine Vapor at 32% relative Humidity and 24 °C

Rapid, Subsurface, In Situ Field Screening of Petroleum Hydrocarbon Contamination Using Laser Induced Fluorescence Over Optical Fibers

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ABSTRACT

A new field screening method is described that couples a fiber optic-based chemical sensor system to a truck mounted cone penetrometer. The system provides the capability for real-time, simultaneous measurement of chemical contaminants and soil type to depths of 50 meters. Standard sampling rates yield a vertical spatial resolution of approximately 2-cm as the penetrometer probe is pushed into the ground at a rate of 1-m min^{-1}

The system employs a hydraulic ram mounted in a truck with a 20-ton reaction mass to push 1 meter long, threaded, steel pipes into the ground. The first section of pipe is terminated in a 60-degree cone and includes strain gauges for measurement of tip resistance and sleeve friction. A sapphire window mounted in the side of the pipe, approximately 60-cm above the probe tip, provides a view port for a fiber optic-based fluorometer system. The soil sample is excited through the sapphire window by light transmitted down the probe over a 500 micron diameter, 60 meter long fiber coupled to a pulsed nitrogen laser located at the surface. Fluorescence generated in the soil sample is carried back to the surface by a second fiber where it is dispersed using a spectrograph and quantified with a time-gated, one-dimensional photodiode array. Readout of a fluorescence emission spectrum requires approximately 16 milli-seconds. A micro-computer based data acquisition and processing system controls the fluorometer system, acquires and stores sensor data once a second, and plots the data in real-time as vertical profiles on a CRT display.

Results are presented from the first field tests of the system at a POL (Petroleum-Oil-Lubricant) contaminated hazardous waste site. Initial results from a series of more than thirty pushes indicate that the system is useful for rapid characterization, in three-dimensions, of the boundaries of a POL contaminant plume at concentrations equivalent to sub-parts-per-thousand of diesel fuel marine. Vertical fluorescence profiles show significant small scale vertical structure on spatial scales of a few cm. This vertical micro-structure appears to correlate with soil characteristics estimated from point resistance and sleeve friction. Field and laboratory calibration of the fiber optic sensor system using different fuel products is presented and discussed. Sensor performance is characterized as a function of soil moisture content.

Introduction

Defining the location and extent of subsurface chemical contamination is a difficult task. Detailed site investigations require installation of many monitoring wells and subsequent analysis of discrete soil and groundwater samples. Effective site characterization is often limited by the ability to select optimal locations for monitoring wells. Furthermore, the ability to resolve horizontal and vertical features in the distribution of chemical contaminates is a function of limitations imposed by the spacing between wells and the vertical spacing between samples.

At present, locations for monitoring wells are usually based on information gleaned from site historical data, ground water hydrology, and/or indirect chemical screening such as soil gas measurements. Because of uncertainties in the information available, well placement is at best an inexact science. Historical data is often incomplete or inaccurate. Knowledge of groundwater hydrology at the site may not provide the level of detail required to understand site characteristics. Interpretations of soil gas measurements may be complicated by erratic movement of vapor in the soil due to impervious layers and changes in atmospheric temperature and pressure. Consequently, many wells are not properly positioned and, therefore, yield information of marginal utility.

Accurate delineation of the boundaries of contaminant plumes and defining small scale vertical structure in the distribution of contamination has important implication with respect to site remediation. The more precisely the area of contamination is defined, the less likely it is that "clean" material will be unnecessarily removed or subjected to costly remediation procedures.

Improved techniques for *in situ*, subsurface, field screening would have several benefits. Knowledge of the distribution of chemical contamination in soils and groundwater could be used to more effectively guide the placement of monitoring wells and thereby, greatly reduce the number of wells required. Field screening methods that provide real-time chemical information at closely spaced intervals could be used to rapidly delineate small scale horizontal and vertical structure in contaminant plumes. In addition to increasing the effectiveness of site characterization there should also be a significant cost savings

Figure 1. Photograph of penetrometer truck developed for use with the fiber optic fluorometer system. The data acquisition system and fluorometer system are located in the rear compartment. The hydraulic system used to push the penetrometer probe into the soil is in the foward compartment.

associated with the reduced requirement for monitoring wells and associated analytics.

Towards this goal of improving capabilities for rapid site characterization, we have equipped a truck-mounted cone penetrometer system (Fig. 1) with a fiber optic based, laser-induced fluorometer system. Cone penetrometers have been widely used for determining soil strength and soil type from measurements of tip resistance and sleeve friction on an instrumented probe (1). The probe is normally pushed into the ground at a rate of approximately 2-cm sec^{-1} using hydraulic rams working against the reaction mass of the truck. For a 20 ton vehicle, the standard (35-mm diameter) penetrometer rod can be pushed to a depth of approximately 50-m in normally compacted soils. In order to extend the measurement capabilities of the penetrometer system to chemical contaminants of environmental concern, it is possible to use the penetrometer system as a platform for insertion of other sensors into the soil. To date, use of penetrometers for direct sensing of chemical constituents in soils has been limited to resistivity measurements (2) and sensors for measuring radioactivity (3).

This report describes the development of an optical based sensor for direct *in situ* screening of chemical contaminants. The system employs optical fibers to make remote laser-induced fluorescence measurements through a window in the probe tip. The system can be used to characterize contaminant plumes that contain compounds that fluoresce when exposed to ultra-violet light. In its present configuration, which uses a nitrogen (N_2) laser (337 nm) excitation source, the system is selective for polycyclic aromatic hydrocarbon compounds which are components of POL products. Coupling the optical fiber sensor with the cone penetrometer provides a capability for direct, real-time sensing of petroleum hydrocarbon compounds in soils that has not previously existed.

System Description

A schematic diagram of the fiber optic fluorometer system is shown in Fig. 2. The system was adapted from a design originally developed for *in situ* fluorescence measurements in seawater (4-5). The penetrometer system uses two silica clad silica UV/visible transmitting optical fibers. One fiber is used to carry excitation radiation down through the center of penetrometer pipe and a second fiber collects the fluorescence generated in the soil sample and carries it back to the detector system. Excitation and emission fibers are isolated from the sample at the probe tip by a 6.35-mm diameter sapphire window mounted flush with the outside of the probe approximately 60-cm from the tip. Although different fibers from several sources have been employed, the fibers used in studies reported here were 500-μm in diameter and 60-m in length, unless otherwise noted. Attenuation was specified by the supplier to be about 100 dB/km at 337 nm (this corresponds to 25% transmission at 337 nm for a 60 m fiber .

Excitation radiation is provided by a pulsed N_2 laser (Model PL2300, Photon Technology, Inc) that operates at 337 nm with a pulse width of 0.8 nsec and a pulse energy of 1.4 mJ. The beam is coupled into the excitation fiber using a 2.5-cm quartz lens. Because of asymmetry in the beam dimensions, 6-mm x 9-mm at the laser aperture, coupling losses into the fiber are somewhat greater than what would be expected for a conventional Gaussian resonator type laser. No attempt has been made to reshape the beam to improve coupling. Instead, we take advantage of the non-symmetrical beam shape by using a separate length of optical fiber to intercept a portion of the laser beam that would not normally be coupled into the excitation fiber. This auxiliary fiber is coupled to a photodiode that is used to provide an optical trigger for time gating the detector. Optical triggering of the detector eliminates problems associated with laser jitter that are experienced with electronic triggering of

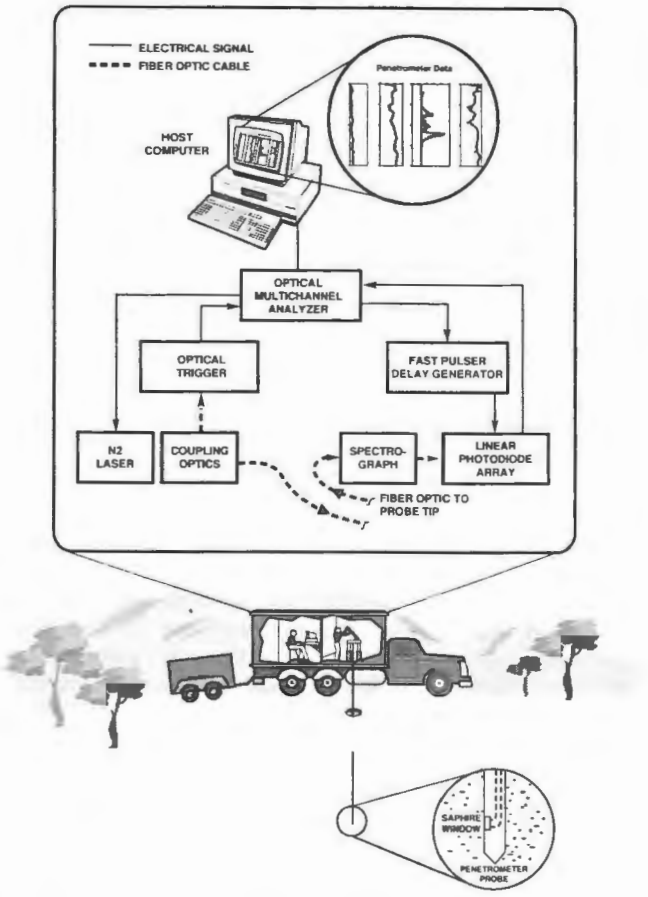

Figure 2. Schematic of laser induced fiber optic fluorometer system.

the detector.

A photodiode array detector system is used to quantify the fluorescence emission spectrum brought back to the surface over the second 60-m fiber. The detector system consists of a Model 1420 Intensified Photodiode Array Detector (EG&G PARC) coupled to a quarter-meter spectrograph which houses a 300 line/mm diffraction grating. The 1024 element array consists of 25 micron wide diodes centered at 25 micron increments. For the 300 line/mm grating the dispersion of the spectrograph translates to a spectral resolution of 0.45 nm per pixel at the array surface when a 25 micron input slit is used. The resolution may be increased to 0.075 nm per pixel by using an 1800 line/mm grating. Readout of an emission spectra requires approximately 16 msec. Because the detector can be readout quickly it is possible to add spectra from multiple laser shots in order to improve the signal to noise ratio of the measurement. Typically, 10 laser shots are used per sample interval.

Control and readout of the detector is performed by a Model 1460 optical multichannel analyzer (OMA) (EG&G PARC). Measurements are initiated by an electronic signal from the OMA that fires the laser. The laser pulse then triggers an optical trigger (Model 1303, EG&G PARC) which sends an electronic signal to a fast pulser (Model 1302, EG&G PARC). The fast pulser implements an appropriate delay and gates the detector "on" for a period of 20 nanoseconds. Fast-gating of the detector activates it only during the time period when the fluorescence signal is present, thereby minimizing any contribution to the signal from background light and detector noise.

Incrementing the delay of the detector gate for successive laser pulses also permits determination of fluorescence decay times. Other studies have shown that differences in fluorescence decay times are useful for discriminating compounds of environmental interest (eg., polycyclic aromatic hydrocarbons) that cannot be resolved based on differences in their fluorescence emission spectra (5). At present, fluorescence lifetime measurements are not performed routinely with the penetrometer system because additional measurement and processing time would be required. In the future, however, fluorescence decay measurements could easily be implemented via software control to take advantage of "dead time" that is currently not utilized when the push is halted every meter in order to install the next section of pipe.

An Intel 386 based microprocessor host computer is used to automate the overall measurement process. The host computer controls the OMA system and stores fluorescence emission data received from the OMA and data from strain gauges on the probe tip. A representative fluorescence spectrum obtained

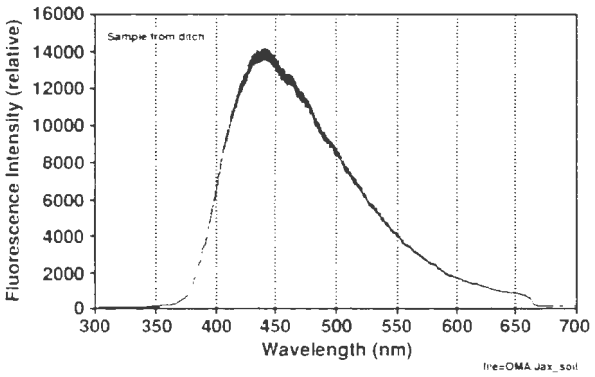

Figure 3. Fluorescnece emission spectum measured for contaminated soil using fiber optic fluorometer system.

from contaminated soil at the first test site is shown in Figure 3. The host computer is also used to generate real-time depth plots on a CRT of the chemical fluorescence measurements and soil characteristics as interpreted from the strain gauge data. Under normal operating conditions, fluorescence measurements are made at a rate of approximately once a second. For the standard push rate of 2-cm sec^{-1} this corresponds to a vertical spacial resolution between measurements of 2-cm. Because each fluorescence measurement consists of intensities measured at 1024 wavelength points, a push to a depth of only 10 meters will generate more than 500,000 data points. In order to simplify data presentation a window (approximately 50 nm wide) is set in the spectral region anticipated to contain the maximum fluorescence intensity. The average fluorescence intensity in the spectral window is then plotted as a function of depth, in real-time, as the probe is pushed into the soil. A typical data plot is shown in Figure 4. The entire fluorescence emission spectrum is stored on a fixed disk to facilitate post-processing of the data

Characterization and Calibration of Sensor Response

Initially, there were several practical concerns about the viability of using an optical fiber system to make *in situ* measurements in soil in conjunction with the cone penetrometer. Issues of concern included: (1)Would the sapphire viewing window retain contaminant after exposure and thereby exhibit a memory effect? (2)Could the optical fiber withstand the necessary handling required to thread it through the penetrometer pipe during insertion and removal? (3)Would the constant flexing of the fiber during measurement significantly alter the attenuation characteristics of the fiber and thus, invalidate quantitative measurements? Experience gained to date, suggests that none of these issues appears to be a problem. Inspection of data in Fig. 4 shows that when the probe was pushed through layers of soil containing relatively high concentrations of contaminant, fluorescence intensities rapidly approached background levels as soon as the probe moves out of the contaminant zone. This suggests that the high pressures acting on the window as the probe is forced through the soil are effective in removing any residual contamination that might be adsorbed on the window. Field experience to date demonstrates that the fibers can withstand the normal handling required for operations with the penetrometer. No fiber failures have occurred during the more than 80 cone penetrometer tests (CPTs) that have been made so far. Finally, measurements in the field showed that there was no measurable difference in the amount of laser energy transmitted through the 60-m excitation fiber depending on whether the fiber was laid out on the ground with no bends or threaded through 50 meters of penetrometer rod with a 180 degree bend approximately every meter (as was normally the case). It appears that as long as the minimum fiber bend radius, for which total internal reflection is maintained for all modes, is not exceeded there is no significant variation in throughput loss.

Response of the fiber optic fluorescence sensor has been calibrated both in the laboratory and in the field using different fuel products added to soils. We have elected to use fuel

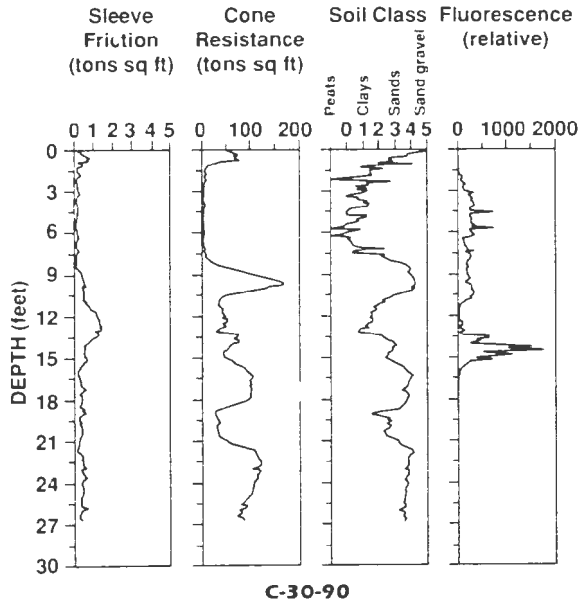

Figure 4. Example of real-time display showing vertical profiles of soil characteristics and chemical fluorescence measurements.

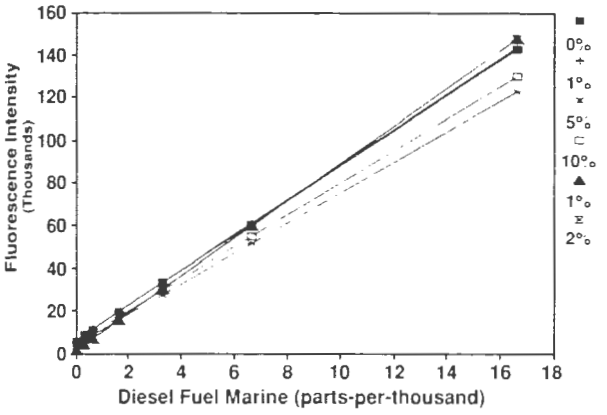

Figure 5. Laboratory calibration curves for DFM in soil as a function of soil moisture content.

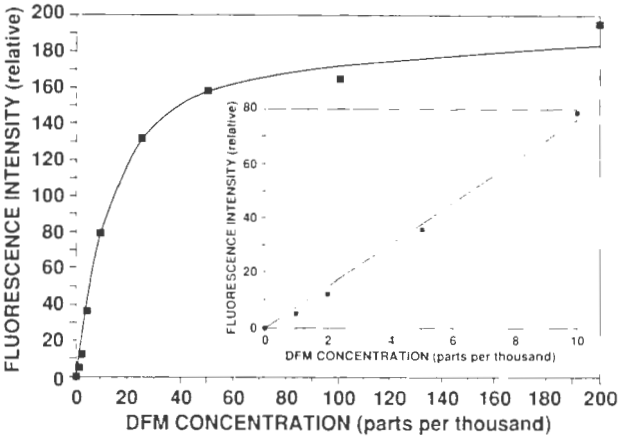

Figure 6. Field calibration of penetrometer fiber optic sensor using diesle fuel marine in sand. Inset shows response is linear below 10 ppt.

products rather than pure compounds because fuel products contain a representative mixture of the compounds that may fluoresce in environmental samples. Obviously, there is no way to be sure that the distribution of compounds that respond to our measurement system in the field is an exact match to the product we select for calibration. In fact, in many cases there will undoubtedly be a mismatch between the distribution of compounds in the product used for standardization and the mixture of compounds present at environmental "dump" sites. These sites may contain a potpourri of products that have had time to undergo degradation and loss of more volatile components. However, at sites such as tank farms that contain recent or ongoing fuel leaks, it may be possible to get a good match between the product used to calibrate the sensor and the product in the ground. Therefore, it should be stressed that the utility of the system, in its present form, is for rapid delineation of hydrocarbon contaminant plumes in order to guide the placement of monitoring wells. With these qualifications with respect to calibration in mind, data is presented which shows that the fluorescence sensor appears to be at least a semi-quantitative sensor for *in situ* screening of petroleum hydrocarbons.

Laboratory results (Fig. 5) show that measured fluorescence intensities increased linearly as a function of diesel fuel marine (DFM) added to uncleaned beach sand. Added quantities of DFM ranged from 500 to 20,000 parts-per-million (ppm) for this experiment. Standards were generated by adding known quantities of fuel product to weighed samples of "clean" soil and tumbling the mixture overnight in tightly sealed glass containers. Figure 5 also shows that the measured response did not change significantly when the water content of the soil was varied from 0 to 10%. Other calibrations using jet fuel (JP-5) in sand also showed that the fluorescence response did not change when the water content of the soil sample was varied from 0 to 25%. This suggests that the response of the fluorescence sensor should be relatively insensitive to changes in soil moisture content as the probe moves through the vadose zone into the saturated zone.

The penetrometer fluorescence sensor was also calibrated in the field by placing a cylinder over the sapphire window and filling it with "clean" beach sand (Fisher Scientific) containing added quantities of DFM. Results (Fig. 6, inset) show linear response ($r^2 = 0.99$) for concentrations in the range of 1000 - 10000 ppm. This is similar to laboratory results discussed above. Figure 6 shows that for higher concentrations, fluorescence intensities appear to approach a saturation value at about 10% DFM in sand (weight/weight). This appears to set an upper limit on the concentrations that can be quantified with this system. We believe this saturation effect arises because the fluorescence response of the sample is to a large extent a surface phenomena. At high concentrations of fluorophore, the surface of the soil particles become saturated with product and therefore, the fluorescence approaches a limiting value. The lower limit of detection for the system configuration described in this report is approximately 100 ppm (two times noise) using 10 laser shots. Detection limits can be improved, at the expense of analysis time, by increasing the number of laser shots that are stacked for each sample interval. Efforts are currently in progress to determine the effect of soil type on fluorescence response and to evaluate the "depth of view" of the fluorescence measurement (ie., how far into the sediment adjacent to the sapphire window does the measurement penetrate).

Results of initial field tests

Initial field tests of the fiber optic fluorometer equipped penetrometer were conducted at a hazardous waste site in the southeastern United States. The site, which dates back to the 1940's, had been used for several decades as a disposal area for mixed petroleum wastes. In the mid-1980's a ditch was dug around the site and a recovery system installed. A map of the site showing locations of the CPTs is given in Figure 7. Figure 8 shows representative results from a transect paralleling the recovery ditch (CPTs 30-37). The depth of sampling in this study was limited to 30 ft by a hard limestone layer. Inspection of the fluorescence profiles indicates that hydrocarbon related fluorescence was detected at locations 30, 32, 33, 35 and 36 but not at location 34 or 37. These results illustrate how it is possible to rapidly delineate the horizontal extent of the contaminated area by making a series of CPTs at the site. Each CPT required

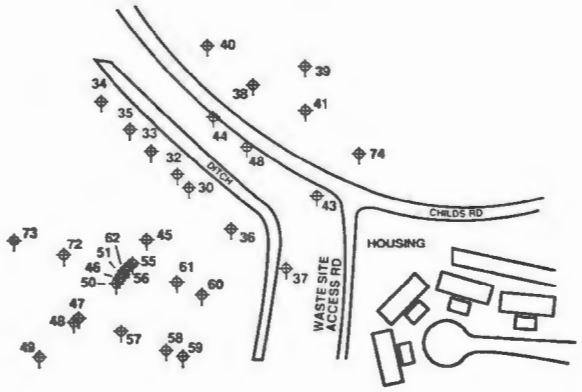

Figure 7. Map showing locations of cone penetrometer tests (CPT's) at test site.

approximately 20 minutes to complete. Detailed inspection of the vertical structure in fluorescence profiles at the locations with the highest fluorescence intensities (CPTs 30, 32 and 36) shows marked similarities. Highest intensities were observed at a depth of approximately 15 feet with a secondary maximum at about 10 feet and background levels at the surface and at the bottom of each profile. Similarity in the vertical structure exhibited by the fluorescence profiles at the three locations and the covariance with measured soil characteristics supports the hydrogeological consistency of the data. The observation that CPTs 34 and 37 showed no measurable fluorescence suggests that at this site naturally occurring organic material did not contribute to measured fluorescence signals. In order to facilitate interpretation, fluorescence and soil property data from individual CPTs can be combined with position information and transformed (Dynamic Graphics, Inc) into a 3-dimensional gridded file for visualization on a minicomputer system. Figure 9 shows an example of a 3-dimensional representation of the fluorescence data from the CPTs at the sites indicated on the map in Figure 7. For this example, fluorescence intensities have been converted into diesel fuel equivalents using the linear portion of the calibration curve presented in Figure 6.

Conclusions and future efforts

Efforts to date suggest that use of a fiber optic based fluorometer system in conjunction with a cone penetrometer may be useful for rapid delineation of subsurface petroleum hydrocarbon contamination at hazardous waste sites. Laboratory and field calibration of the fluorometer system using fuel products (diesel fuel marine and JP-5) indicates that the fluorometer system is quantitative for direct determination of these products in soil

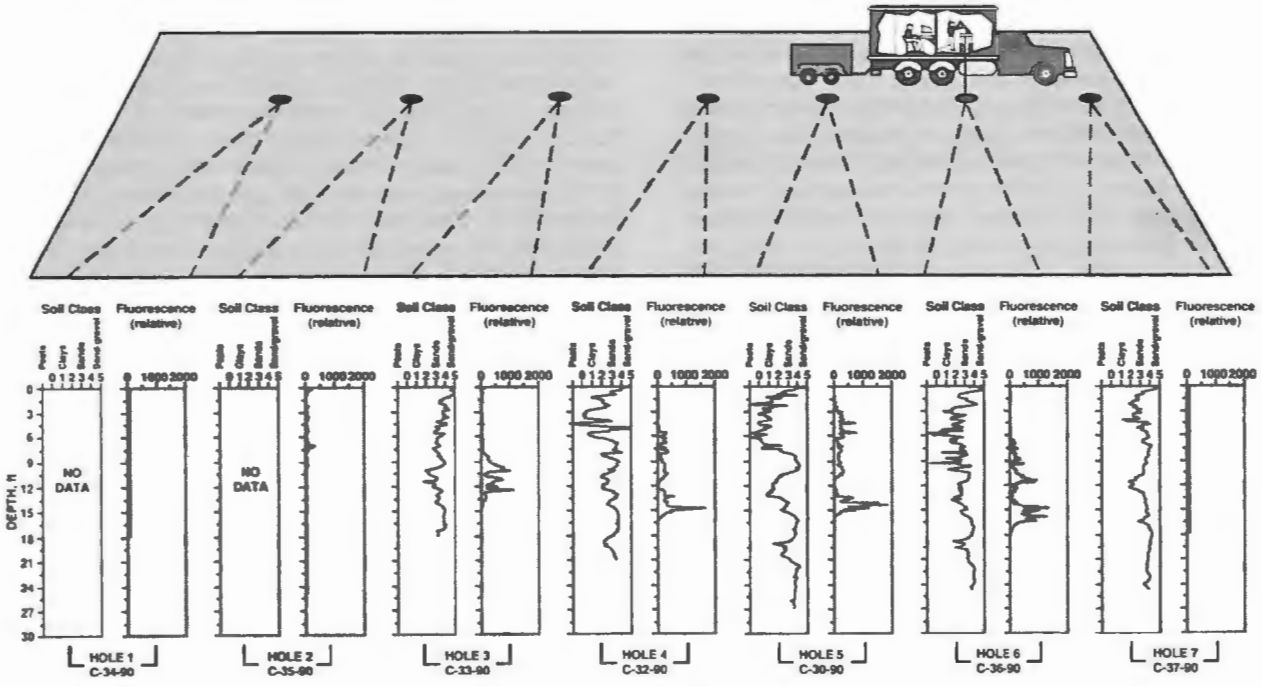

Figure 8. Test data showing the use of the fiber optic fluorescence sensor for locating the boundaries of a hydrocarbon plume.

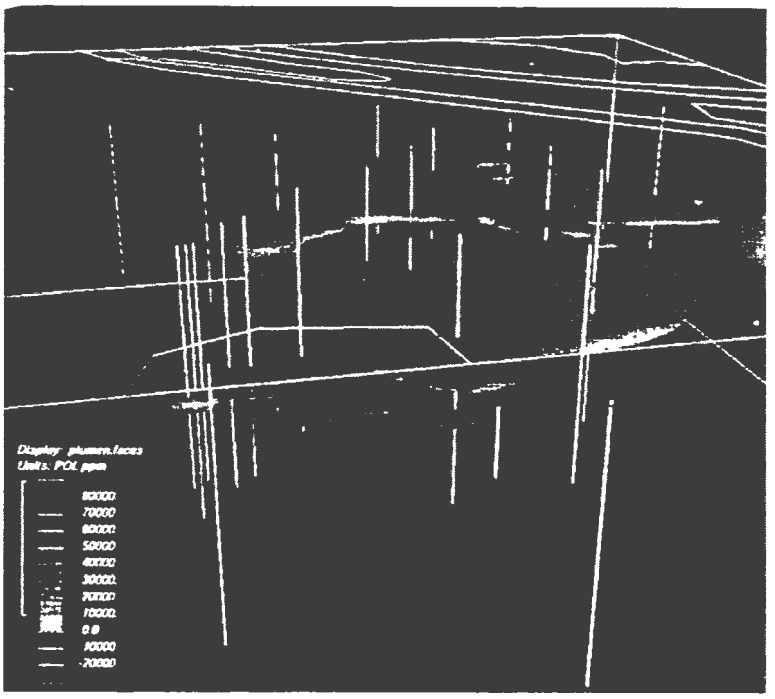

Figure 9. Eample of 3-dimensional visulation of soil contamination based on CPT data. The volume shown represents areas that had fluorescence intensities equivalent to 1000 ppm or more diesel fuel marine. The lines on the upper surface represent cultural features (ditches and roads) present at the site.

(sands) for concentrations in the range of 100 ppm to 10000 ppm. At present, the greatest utility of the system is for rapid screening for POL contamination in order to more precisely locate contaminated zones, and thus significantly reduce the number of monitoring wells required for site characterization. The accuracy of converting measured fluorescence intensities to concentration units will depend on how closely the product used for sensor calibration emulates the product in the soil. Experience in the field indicates that the optical fiber system is rugged enough to withstand normal deployment procedures with the penetrometer system and that the sapphire viewing window appears to be self-cleaning, thereby avoiding memory effects.

Efforts currently planned, or in progress, include: (1) rigorous intercomparison of penetrometer field measurements with conventional sampling and standard analytical methods, (2) characterization of the effect of different soil types and characteristics on system calibration, (3) enhancing the capabilities of the sensor system for measuring compounds that are excited at higher energies by replacing the N_2 excitation source with a Nd-YAG operating at the third and fourth harmonics (355 and 266 nm).

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DISCUSSION

The following is a panel discussion in which questions were posed to the first three authors of papers in the Chemical Sensors Session.

DICK GAMMAGE: Most of the data you showed was for sand. You're going to have different quenching problems, different degrees of quenching for different soils. Can that throw you out at all? Also, I thought the original intent of this device was to be able to lower it directly into groundwater and take in water measurements. And I'm wondering why your focus seems to be totally on the headspace at this stage?

STEPHEN LIEBERMAN: I'll talk about this soil type question. That's a good question. It's something that has been on our mind. We actually have a laboratory study going right now where we're going to evaluate the effect of soil type on the response of the sensor. One of the other considerations with soil type, and this was something we visually observed, is if you have a sand the sample volume is going to be different than if you have a very fine grain clay or something like that. We have not parameterized that or really documented what that effect is yet, but we are looking at that. That's kind of one of the drawbacks of rushing some of the stuff out in the field, just to see if you can get that fiber down there without breaking in and some of those very basic questions. But we haven't ignored that.

FRED MILANOVICH: The answer to the second part is a quite complicated answer. The experience we've had is that headspace measurement is far and away more reproducible. And since this is a result-driven technology, we want something that works. When we designed the continuous probe the reagent is now in contact with a membrane. When we wet it on the other side with water, we have problems. In the original probe there was an air space, and you could stick that probe into the water. With the membrane being teflon, the wetting phenomenon was different than what has been exposed to the pyridine. So some work would have to be done there. But I don't see there's a great liability to stay with headspace.

JOHN SCHABRON: How often do you have to recalibrate the probe? I guess now that you can introduce solution into it, you can calibrate it more frequently. Could you also address the issue that, with the two diodes, the red and the green, you're not compensating for the difference in output of the two diodes as you would if you had a single lamp and a monochromator with two different wavelengths.

FRED MILANOVICH: The calibration issue is a function again of a lot of factors. If you make enough reagent and it's stored cold, you can go with the calibration. We've gone months with the calibration. But if you mix a new reagent, open a new bottle of pyridine, chemistries are different. So you'd have to recalibrate.

MARY BETH TABACCO: Basically we found that you can adjust the output from those two diodes to make them match, make one greater or one less. The ability for the ratio to remain constant isn't dependent on the output from the diodes. In the graph that I showed you, the green output was lower. In fact, the system electronics that we've built, the green is just about the same output value. By adjusting the current to the LED, you adjust the output value.

DeLYLE EASTWOOD: As some of you may know, there is a fiber optic committee chaired by Dr. Tuan Vo-Dinh of Oakridge which is working on developing the calibration standards, fluorescence standards and standards for terminology, and collecting a data base for fiber optic chemical sensors. We use the term fiber optic chemical sensors because as some of you know, Optrode is a registered trademark. Dr. Vo-Dinh is giving a presentation on that at the Pittsburgh conference in Chicago, Monday, March 4. I will also chair a meeting on luminescence at that conference.

There's been a lot of previous work on classification and identification of oils, some of which is in the literature, and is the basis for a couple of ASTM methods. My question is, do you plan to use another laser and fiber to measure BTX?

STEPHEN LIEBERMAN: Yes, but I'm not sure we're going to get down to BTX. We did have plans to use a different excitation source. That should be coming on line, should at least be available to us about the end of this month. That will give us the 266 and 355 excitation. But I think benzene and others are even excited at lower wavelengths. The thing we're bucking there is the transmission down the fiber. As you know, the attenuation dramatically increases as you go down in the UV. So right now the 337 is kind of a nice compromise between what we can get down there and a wavelength that will excite some of the 2, 3, 4-type ring compounds. But if we could get the energy down there, it would be real nice to try to go 200 or so. But I don't see that happening right now. I think 260 is going to be pushing it. Even at that, we're going to be brute forcing the energy down there. So I think we may be approaching the damage threshold of the fiber, versus what we can get out the other end.

GORMAN BAYKUT: I have a question about telling compounds apart in a mixture. You gave an example of a mixture of three compounds. If you have a high concentration of some compounds with a very low concentration of another compound, do you have any problems with determining them just using the slopes?

STEPHEN LIEBERMAN: We have not actually done experiments where we've juggled concentrations of these different compounds and really determined what the range of concentrations we're able to discriminate. Obviously that's a concern. We've done a little bit of work using Lifetimes as a way to discriminate different metal ions that complex with a particular indicator molecule. We've had some success fitting biexponential curves to those compounds. But again, we haven't really pushed the limit by having tremendous differences in concentration. Our current thinking is it's going to take a combination of techniques and maybe a smart pattern recognition-type techniques. We may be looking a neural networks as a way. But obviously, there's going to be some point in the differences in concentration that you're going to be able to determine.

FRED MILANOVICH: In these experiments we actually prepared the solution so that they'd give a similar initial intensities.

BRIAN PIERCE: I have four questions: (1) These indicators in your porous meter, are these reactions reversible? (2) What are the polymers you're using in your porous polymer monitor or sensors? (3) Have you considered waveguide configurations? (4) How is it possible to construct these 3-D visualizations from the finite number of points that you've sampled? What kind of assumptions go into that?

MARY BETH TABACCO: We're working with both reversible and irreversible systems. The pH Optrodes, the ammonia sensors are all fully reversible. Right now, for some of the other vapors sensors for hydrazines, carbon monoxide, we have irreversible indicator systems. But as I mentioned, in e case of the irreversible systems we've demonstrated that by monitoring the slope you can look at real time changes in concentration. For example, with ethylene, we've cycled concentrations from 100 ppb to 100 ppm and you basically can monitor the change in the slope to pull out real time information.

Your third question was about waveguiding. And no, we've not considered that approach here.

Concerning the actual polymers we're working with, we're using a variety of polymer systems, both hydrophilic and hydrophobic. These are methylmethacrylate systems with bis-acrylamide cross-linkers. The actual formulation varies depending on the sensor. We have applied for a patent for the pH Optrode under development. But as I mentioned, it is kind of a witch's brew at this point.

STEPHEN LIEBERMAN: By the 3-D visualization I assume you mean the fancy three-dimensional figure of field data. I'm not quite sure if I understand the question. There's actually a lot of data points here that represents about 30

DISCUSSION

pushes. We're firing that laser about once a second as we're pushing it into the ground. So we're getting a point in the vertical about every two centimeters. Now obviously you have to be careful in any kind of three-dimensional visualization — it only represents reality as good as those contouring algorithms. I think the proper way is to first plot out your raw data in cross-section or by profile. You have to make sure that the visualization you generate by the more sophisticated computer program reflects the reality of what you saw in those individual profiles.

MARTY HARSHBARGER-KELLY: What is the software package you're using on that MacIntosh for data manipulation and who's the software manufacturer?

FRED MILANOVICH: The software package is Lab View. It's all icon driven, so no words are typed to do all that interfacing, just moving icons around. I believe the software manufacturer is National Instruments.

BERT FISHER: Your instrument is measuring polyaromatic hydrocarbons, so it's a bit misleading to say that you're measuring product, because you're measuring some chunk of that. Also, this really should be able to look at historical spills. Have you looked at weathered materials, because the PAH's will hang around. And my comment on the three-dimensional visualization is, it's a lot like doing geology. You have great resolution in the vertical and you accept the horizontal on faith. So it's like doing stratigraphy.

STEPHEN LIEBERMAN: As to your question regarding weathered product, I showed you data from a Jacksonville site that has a rather checkered past. Those deposits go back 30 or 40 years. Now in geological terms that may not be your idea of a weathered product, but it's not a fresh product. Actually there's some work I know out of the petroleum people that shows that those PAH spectra don't seem to change very much as a function of time, at least with the PAH components, but we don't have any real evidence. This is also sort of a brute force method here. We're taking this thing out on the field and we're sticking it in the ground. We don't know very well what's down there or what we're even looking at. Personally I think it would be much nicer to go to some sites where we have some more recent leaks from a tank farm or something like that where we could put ourselves to a better test of whether we can discriminate for instance JP5 from diesel fuel. Hopefully we would also have information on how old the product is and how long it's been in the ground.

BERT FISHER: That really was my concern, in that you would be seeing stuff where there in fact was no product, but you were looking at a tremendous amount of PAHs that had been hanging around for many years.

STEPHEN LIEBERMAN: That may be the case in that example.

PETER KESNERS: As I understand your apparatus, there's a membrane permeation front on it. What sort of membrane types have you investigated? Do you think it's feasible to measure pyridine in water with other membranes with the sensor working the other way around?

FRED MILANOVICH: That's a real interesting plot. Our concern with the membrane is to keep pyridine out of the water, so we have solicited help anywhere we can. The current membrane that works the best is plumber's tape, simple expandable teflon plumber's tape. And that's a result of trial and error from attempts too numerous to mention. Probably 40 or 50 membranes have been tried and plumber's tape is the best. We do have some proprietary technology from companies that we aren't able to speak about yet that could exceed the plumber's tape.

TODD TAYLOR: It seems to me that the calibration curve that you showed on the screen is going to depend on quite a few things in addition to the soil type. It seems to me it's going to depend on the water content, because water is going to affect the amount of oxygen quenching going on in the soil. It's going to depend on the oxygen concentration. Surface soils are known to contain a lot of humic materials, and those materials naturally fluoresce. Their fluorescence, in fact, depends on metal concentration in the soil. So it seems to me there are quite a few factors which may be involved in looking at the fluorescence of the soil. And the last question is not really a question. It's more the fact that I think that you have a lot more work to do in characterizing your system.

STEPHEN LIEBERMAN: In the previous graph, I did show that we have looked at varying the water content over from all the way dry to up to 10% in the data I showed you and 25% with JP5. And seeing, somewhat surprisingly to me, no real significant change in the response of the sensor. And so I think at least as a first cut we have addressed that. As to the question of humics, we've also considered that question. In the case of the Jacksonville data, we showed the fact that we could leave the area that historically was the site where the contamination was and get down the background fluorescence, at least at that site. I don't think we have a problem with background fluorescence due to the humic substances, although we have done some other tests where we've measured humic substances. We've looked at their spectra characteristics and also looked at their decay times. The decay times for the humic substances appear to be much shorter than what we're seeing for the petroleum products. So if we do run into a case where we are getting background fluorescence due to naturally occurring organics, there's at least some hope that we may be able to resolve that based on their emission curves.

I agree with you, there's tons of problems out there that need to be addressed and looked at in more detail. Our approach has been one to let's push this thing out in the field and see what happens. Let's fill in some of these questions later, when we get some handle on what we are seeing. But I think that the true proof of this thing, and this is where we stand right now, is going to be to do some of these profiles and then rigorous validation of it: to collect samples and analyze them by the more conventional methods. Obviously that needs to be done. And that's going to be the thrust of our effort now.

SPECTROELECTROCHEMICAL SENSING OF CHLORINATED HYDROCARBONS FOR FIELD SCREENING AND IN SITU MONITORING APPLICATIONS

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ABSTRACT

The detection and identification of chlorinated hydrocarbon solvents (CHS) have been demonstrated by combining the principles of spectroscopy and electrochemistry. The successful observation of the CHS is highly dependent on the analysis procedure. The procedure is based on a photon induced electrochemical reaction which is detected by surface enhanced Raman spectroscopy (SERS) on electrodes. The results and methodology of the technique will be discussed.

INTRODUCTION

The importance of techniques to sense and monitor chlorinated hydrocarbon solvents (CHS) are becoming increasingly more important with the intensifying presence of groundwater contaminations. Our research and development effort is aimed at producing a commercial, low cost, field portable instrument for the field screening/in situ monitoring of contamination from chlorinated organic solvents based on spectroelectrochemical fiber optic probes. Some of the advantages of this technique for monitoring a contamination site are cost, small size of sampling probe, real-time analysis, the capability of sensing in adverse environments, and the ability of using a central detection facility. The technique has an advantage over current fiber optic chemical sensing methods for chlorinated organics in that the sensing only takes place when the electrochemical device is turned on. This should enable long term monitoring of a well to be accomplished with only one probe.

Our monitoring system for chlorinated organic solvents is based on the principle of combining spectroscopic, electrochemical and fiber optic techniques (Spectro-electrochemical Fiber Optic Sensing (SEFOS)). SEFOS is, in principle, a generic technique which can be adapted to many different sensing applications. With the SEFOS technique, we use electrochemical methods to reduce the chlorinated organic solvents into reactive intermediates. The reactive intermediates can then react with the "trapping" reagent and spectroscopic changes, such as surface enhanced Raman spectra, are used to sense the chlorinated organics at levels far below their detection means by electrochemical methods alone. Previous work (1) has shown the usefulness of using surface enhanced Raman spectroscopy (SERS) for the detection of groundwater contaminations and the technique has also been successfully applied to fiber optics (2). However, these past experiments have mainly been restricted to aromatic hydrocarbons.

In this manuscript we will discuss some of the fundamental aspects of using SERS for the examination of the following chlorinated hydrocarbons or organochlorides: carbon tetrachloride, 1,2-dichloroethane (DCE), chloroform and trichloroethylene (TCE). Our interest in these compounds stems from their existence in the groundwater at the Department of Energy hazardous waste sites.

EXPERIMENTAL

The Raman spectroscopy system for conducting the SERS experiments at EIC has been previously described (2). The system used at Oak Ridge National Laboratory (ORNL) is shown in Figure 1 and, with the use of an optical fiber for excitation, represents a first step toward a remote fieldable Raman system. Of note in the optical system is placement of the laser line pass filter (BP) after the optical fiber to remove interfering Raman scattering from the fiber itself

(3). Both research groups employed high-resolution spectrometers and diode array detectors for measuring Raman scattering from similar spectroelectrochemical cells. As shown in Figure 2A, each cell was fabricated from a 3 x 6 x 3 cm quartz cuvette with O-ring joints fused into three sides and the top. Electrodes were fed into the cell through O-ring joints and consisted of Pt counter, Ag/AgCl reference, and copper working electrode. The working electrode was placed about 2 mm from the (large) face of the cell between the two electrodes. This orientation minimized the path length of incident and scattered light through the sample solution and simplified alignment of the electrode in the optical system. For transport/concentration studies, a membrane could be sandwiched between the spectroelectrochemical cell and a second cuvette with matching O-ring joint fused into the bottom (Figure 2B).

The spectroelectrochemical procedures were first developed at EIC and then used at ORNL. Electrochemical roughening of polished copper electrodes, consisting of high purity 1.0 mm copper wire, was achieved with an oxidation/reduction cycle (ORC) from -0.6 to +0.2V in a 0.1M KCl electrolyte at 25 mV/sec. Saturated solutions of the chlorohydrocarbon solvents (CHS) in distilled water or 100 µg/ml solutions of CHS in 0.1M KCl were cycled several times under the same conditions and optimum SERS spectra were acquired at -0.2V on the cathodic sweep. All cycling occurred under laser illumination at 625 nm at EIC or 647 nm Krypton illumination at ORNL. The use of the slightly different wavelengths for illumination and Raman spectroscopy did not produce significantly different results at the two labs.

RESULTS AND DISCUSSION

Our results confirmed previous experiments (1) which indicated that carbon tetrachloride was not observable on Ag substrates. In addition, we were unable to observe the chlorinated hydrocarbons on Ag or Au substrates. However, when we examined the chlorinated hydrocarbons with a Cu electrode, we were able to observe the SERS spectra of carbon tetrachloride (Figure 3) as well as the SERS spectra of TCE, DCE and chloroform (Figure 4).

The best SERS spectra were obtained when the ORC cycle was stopped during the reduction step at the potential of zero charge for Cu(-0.2V) (4). The observation of the SERS spectra was also highly dependent on illumination during the cycling. Previous work by Thierry and Leygraf (5) has indicated the importance of illumination during the electrochemical roughening of Cu electrodes to produce Raman active sites.

The vibrational features in Figure 4 indicate that a reaction is occurring on the electrode surface (see Table 1 for vibrational assignments). From the spectra, it appears that ring formation is occurring due to an electrochemical and/or photochemical process. However, in our experiments no SERS spectra of the CHS were observed unless the electrode was illuminated during the reduction step and thus a strictly electrochemical reaction can be ruled out.

This "photo" induced result indicates the possibility of a photoelectrochemical process. Copper oxides are known to be p-type semiconductors which eject electrons under illumination (Equation 1) (6). The band gaps for the two possible copper oxides are 2.0-2.6 eV (620-477 nm) for Cu_2O and 1.7 eV (730 nm) for CuO. These electrons can then electrochemically reduce the chlorinated hydrocarbon solvents.

$$Cu_2O + \lambda \rightarrow Cu_2O(h^+,e^-)$$

This electrochemical reduction is similar to a reaction scheme for the electrochemical reduction of chloroform which has been determined by Fritz and Kornrumpf (6) to be :

$$CHCl_3 + 2e^- \rightarrow CHCl_2^- + Cl^-$$

$$CHCl_2^- + CHCl_3 \rightarrow CH_2Cl_2 + CCl_3^-$$

$$CCl_3^- \rightarrow :CCl_2 + Cl^-$$

The formation of the dichlorocarbene during the electrochemical reduction process would tend to form a ring type structure (6). This ring type structure is indicated in our SERS spectra with the strong band at 1380 cm^{-1}.

A preliminary observation has indicated that the SERS spectrum is only observable for a finite amount of time. The result is either due to the degradation of the electrode or the sample. If the electrode was replaced with a new SERS surface and then placed in the same solution, the spectrum was still not observable. This indicates that the chlorinated hydrocarbons were being consumed during the experiments in the small volume (10 ml) of analyte. Confirmation of this result would indicate that the SERS on Cu surfaces is a method which is capable of both sensing and removing the chlorinated hydrocarbons from the solution.

To determine the cause of the disappearing SERS signal, a series of SERS/GC experiments which determined the TCE concentration before and after the SERS experiments were performed. Saturated samples of trichloroethylene (TCE) in 0.1M KCl and distilled H_20 were cycled in a sealed glass SERS cell to prevent the possibility of outgassing of the TCE. Samples of the saturated TCE solutions were collected both before and after the electrochemical cycling. These samples were analyzed on a Hewlett-Packard Model HP 5730A Gas Chromatograph. Chromatograms were recorded and the magnitudes of retention peaks were examined for the TCE peak in the experiments. Large spikes at the 45 second retention time were due to impurities in the distilled water. The chromatograms showed that a large amount of TCE was consumed during electrochemical cycling. Figure 5 represents a typical "before" and "after" chromatogram.

Analysis of "before" and "after" chromatograms showed an average consumption of 66% of the trichloroethylene during the electrochemical cycling and SERS experiments. This is consistent with our observation that a film was being formed on the roughened copper surface of our working electrode. The formation of a film also indicated the carbene may be originating a radical induced polymerization. Methods for determining the exact structure of the products formed during electrochemical cycling are currently under investigation.

CONCLUSION

The observation of a "photo" induced SERS process in the analysis of the chlorinated hydrocarbon solvents has future implications for environmental sensors. Previous to this work it was thought that the CHS type compounds were not observable by the SERS technique. Upon completetion of our fundamental experiments, future work will concentrate on the analytical applications of the process and the development of field portable Raman instrumentation.

ACKNOWLEDGMENT

This work was conducted in part under a collaborative research agreement (CR-90-003) between EIC and ORNL (Martin Marietta Energy Systems). Financial support for this work was derived in part from the Office of Health and Environmental Research Division of the Department of Energy under the Small Business Innovative Research program.

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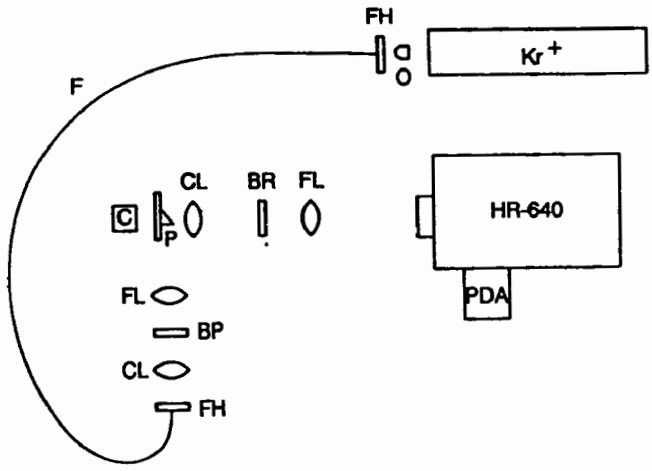

Figure 1. Experimental setup for "photo" induced SERS experiments at ORNL. F = optical fiber, O - microscope objective, CL- collimating lens, FL = focusing lens, P = right angle prism, BP = laser line pass filter, BR = laser line rejection filter, C = spectroelectrochemical cell.

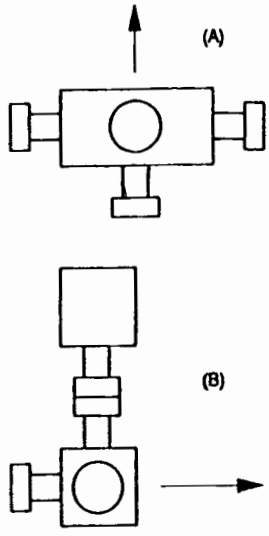

Figure 2. Diagram of spectroelectrochemical cell. (A) Top view showing 3 electrode ports and O-ring joint opening in the top of the cell. (B) side view showing sample reservoir attached to the top for membrane concentration/transport studies. Only 2 of the 3 electrode ports are visible. In both diagrams the arrows point along the optical axis as shown in Figure 1.

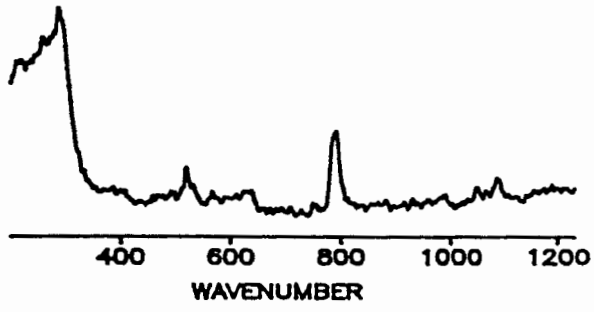

Figure 3. The SER spectrum of a saturated solution in water on a Cu electrode of carbon tetrachloride. The spectrum has been smoothed for clarity.

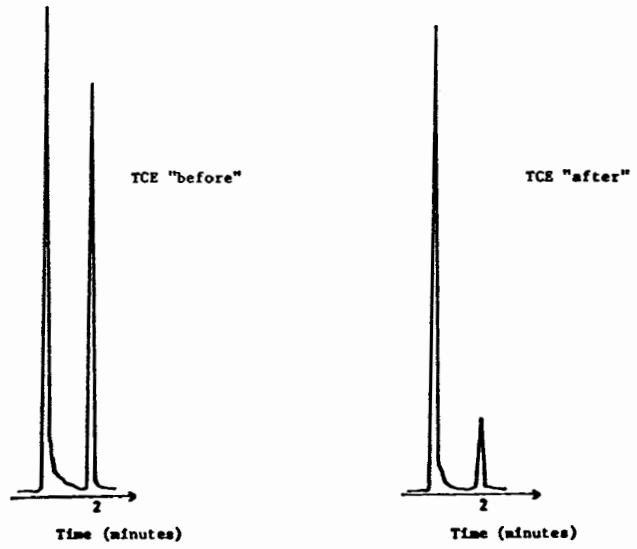

Figure 5. Gas chromatograms of TCE solution before and after the SERS experiment. Retention time for the TCE peak was 2 minutes.

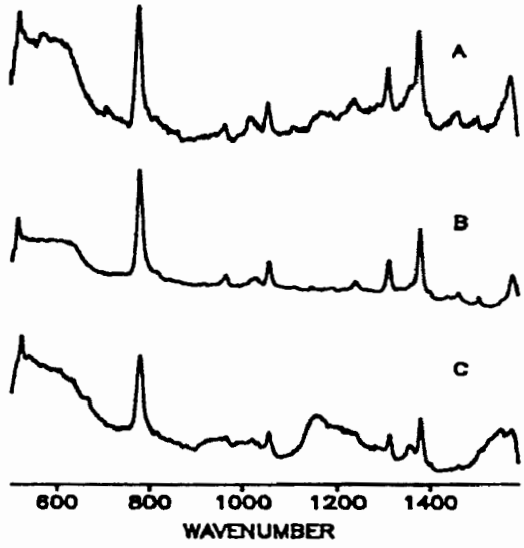

Figure 4. The SER spectra of saturated solutions in water on a Cu electrode of (A) trichloroethylene, (B) 1,2,-dichloroethane and (C) chloroform.

Table 1
Major Raman/SERS Peak Positions (cm^{-1}) and Vibrational Assignment for the Chlorinated Hydrocarbon Solvents

CCl_4		$CHCl_3$		DCE		TCE		Vibrational Assignment
Raman	SERS	Raman	SERS	Raman	SERS	Raman	SERS	
227 s	220 w							Cu-C ?
	261 w							Cu-C ?
	288 w							Cu-C ?
319 s								"chain expansion"
462 s								symmetric CCl_4 str.
	521 w		526 m		521 m		524 m	CCl str., Cu-C stretch?
						628 s		CCl str. - secondary CA
		689 s	670 w	656 s				CCl str. - primary CA symmetric CCl_3 str.
				674 m				CCl str. - primary CA
762 w								CCl str. - primary CA
787 w	791 m	760 m	783 s	755 s	782 s	780 m	781 s	CCl str. - primary CA
				882 w		842 w	862 w	CC skeletal str.
				944 w	965 w	930 w	963 w	CC skeletal str., ring "breathing"
			1021 w		1024 w		1018 w	in-plane CH deformation, CC str., ring "breathing"
	1051 w		1056 m	1055 w	1058 m		1055 m	CC str., ring "breathing"
	1089 w				1101 w		1105 w	CC str., ring "breathing"
			1151 w		1148 w		1167 w	ring "breathing" - cyclopropane type
		1218 w		1209 w				CH_2 twist and rock
			1234 w		1239 w	1247 m	1237 w	CH_2 twist and rock, in-plane CH deformation
			1313 m	1306 w	1312 m		1312 m	CH_2 in-phase twist, CH_2 twist and rock, in-plane CH deformation
			1352 m				1358 m	CH deformation
			1381 s		1379 s		1379 s	ring str.,
				1433 w				CH_2 deformation
			1465 w		1464 w		1463 w	CH_2 deformation
					1509 w		1505 w	symmetric C=C str. - cyclo
			1550 w					C=C str. - cyclobutene
			1581 w		1582 m	1585 s	1580 s	C=C str. CA, 3 or C=C couple str. - polyene

s - strong intensity, m - moderate intensity, w - weak intensity
CA = Chloroalkane, str. = stretch

DISCUSSION

ARTHUR D'SILVA: In the E.I.C. experiments at what wavelength did you measure the fluorescence?

MICHAEL CARRABBA: We're looking at the complete spectrum, in this case a very simple proof of concept. We weren't trying to develop a highly skilled system as the Livermore people have developed, or as the people at GEO-Centers. We're proving the concept here. We just monitored the intensity under the total fluorescence band.

ARTHUR D'SILVA: What is the excitation wavelength?

MICHAEL CARRABBA: The excitation wavelength was 514 nanometers. We added an argon-ion laser. We believe we could use just about any of the wavelengths from 488 up to about possibly 600, but we really didn't try the 600.

EDWARD POZIOMEK: In the experiment where you described the photon induced reaction, did you utilize a base?

MICHAEL CARRABBA: In the electrochemical experiment you don't need the base. We use it as our bench mark, and then put the electrodes in. I believe we don't need the base, and that's probably the important point.

EDWARD POZIOMEK: If you had the opportunity to solve a technology barrier, which one would you go after first in this area to move it faster?

MICHAEL CARRABBA: The implication of the dichlorocarbene, going after a double bond, could be quite lucrative in the future. And we believe we can make probe systems that have been coded right onto an optical fiber and a very simple sensor. That's where I think we'd pursue it at this point. Basically we'd use some particular dyes that when the dichlorocarbene attacks the double bond it breaks the conjugation and the fluorescence disappears or new fluorescence appears. That's the direction that we're working on right now.

SURFACE ACOUSTIC WAVE (SAW) PERSONAL MONITOR FOR TOXIC GASES

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ABSTRACT

A demonstration model 4-sensor Surface Acoustic Wave (SAW) Personal Monitor for Toxic Gases was designed and built, with emphasis on minimizing the overall system size, weight, power consumption, and complexity. The completed demonstration unit contained four 158 MHz SAW delay lines, supporting RF electronics, microcomputer (microcontroller), a miniature pump, valve, gas transfer lines, and a small scrubber to provide a clean, dry, air source to establish sensor baseline frequencies. The demonstration unit weighs approximately 2 pounds. The projected size of the follow-on unit is expected to be 6" x 3" x 1". Unlike previous SAW vapor sensor arrays, which utilized coatings that interact reversibly with specific classes of toxic organic vapors, this SAW Personal Monitor takes advantage of sensor coatings that react irreversibly with toxic chemicals. Thus it can more easily and effectively determine total exposure to a given toxic gas. The following toxic inorganic gases were selected for study with the demonstration system: HCl, NO_2, SO_2, NO_2, H_2S and NH_3. Coating materials were selected that react irreversibly with each gas. The coatings were applied to the SAW sensors and their performance evaluated for exposure to a single gas. The results show that suitable materials are available for use as dosimeter coatings for SAW sensors. Thus the potential exists for developing an effective SAW Personal Monitor for detecting and monitoring each of the above gases, except NO_2, at concentrations well below the OSHA "action levels".

INTRODUCTION

In all areas of environmental monitoring, as well as industrial hygiene, there is a need for smaller, more sensitive, and inexpensive personal monitors (e.g., dosimeters) for toxic gases and vapors. For example, personnel involved in field screening must be concerned with their personal health and safety when working at a field site, and may often require accumulated exposure data for various toxic gases. SAW sensor technology, however, is not limited to use in a Personal Monitor (e.g., a toxic gas monitor that can be worn on clothing). The same sensor technology could be extended to the development of small, hand-held or in-situ monitors for a variety of field screening applications.

There are a number of techniques currently being used to acquire toxic exposure data, however, each have their limitations. In the future large numbers of more effective monitors will be required for the rapid and reliable detection and/or monitoring of toxic gases and vapors at ever lower concentrations, in response to increasingly stringent state and federal health and environmental regulations. Chemical microsensors have demonstrated the sensitivities and physical properties needed to meet the size, cost, and performance requirements of a new generation of personal monitors, and should ultimately find a wide range of applications within the industrial, medical, and environmental communities (1 - 13).

Of the chemical microsensors that have been investigated to date, SAW devices, which measure changes in mass when a chemically specific surface coating adsorbs or reacts with an appropriate gas, are the best characterized and the most promising for rapid development. SAW devices have been shown to respond in just seconds to selected vapors at concentrations down to the parts per billion range for specific organic chemicals. Because of their solid state construction and compatibility with integrated electronics, they can be easily incorporated into very small, lightweight instruments, small enough to be worn on clothing. The primary challenge remaining in the development of SAW based microinstruments is the development of more selective and sensitive SAW coatings for specific gases and vapors. Other technical areas to be addressed are the miniaturization of supporting electronic components and the development of computer software to facilitate sensor operation, data analysis, and data reporting.

OBJECTIVE

The objective of the present study was to demonstrate the feasibility of developing a miniaturized Surface Acoustic Wave (SAW) Personal Monitor with the size, sensitivity, selectivity, reliability, and low power consumption appropriate for wearing on clothing. To achieve this objective it was necessary demonstrate that: (1) the SAW sensors and necessary support electronics can be sufficiently miniaturized; (2) chemically selective SAW coating materials are available or can be developed for the detection of a wide range of toxic gases; and (3) the SAW sensors and their coatings can be sufficiently sensitive to specific toxic gases to meet the requirements of field screening, personal safety, and related monitoring applications.

SAW SENSOR INSTRUMENTATION

1. SAW Sensor Operating Principles

SAW devices are mechanically resonant structures whose resonance frequency is perturbed by the mass or elastic properties of materials in contact with the device surface. Rayleigh surface waves can be generated on very small polished chips of piezoelectric materials (e.g. quartz) on which an interdigital electrode array is lithographically patterned. When the electrode is excited with a radio frequency voltage, a Rayleigh wave is generated that travels across the device surface until it is "received" by a second electrode. The Rayleigh wave has most of its energy constrained to the surface of the device and thus interacts very strongly with any material that is in contact with the surface. Changes in mass or mechanical modulus of a surface coating applied to the device produce corresponding changes in wave velocity. The most common configuration for a SAW vapor/gas sensor is that of a delay line oscillator in which the RF voltage output of one electrode is amplified and fed to the other. In this way the device resonates at a frequency determined by the Rayleigh wave velocity and the electrode spacing. If the mass of the coating is altered, the resulting change in wave velocity can be measured as a shift in resonant frequency. SAW vapor/gas sensors are similar to bulk wave piezoelectric crystal sensors, except they have the distinct advantages of substantially higher sensitivity, smaller size, greater ease of coating, uniform surface mass sensitivity, and improved ruggedness. Practical SAW sensors currently have active surface areas of a few square millimeters and resonance frequencies in the range of hundreds of MHz. However, SAW devices having total surface areas significantly less than a square millimeter and resonant frequencies in the gigahertz range are possible using modern microlithographic techniques. Such devices would ultimately increase device sensitivity as well as decrease size. Most of the SAW vapor sensors reported in the literature employ two delay line oscillators fabricated side by side on the same chip, with one delay line used to monitor the toxic chemical and the other to act as a reference to compensate for changes in ambient temperature and pressure.

2. SAW Sensitivity and Selectivity

A 158 MHz SAW device having an active area of 8 mm^2 will give a resonant frequency shift of about 365 Hz when perturbed by a surface mass change of 1 nanogram. This sensitivity is predicted theoretically and has been confirmed experimentally. The same device exhibits a typical frequency "noise" of less than 15 Hz RMS over a 1 second measurement interval (i.e. 1 part in 10^7). Thus, the 1 nanogram mass change gives a signal to noise ratio of about 24 to 1. For vapor or gas sensing applications, the objective is to have the chemical selectively adsorb onto the mass sensitive surface of the device. Chemically selective coatings are used for this critical operation.

3. Selective Coatings

The operational behavior of a Surface Acoustic Wave device can be very sensitive to changes in density, elastic modulus, and viscosity of the surrounding medium; however, SAW devices are not inherently sensitive to the chemical properties of the medium surrounding the device. When coated with a chemically selective thin film they can exhibit remarkable sensitivity to small quantities of a chemical vapor or gas. The development of such selective coatings for toxic chemicals can take two directions, (1) coatings that will selectively and reversibly adsorb a selected vapor or gas by matching "solubility" characteristics; and (2) coatings that react chemically and irreversibly with a selected vapor or gas. SAW selectivities in excess of 10,000 to 1 for certain toxic chemical agents have been demonstrated using the "solubility" approach. Much greater selectivities should be possible using chemically reactive coating/vapor (gas) combinations.

SAW INSTRUMENTATION DEVELOPMENT

1. Miniaturization of SAW Sensor Array and RF Electronics

Ultimate miniaturization would be achieved by going to hybrid circuitry, where the sensors and support RF electronics could be reduced in size to a few cm^2 or less. Hybridization, however, will require a major engineering effort and was beyond the scope of this study. The emphasis was therefore on the selection and arrangement of the discrete components and electronic packages to minimize the size of the demonstration unit. The basic design of the system is essentially the same as used in previous SAW Vapor Monitors. The four coated SAW dual delay line devices were mounted in small, gold IC packages. The lids of each package were modified with short, 1/16" ID, gold plated gas inlet and outlet tubes to provide the toxic gases access to the sensors. A fifth SAW dual delay line, sealed to prevent exposure to the ambient environment, was place in a separate package. In the demonstration unit, this fifth device was used as a reference for all other sensors to compensate for changes in temperature and pressure. The output of the 4 SAW Sensor Array was integrated with a 4 channel frequency interface card to generate the measured

frequency differences, Δf, and with an onboard microcomputer (microcontroller) for data analysis.

2. Instrument Configuration

The system was designed with three circuit cards: a sensor card, a four channel frequency interface card, and a microcomputer card. The entire instrument will fit in an enclosure 4-3/4" x 8" x 3", allowing room for the necessary pumps, valves and gas transfer lines. The system was designed for either battery operation or with a 120 VAC 50-60 Hz power supply. 1/8" Swagelok bulkhead fittings on the enclosure provided gas inlet and outlet to the system. Except for the stainless steel Swagelok fittings on the front of the enclosure, all surfaces in contact with the gas up to the SAW devices are either Teflon or gold.

The four channel microcomputer controlled frequency counter measures and reports the frequency of each SAW sensor every two seconds while controlling the solenoid valves by means of a solid state relay. For laboratory evaluation of the demonstration model SAW Personal Monitor for Toxic Gases, the counter output is provided on a 9600 baud RS-232C serial communications line. For better control and monitoring of the demonstration model, and it's subsystems, all communication with the unit was through the RS-232 line and a personal computer with a serial communication port. In a follow-on program, a different communication scheme will be devised so that the user will have the option of entering all instructions directly on the instrument. Also, all concentration data and/or signals will be presented on visual (LCD) displays or by audio alarms mounted on the instrument enclosure. There will still be the option of communicating with the SAW Personal Monitor via a personal computer to retrieve data stored in memory.

In the demonstration unit, the onboard Octagon SB S-150 microcomputer was programmed to control operation of the system, but not for analysis of the sensor array data. Development of a sensor array data analysis program is planned for the follow-on effort. With the demonstration unit, the performance of each SAW sensor, and it's coating, was evaluated individually against a specific toxic gas. There are a number of experimental variables that also require computer control and or analysis. For example, due to the possible adsorption/desorption of ambient gases (especially water vapor) on the coatings, the computer must continually determine the actual baseline for each sensor, by intermittently providing clean, dry (filtered) air to the sensors. The computer must also store calibration data for each sensor and provide total exposure values on demand and/or activate an alarm when certain values are exceeded. Figure 1 provides a pictorial layout of a SAW Array Personal Exposure Monitor.

SAW COATING SELECTION

1. Selection of Candidate Coatings

A series of candidate materials was selected for screening as coatings for the SAW devices. They were selected on the basis of their known reactivity with the toxic gases chosen for evaluation. The coatings selected for screening against the reactive gases are given in Table 1.

Table 1. Candidate Coating Materials for SAW Sensors

Candidate Coating	Reactive Gas
Diphenylbenzidine	NO_2
2,4, Dinitrophenylhydrazine	NO_2
o-Toluidine	NO_2
Triethylenediamine (TEDA)	SO_2
$Na[HgCl_2]$ (hydrate)	SO_2
$Pb(C_2H_3O_2)_2 \cdot 5H_2O$	H_2S
$CuSO4 \cdot 5H_2O$	H_2S
$K[Ag(CN)_2]$	H_2S
Ninhydrin	NH_3
$CoCl_2 \cdot 6H_2O$	NH_3
Polyvinylpyridine (PVP)	HCl

2. Coating of SAW Devices

Each of the above coatings was applied to two 158 MHz Saw devices. Each SAW device to be coated was inserted into a suitable connector mounted on a circuit board that contained the necessary electronics to operate the device and provide frequency signals to an external data aquisition system. Prior to coating, each dual 158 MHz SAW device was ultrasonically cleaned in isopropanol or chloroform, dried in a stream of compressed dry, zero air, and positioned in the coating apparatus. In all but a few instances, the coatings were applied by a spray deposition technique developed by Microsensor Systems. The primary requirement is that the coating material must be soluble in a volatile solvent. Zero air was used to generate a fine mist of the specific coating solution. A mask was placed over the SAW device so that only the interdigitated delay lines were coated.

The quantity of coating material deposited on each delay line was closely monitored by the computer data system which reported the mass of material deposited as an increase in frequency, Δf. The amount of coating material applied was held closely to 250 KHz ± 50 KHz. The frequency shift, Δf, corresponds to coating thickness, assuming uniform surface coverage. Once the coatings were applied, the SAW devices were covered and stored in a low humidity (≤ 10% RH) environment until ready for testing. As the candidate coating materials given in Table 1 are generally hygroscopic, it can be assumed that a certain amount of water will be associated with each coating and must be considered in subsequent gas interactions.

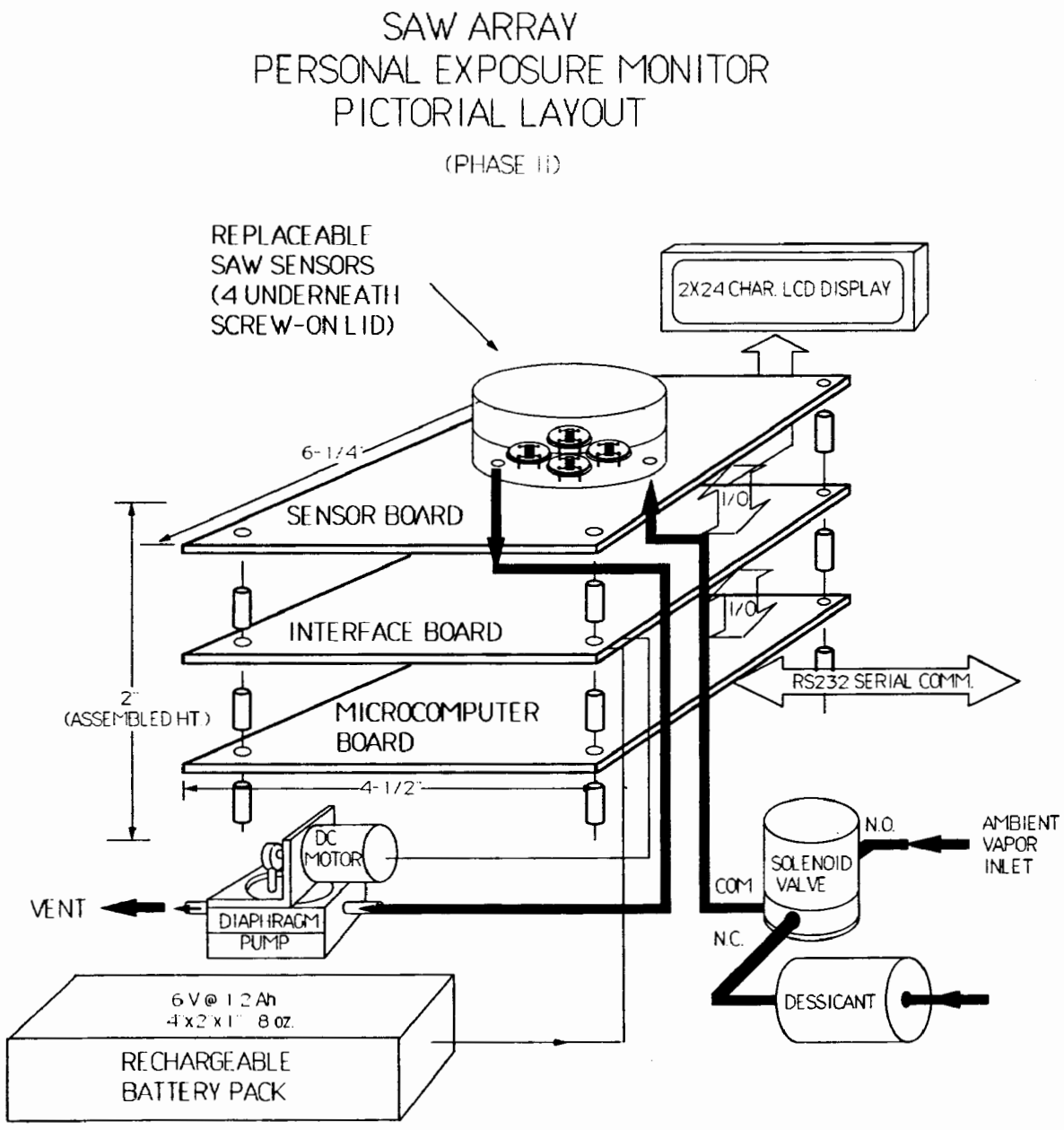

Figure 1. Pictorial Layout of SAW Array Personal Exposure Monitor

3. Screening and Selection of Coatings for SAW Test and Evaluation

The following criteria were established to define a successful candidate material: (1) that a coating give a frequency shift equivalent to a 100:1 signal to noise ratio when exposed to the toxic gas at a concentration of approximately 100 ppm for 1 minute or less; and (2) that the coating react irreversibly with the test gas. With a baseline noise level of approximately 15 Hz, a 100:1 signal to noise ratio would be equivalent to a frequency shift on the order of 1500 Hz. Thin film coatings showing less response would not have sufficient sensitivity nor capacity to be useful in field monitoring applications.

A calibrated cylinder of each of the test gases (NO_2, SO_2, HCl, H_2S, NH_3) in air was obtained from the Scott Specialty Gas Co. The concentration of each gas source was:

Toxic Gas	Source Concentration
HCl	103.3 ppm
NH_3	106.5 ppm
H_2S	100.6 ppm
NO_2	108.0 ppm
SO_2	102.5 ppm

By simple dilution of the compressed gas with clean, dry, zero air, a steady state concentration at any value less than 100 ppm could be easily prepared. A constant gas flow rate of 200 cc/min was maintained. A valve was arranged so that clean air, or a known concentration of the specific test gas, could be alternately delivered to the sensor. A lid with 1/8" gold gas inlet and outlet tubes was placed over the device and was connected to the output of the gas dilution chamber. The frequency output of the dual delay lines could be monitored using a small frequency counter.

In the tests, a coated SAW device was first exposed to clean, dry air at 200 cc/min to obtain a steady baseline frequency. The valve was then turned to expose the sensor to a known concentration of the toxic gas, at the same flow rate, for a pre-determined period of time. The sensor was then exposed once again to clean, dry air to establish a new baseline. If the clean air baseline, after exposure to the toxic gas, was significantly different from the initial clean air baseline, it was assumed the change in frequency was due to an increase in coating mass resulting from the irreversible reaction with the challenge gas. If there was no significant change in SAW frequency, the device was exposed to higher gas concentrations for longer periods of times. If there was still no permanent change in baseline, it was assumed there was no reaction and that the coating, in its present form at least, was ineffective. All tests were performed with dry air, unless otherwise specified in the text.

The results of the initial screening tests are given in Table 2. They show that for each toxic gas there was at least one coating that gave an acceptable response. However, in several instances there were rather unexpected results. For example, NO_2 did not appear to react at all with 2,4 Dinitrophenyl hydrazine unless there was a relatively high moisture content (≈ 80% RH) in the carrier gas. It was also surprising that H_2S did not react readily with the lead acetate coating, even though we have observed this surface reaction in a previous study. Copper sulfate seemed unreactive initially, however, after repeated cycling it did react to give a very large and permanent frequency shift. The reaction, or lack of it, in each case may depend to a large extent upon the amount of water present in the film.

Table 2. Results of Initial Coating Screening Test
(Thickness of all coatings approx. 250 Hz)

Coating	Gas	Conc./Time	Δf (Hz)	Stable Reaction
Diphenylbenzidine	NO_2	50 ppm/60 s.	900	No
2,4, Dinitrophenyl hydrazine	NO_2	50 ppm/60 s.	2,800	Yes
o-Toluidine	NO_2	50 ppm/60 s.	<100	---
TEDA	SO_2	50 ppm/60	1,000	Yes
$Na[HgCl_2]$	SO_2	50 ppm/60 s.	---	---
$Pb(C_2H_3O_2)_2$**	H_2S		---	---
$CuSO_4$***	H_2S	50 ppm/60 s.	2,000	Yes
Ninhydrin	NH_3	50 ppm/ 60 s.	100	---
$CoCl_2$	NH_3	50 ppm/ 20 s	2,700	Yes
PVP	HCl	(known to react)		

* Reacted only in presence of high RH
** Reacted in a previous study, but now
*** Reaction occurred after repeated H_2S exposure

Based on the results of Table 2, the following coatings were selected for more careful evaluation. 2,4 Dinitrophenyl-hydrazine was not used for NO_2. Rather TEDA was used for both SO_2 and NO_2.

Coating Material	Toxic Gas
Polyvinylpyridine (PVP)	HCl
Triethylenediamine (TEDA)	NO_2 and SO_2
Copper sulfate ($CuSO_4$)	H_2S
Cobaltous chloride ($CoCl_2$)	NH_3

TEST AND EVALUATION OF SAW SENSORS AS MONITORS FOR TOXIC GASES

1. Coating of SAW Sensors

The coating procedure used was the same as described above. Both SAW delay lines on each device were coated simultaneously, and the amount deposited was measured and recorded. The identification number of each device and the coating mass (in terms of frequency shift, Δf) are given in Table 3. The coatings applied are very thin, on the order of a micron or so in thickness, on the average.

2. Evaluation of SAW Sensors as Monitors for Toxic Gases

The frequency difference, Δf, of each SAW device being tested was input to a Apple Macintosh computer where the data was collected and displayed. The test system evaluated

only one sensor at a time against a single toxic gas. Even though each of the coating materials being tested could very likely react with more than one gas, binary gas mixtures and interference studies were not included in this preliminary investigation. Interference studies will be a part of the follow-on study, using multiple sensor arrays and other techniques to address the problem of sensor specificity.

The gas dilution chamber was again used to deliver known concentrations of each test gas to the SAW sensors at a constant flow rate of 200 cc/min at ambient pressure, and a constant "baseline" frequency established for each SAW device by exposing it to a clean, dry air stream. Once a constant baseline frequency was established, the sensor was exposed to a predetermined "dose" of the selected toxic gas. The size of the dose could be varied from 10 to 100 ppm over any selected time interval. After exposure to the toxic gas, the sensor was again exposed to clean, zero air until a new baseline frequency was established. The difference between the initial baseline and the final baseline was taken as the frequency shift due to the irreversible reaction of the toxic gas with the coating material. The magnitude of this frequency shift could be correlated with the amount of toxic gas interacting with the sensor.

The intent of the tests was to quickly look for order of magnitude changes in frequency and general reproducibility of performance when exposed to moderate changes in gas concentrations: i.e., to identify coatings that could be used in a more comprehensive follow-on development program. This study did not include a careful characterization of each coating reaction. In any event an accurate characterization of the surface reactions would be difficult without a more careful control of trace water, both in the hygroscopic coating materials and the gas delivery system.

3. Exposure of NH_3 to $CoCl_2$ Coated SAW Sensor

The SAW devices were at ambient temperature and thus subject to the room temperature fluctuations (≈ 25° +/- 1 C). Although a reference SAW device was used to compensate for both temperature and pressure changes, the compensation is not exact, and may have caused some small, random drift in device background frequency. These slow changes occurred in cycles of many minutes and thus did not adversely effect the measurements. Even though a number of the coating materials have a small volatility, the signal drift reflected "apparent" increases as well as decreases in weight. Thus volatility did not have a measurable effect on the measurements. Once a device was equilibrated with the laboratory environment (temperature and pressure) the slow baseline drift was usually on the order of ± 50 Hz. In addition to temperature changes and the possibility of volatility, the baseline drift may also be due in part to changes in gas flow rate (due to changes in flow through the non-precision needle valve used to set the flow rate). Even with the small observed background drift, the following data show that system performance was excellent and clearly able to detect and monitor changes in SAW frequency upon exposure to the challenge gases. Sensor drift will be corrected for in the follow-on Personal Monitor development program.

An example of data for the exposure of ammonia to the $CoCl_2$ coated SAW devices is shown in Figures 1. An exposure of 20 ppm NH_3 for 20 seconds was selected for testing the $CoCl_2$ coated sensors. When the NH_3 was introduced, there was a large initial decrease in SAW frequency followed by a rapid increase. Each point on the curve corresponds to a 2 second time interval. After 20 seconds, when the clean air at 200 cc/min was again introduced, Δf continued to increase through a small maximum and then level off to a new, higher, baseline value. The initial negative "spike" in the Δf vs time plot may be due in part to disruption and re-establishment of a constant gas flow rate, while the subsequent increase in Δf most probably results from both adsorption and reaction of the NH_3 with the $CoCl_2$ coating. The maximum may result from a more gradual desorption of non-reacted NH_3 from the coating. The equilibrium frequency shift values for all devices are shown in Table 4.

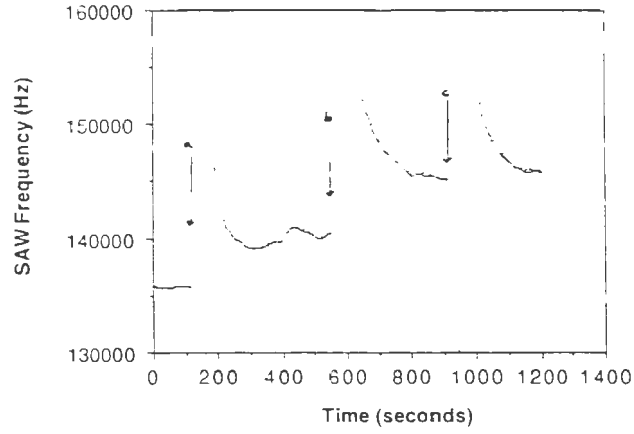

Figure 1. Frequency Shift (Hz) vs. Time for Repeat Exposure of $CoCl_2$ Coated SAW Device (9024-11) to 20 ppm NH_3 for 20 Sec.

Table 3. Thickness of SAW Device Coatings

Coating Material	Coating Thickness (KHz) Device Number	Side "A"
PVP	9024-1	255
	9024-2	198
	9024-3	198
$CuSO_4$	9024-7	149
	9024-8	150
	9024-9	196
$CoCl_2$	9024-10	136
	9024-11	112
	9024-12	106
TEDA	9024-4	149
	9024-5	178
	9024-6	300

Table 4. Frequency Shifts for $CoCl_2$ Coated SAW Devices Upon Repeated Exposure to 20 ppm NH_3 for 20 seconds

Device Number	Exposure	Frequency Shift
9024-10	a. - d.	(dose optimization test)
(Coating 112 KHz)	e.	1,200 Hz
	f.	0 Hz
9024-11	a.	4,000 Hz
(Coating 136 KHz)	b.	4,000 Hz
	c.	1,000 Hz
9024-12	a.	2,600 Hz
(Coating 106 KHz)	b.	2,000 Hz
	c.	1,200 Hz
	d.	1,600 Hz
	e.	2,000 Hz
	f.	0 Hz

From the data in Table 4 it is evident that $CoCl_2$ coated SAW devices show large (Kilohertz), irreversible shifts in frequency when exposed to small doses of ammonia, and that with continued exposure the coatings saturate as expected. Even allowing for the variation is response of the different sensors, the sensitivity of the $CoCl_2$ coatings, i.e., those with some residual capacity, is on the order of 5 to 10 Hz/ppm/sec. Considering that the background noise level of the SAW sensors is on the order of 15 Hz, a ten seconds exposure of a sensor to 1 ppm NH_3 would give a signal of better than 50 Hz, at least three times the background noise. Thus the $CoCl_2$ coatings have more than enough sensitivity to detect ammonia at concentrations below the OSHA Exposure Limit of 50 ppm NH_3 for an 8 hour weighted average.

4. Exposure of $CuSO_4$ Coated SAW Sensor to H_2S Gas

The test procedure was essentially the same as described above. Typical results are shown in Figure 2 for device 9024-7. H_2S shows a decrease in SAW frequency with exposure rather than an increase in Δf as observed with the reaction of NH_3 with the $CoCl_2$. Also, there was no initial "spike" in Δf when the challenge gas was introduced. Upon repeated exposure, the frequency shifts became progressively smaller, due to saturation of the reactive sites of the $CuSO_4$ coating.

The Δf values for the $CuSO_4$ coated sensors 9024-7 and 9024-8 are given in Table 5. SAW device 9024-9 apparently became defective during the coating process. SAW device 9024-7 was exposed five times to 20 ppm of H_2S for 20 seconds. With the initial dose of H_2S, Δf decreased by 1,400 Hz. The second exposure decreased Δf by only 400 Hz. Subsequent doses caused essentially no further change in Δf. Thus the $CuSO_4$ coatings were essentially saturated by a single 20 ppm dose of H_2S for 20 seconds.

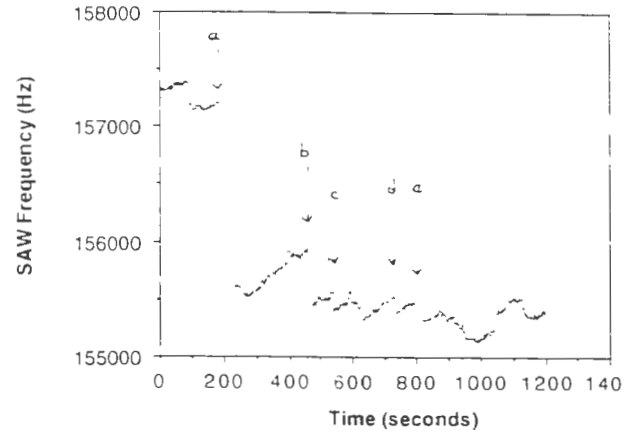

Figure 2. Frequency Shift (Hz) vs. Time for Repeat Exposure of CuSO4 Coated SAW Device (9024-7) to 20 ppm H2S for 20 Sec.

Table 5. Frequency Shifts for $CuSO_4$ Coated SAW Devices Upon Exposures to 20 ppm H_2S for 20 seconds

Device Number	Exposure	Frequency Shift
9024-7	a.	1,400 Hz
(Coating 149 KHz)	b.	400 Hz
	c.	100 Hz
	d.	0 Hz
	e.	0 Hz
9024-8	a.	1,400 Hz
(Coating 150 KHz)		
9024-9	(device defective after coating)	
(Coating 196 KHz)		

Thus the $CuSO_4$ coated SAW devices, like the $CoCl_2$ coated devices, do give large (KHz), irreversible shifts in frequency when exposed to small doses of an appropriately reactive gas, and that with continued exposure the coatings saturate as expected. The sensitivity of a newly prepared $CuSO_4$ coating is on the order of 3 to 4 Hz/ppm/sec. With background noise on the order of 15 Hz, a ten second exposure to 1 ppm H_2S would give a signal of around 30 to 40 Hz, equivalent to a signal to noise ratio of 2:1. The detection limit of this coating is thus also is well below the OSHA Exposure Limit of 20 ppm H_2S for an 8 hour weighted average.

5. Exposure of TEDA Coated SAW Sensor to SO_2 Gas

The procedure used to test the TEDA coated SAW sensors with SO_2 was the same as described above. Typical results are shown in Figure 3 for device 9024-6. The results for device 9024-5 were similar. SAW device 9024-4 was reserved for testing with NO_2, which was expected to react with TEDA in much the same way as SO_2. A rather unexpected behavior was observed when the TEDA coated devices were initially exposed to SO_2. For the first few

exposures of 20 ppm SO_2 (20 seconds), the coatings did not respond significantly. After several repetitions, however, the coatings did begin to respond with positive shifts in Δf with the continuing exposure. Thus it appears there was a "conditioning" period, after which the coatings began to respond. The "conditioning" must be associated with some chemical change in the coatings upon exposure to the test gas, or to the zero air, most likely involving associated water. As each device, after being coated, was covered with a close fitting lid (but not hermetically sealed) and stored in a ≈ 10% RH environment, they must have adsorbed some water vapor (or perhaps another ambient gas) which was subsequently desorbed from the coatings by the dry (< 1% RH) zero air and/or the dry sample (SO_2) air. This "conditioning" or "ageing" effect was not further explored at this time, but will of necessity be investigated in the follow-on study in order to provide coatings that behave predictably and reproducibly.

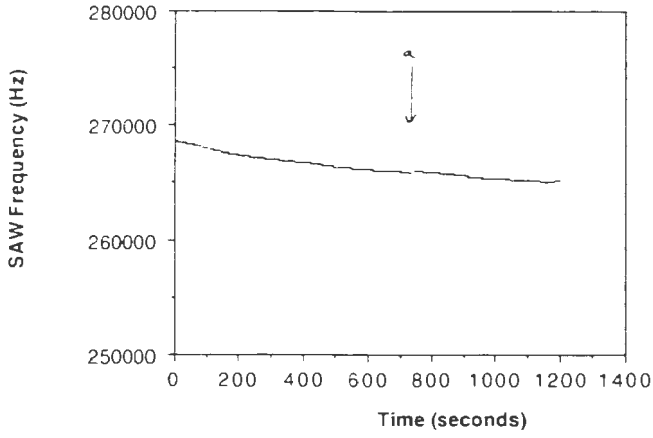

Figure 3(a). Frequency Shift (Hz) vs. Time for Repeat Exposure of TEDA Coated SAW Device (9024-6) to 20 ppm SO_2 for 20 Sec. (First exposure, a)

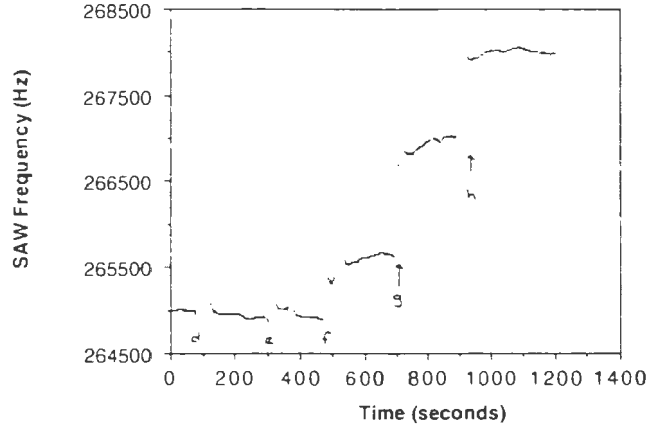

Figure 3(b). Frequency Shift (Hz) vs. Time for Repeat Exposure of TEDA Coated SAW Device (9024-5) to 20 ppm SO_2 for 20 Sec. (Exposures d to h)

After the initial induction period, the frequency shift vs time plot in both Figure 3(b) shows an increase in the SAW baseline with each 20 second dose of SO_2, after the initial "spike" in Δf. Device 9024-5 was allowed to stand in the test apparatus for approximately two hours with continuous exposure to zero air, before the run. Even so, it wasn't until exposure f that the device began to respond. Somewhat similar behavior was observed for device 9024-6, however the conditioning period was much shorter. For both device 9024-5 and 9024-6, once the coatings became reactive, the shifts in frequency were regular and irreversible.

The frequency shifts are given in Table 6. The data clearly show the induction period during which there was no effect of SO_2 exposure, and the subsequent increases in Δf when reaction began to occur. If we assume an average response of 1,200 Hz for device 9024-5 and 1,800 Hz for device 9024-6, the sensitivities are approximately 3 and 4.5 Hz/ppm/sec, respectively. The coating on device 9024-6 was a third again the mass of the coating on 9024-5 (300 KHz to 178 KHz), thus one would expect the sensitivity to SO_2 to be a third again as high, which was observed. Thus the two coated devices had essentially equivalent sensitivities.

Table 6. Frequency Shifts for TEDA Coated SAW Devices Upon Repeated Exposure to 20 ppm SO_2 for 20 seconds

Device Number	Exposure	Frequency Shift
9024-5	a.	0 Hz
(Coating 178 KHz)	b.	0 Hz
	c.	0 Hz
	d.	0 Hz
	e.	0 Hz
	f.	800 Hz
	g.	1,400 Hz
	h.	1,000 Hz
9024-6	a.	0 Hz
(Coating 300 KHz)	b.	0 Hz
	c.	200 Hz
	d.	1,600 Hz
	e.	2,000 Hz
	f.	1,800 Hz

With sensitivities of about 3 to 4 Hz/ppm/sec, depending upon coating thickness, and a background noise level of 15 Hz for the SAW devices, the sensors should ultimately detect concentrations of SO_2 as low as 1 ppm within 10 seconds at a signal to noise ratio of about 2:1. With this sensitivity, these coatings should easily detect SO_2 at or below the OSHA Exposure Limit of 5 ppm SO_2 for an 8 hour weighted average.

6. Exposure of TEDA Coated SAW Sensor to NO_2 Gas

It was anticipated that TEDA would respond to NO_2 in much the same manner as to SO_2; however, the data for the one available sensor showed quite different behavior. First, no conditioning period was observed. The first 20 second dose of 20 ppm NO_2 gave a relatively small but definite increase in SAW frequency which apparently saturated the sensor, as no further increase in Δf was observed with additional exposure to NO_2. The frequency shift data are given in Table 7. The baseline shift of approximately 350 Hz for an exposure of 20 ppm NO_2 for 20 seconds, is equivalent to about 1 Hz/ppm/sec, well below the sensitivity to SO_2. With a sensitivity of approximately 1 Hz/ppm/sec, and a background noise level of 15 Hz, the TEDA coated sensors would have to be exposed to 1 ppm NO_2 for over 30 seconds to give a 2:1 signal to noise ratio. In addition, the film apparently has a very low capacity for NO_2 (i.e., saturating at a very low exposure concentration). TEDA is therefore of only marginal utility as a dosimeter coating for NO_2.

Table 7. Frequency Shifts for TEDA Coated SAW Devices Upon Repeated Exposure to 20 ppm NO_2 for 20 seconds

Device Number	Exposure	Frequency Shift
9024-4	a.	350 Hz
(Coating 149 KHz)	b. - g.	0 Hz

7. Exposure of PVP Coated SAW Sensors to HCl Gas

Device 9024-1 was given 5 separate exposures to 20 ppm of HCl for 20 seconds, over approximately a 30 minute period, with no apparent reaction of the HCl with the PVP. We know from previous studies that surface films of PVP do react with HCl, thus the lack of response must be similar to the "conditioning" period observed for SO_2 gas on TEDA. To accelerate the reaction, the PVP coated device 9024-1 was exposed to a higher concentration of HCl (100 ppm) for 2 minutes. The result was a very large increase in Δf, over 30,000 Hz in the 2 minute period, as shown in Table 8. A second large dose (100 ppm over a 60 second period) further increased Δf by only 4,800 Hz, indicating that the PVP coating was approaching saturation. The estimated sensitivity, based on the 30,000 Hz shift is about 3 Hz/ppm/sec.

Device 9024-2 was exposed to repetitive doses of HCl at a concentration of 25 ppm for 20 seconds. The results given in Table 8 indicate no conditioning period was needed. The very first exposure gave an increase of about 900 Hz and appeared to be stable with time. Subsequent exposures also increased Δf, until the film began to saturate. Sensitivity based on the initial exposure is about 2 Hz/ppm/sec. Device 9024-3 did require a conditioning period when exposed to 25 ppm HCl for 20 seconds. HCl exposures were increase to 50 ppm for 30, 60 and 90 seconds, before an increase in Δf was observed. With the final exposure, a frequency increase of approximately 6,400 Hz was observed.

Table 8. Frequency Shifts for PVP Coated SAW Devices Upon Repeated Exposure to HCl

Device Number	Exposure	Frequency Shift
9024-1	a.(20 ppm 20 sec)	0 Hz
(Coating 255 KHz)	b.(20 ppm 20 sec)	0 Hz
	c.(20 ppm 20 sec)	0 Hz
	d.(20 ppm 20 sec)	0 Hz
	e.(20 ppm 20 sec)	0 Hz
	f.(100 ppm120 sec)	30,000 Hz
	g.(100 ppm 60 sec)	4,800 Hz
9024-2	a.(25 ppm 20 sec)	900 Hz
(Coating 198 KHz)	b.(25 ppm 20 sec)	600 Hz
	c.(25 ppm 20 sec)	400 Hz
	d.(25 ppm 20 sec)	600 Hz
	e.(25 ppm 20 sec)	400 Hz
	f.(25 ppm 20 sec)	200 Hz
9024-3	a.(25 ppm 20 sec)	0 Hz
(Coating 198 KHz)	b.(25 ppm 20 sec)	0 Hz
	c.(25 ppm 20 sec)	0 Hz
	d.(50 ppm 30 sec)	0 Hz
	e.(50 ppm 60 sec)	0 Hz
	f.(50 ppm 90 sec)	6,400 Hz

The sensitivities of the PVP coated SAW devices were in the range of 1 to 3 Hz/ppm/sec. Device 9024-1, with the greatest apparent sensitivity (3 Hz/ppm/sec), had the highest coating mass, as would be expected. Thus the results for the three devices are consistent. With a sensitivity of 1 to 3 Hz/ppm/sec, a sensor would have to be exposed to 1 ppm HCl for 10 to 30 seconds to give a 2:1 signal to noise ratio. The PVP films do appear to have a high capacity for HCl, as evidenced by the 30,000 Hz shift for device 9024-1. Considering that the OSHA Exposure Limit is 5 ppm HCl for an 8 hour weighted average, the PVP coating should be considered a good candidate for further development as a coating for monitoring acid gases.

CONCLUSION

In the evaluation of the various SAW coatings it was found that for each toxic gas, except NO_2, a relatively large, easily measured SAW response was observed when an appropriate coating was exposed small concentrations. The measured sensitivities show that each toxic gas studied (except NO_2) could be detected by a SAW sensor well below the "action level" set by OHSA, when monitored for a period of one minute or less. The candidate coatings, toxic gases, and the respective OSHSA exposure limits, are:

Candidate Coating	Toxic Gas	OSHA Exposure Limit - 8 hour Weighted Ave.
polyvinylpyridine (PVP)	HCl	5 ppm
triethylenediamine (TEDA)	NO_2 and SO_2	5 ppm
copper sulfate ($CuSO_4$)	H_2S	20 ppm
colbaltous chloride ($CoCl_2$)	NH_3	50 ppm

The study thus successfully achieved it's objective of demonstrating that: (1) the SAW sensors and necessary support electronics can be appropriately miniaturized;

(2) a number of successful coatings are readily available and others can certainly be identified in the literature, or developed, for additional toxic gases; and (3) SAW sensors are sufficiently sensitive to meet OHSA requirements, at least for the toxic gases selected for this demonstration study. A number of technical problems and/or potential limitations of the technology were identified and approaches suggested for their solution. Based on the results of this program, we conclude that a prototype Surface Acoustic Wave Personal Monitor for Toxic Agents could be readily developed in a follow-on program. In addition to use as a Personal Monitor, such a small, sensitive and rugged solid state instrument could possibly find other applications in the field screening for toxic chemicals. In all applications however, the usefulness of SAW sensors will increase with the continued development of more sensitive and selective device coatings.

ACKNOWLEDGEMENT

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DISCUSSION

WILLIAM BOWERS: You showed some data on individual sensor responses for single exposures. Have you done any interference effects on some of these? I am glad to see you're going to resonators now.

N. LYNN JARVIS: We did no interference studies in this particular program. You could probably tell that many of the coatings used would respond to more than one vapor. These were not selective coatings in that sense. Selectivity is much more difficult to get. That's why we end up using an array of sensors to get the selectivity. Resonators are much, much nicer.

MICHAEL CARRABBA: When you put the coating on these SAW devices, and the coating goes over electrodes, is the area on the whole surface sensing the weight or is it just the area between the electrodes, or the area on the electrodes?

N. LYNN JARVIS: The whole area surface senses the weight. The wave will cover most of the surface. Most of the surface is sensitive and you get a response.

PHILLIP GREENBAUM: Have you tried attaching antibodies to these? And if not, do you think that would be a problem?

N. LYNN JARVIS: We have not and you could certainly attach them. The problem is that antibodies are very large, and you're trying to attack very small molecules with the antibody. You may get a very small signal i.e., the change in weight is very small. Sensitivity might be fairly low in this case. It would not be a way we would probably choose to go with these particular sensors. There are probably better sensors for that.

MAHADEVA SINHA: Are these things disposable once you use them? After a certain while do you throw them out?

N. LYNN JARVIS: Yes. In this system, once a sensor is used up, we propose to it throw it away and plug in a new one.

MAHADEVA SINHA: You talked about the reversibility of some of the reactions. What did you mean by that?

N. LYNN JARVIS: There are two ways you can go with a coating on a SAW device. You can use coatings where the vapors absorb onto the coating, depending on solubility characteristics and other factors. They will absorb when the vapor is present. When the vapor challenge is removed, it desorbs again from this polymer and is removed. So it's a completely reversible system with certain vapor coating combinations. You can use a coating where there is no chemical reaction. However, if you have a chemical reaction, then it is completely irreversible, which is what we're looking for in this particular application. In some applications you want reversibility; in some you don't, depending on the intended use.

EDWARD POZIOMEK: In your last viewgraph and also in your comments you mentioned the possibility of the wide applications to environmental measurements, and you said something about putting a SAW down a well. Perhaps you could comment on the state of this SAW technology for use in liquids, because the applications presented here were for vapors or for gases.

N. LYNN JARVIS: If we put a sensor in a well, it would have to be within the well headspace to be monitored, not the liquid. The technology for SAWs in liquid is very poorly developed, and is just barely beginning. We know of no really effective way to monitor using a SAW in solution.

ARRAYS OF SENSORS AND MICROSENSORS FOR FIELD SCREENING OF UNKNOWN CHEMICAL WASTES

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Abstract

The high cost of laboratory-based analysis has driven the development of rapid screening methods for hazardous chemicals in unknown wastes. Screening methods permit the "triage" of samples into those that (a) contain no regulated wastes, (b) definitely contain regulated chemicals, or (c) are ambiguous. Only the last category requires detailed analysis.

The requirements of portability and ease of use place extraordinary demands on the designers of analytical instruments. In this paper, we will discuss several approaches to obtaining qualitative analytical data from multiple sensors or highly-selective sensors. These are: (a) a sensor with a selectivity 1000-10000 times greater for chlorinated or brominated compounds than for unsubstituted ones; and (b) pyrolysis-EC, which uses catalytic pyrolysis, arrays of electrochemical sensors, and pattern recognition methods to identify pure chemicals and mixtures. Two applications of the latter are described, the rapid identification of chemical vapors, and the grading of grain according to "odor".

Introduction

The high cost of laboratory-based analysis has driven the development of rapid screening methods for hazardous chemicals in unknown wastes. A screening method is one that can be done on-site, by non-chemists, inexpensively and safely. On the other hand, a screening method is less likely to provide the definitive data that a full laboratory analysis, perhaps requiring GC/MS or ICP, might give. In the case where no information is available, however, even limited information can be of value, especially if it is used to supplement data gathered from other sources. For example, a suite of simple screening methods may be used for the "triage" of unknown samples into positive, negative, and ambiguous groups. Often, the nature of the chlorinated compounds may be known from purchase or production records, so that only the ambiguous category may require detailed analysis. Screening methods may also be useful for confirming conclusions that have already been drawn from independent data, for example, that a collection of similar barrels do indeed contain the same materials.

The willingness to accept reduced certainty for the sake of economy and practicality opens the door to a wide variety of useful techniques that can be used in the field. In this paper, we will describe two such methods.

A unique semiconductor sensor has been found that is very sensitive to chlorinated and brominated organic compounds (1-3). It shows no detectable response to hydrocarbons, oxygen- or nitrogen-containing organic compounds, or fluorocarbons.

A second method that has given us promising results has been catalytic pyrolysis of chemical vapors combined with electrochemical detection. Compounds that are not normally thought of as electrochemical analytes, such as chloroform or cyclohexane, can be partially oxidized on a hot platinum surface (4). The volatile products always include some that give a response on a porous-electrode electrochemical sensor. We have confirmed over several years that the products of the pyrolysis are reproducible for most organic and some inorganic compounds when the conditions are kept reasonably constant (5). We have also

confirmed the critical requirement that the products are independent of analyte concentration, at least at concentrations of below 200 ppm. We call this method **pyrolysis-EC**.

The present embodiment of pyrolysis-EC is an instrument we call the CPS-100. This device uses an array of electrochemical gas sensors with different, but overlapping, selectivities. The incoming gases are pyrolyzed over noble metal catalysts heated at controlled temperatures. The operation of the instrument is orchestrated by a fairly powerful computer which can perform pattern analysis on the resulting data. In this paper, we report the results of a study on pattern recognition of odors in spoiled grain. The unique properties of neural networks have been shown to have significant potential for handling low-quality information. On reflection, this unique application is not so different from the problems encountered in classifying and handling hazardous wastes.

A simplified implementation of pyrolysis-EC has also been tested that uses a single sensor and a single catalytic filament. This drastically simplified system was still capable of distinguishing many organic chemicals. With fewer parts and lower power consumption, this simplified configuration may be suitable for selective hand-held vapor monitors.

Experimental Methods

Organochlorine sensor. The sensor was made by mounting a coil of platinum wire on a threaded base. A separate platinum wire is also mounted on the base and located axially within the coil. A mixture of lanthanum oxide, lanthanum fluoride, and a binder was applied to the coil. The coil was slowly heated with an electric current until a reaction occurred, forming the active material. The sensor is used by heating it to 550 °C with an electric current; conductivity is measured between the heating coil and the separate platinum electrode. When the sensor contacts the vapor of a chlorinated organic compound, the conductivity increases. A simple circuit can be used to provide a voltage output which is proportional to the concentration.

Permeation device. The permeation sampler consisted of a bundle of 0.025" o.d. dimethylsilicone tubing (Silastic, Dow-Corning) (Figure 1). The bundle could be placed in an aqueous sample containing dissolved organic or organochlorine compounds. A continuous flow of air was circulated through the lumen of the tubing, and organic material diffusing inward through the silicone membrane entered the gas phase. In a typical experiment, two permeators were used to provide separate reference and sample signals (Figure 2).

Pyrolysis-EC. The CPS-100 Toxic Gas Monitor has been described in several earlier publications (5-11); its configuration is diagrammed in Figure 3. The four sensors had platinum or gold working electrodes. For the grain odor experiments, the sensors were biased at differing oxidizing potentials, since reducing potentials gave very low or poor signals. A single rhodium pyrolysis filament was operated at 25, 450, 750, and 850 °C. The combination of four sensors and four temperatures gave an array of sixteen data points per analysis.

The apparatus for simplified pyrolysis-EC consisted of a single platinum filament and a single platinum-electrode gas sensor. A control circuit maintained the catalyst at any one of four preselected temperatures. The filament was enclosed in a Teflon-lined chamber of small volume through which the analyte gas was pumped at about 50 cc/min. The gas then passed through a short tube to the sensor. The experiments were controlled, and data gathered, by a commercial datalogger (Onset Computer Corp., N. Falmouth, MA).

Gas samples. Accurate samples of test compounds in vapor form were made by injecting measured volumes of the liquids into 40-liter Tedlar gas bags and filling with air pumped through a charcoal/Purafil filter. A flowmeter together with a stopwatch was used to determine the volume of air being pumped into the bag. Samples of permanent gases were made from standard mixtures obtained from commercial sources. Volumes of the standard mixtures and air were calculated and pumped into a sample bag, using the flowmeter and stopwatch to determine the volumes.

Samples from grain odors were generated by heating a sample of grain to 60 °C and flushing with a measured volume of air. The effluent air was passed through an ice trap to collect a "non-volatile" fraction and a liquid nitrogen trap to collect the "volatiles". The two fractions were run separately and in duplicate. Grain samples were obtained from Drs. L. Seitz and D. Saur of the USDA Grain Marketing Research Laboratory.

Results and Discussion

Organochlorine sensor. Typical responses of the sensor to different vapors in air are shown in Figure 4. The sensor was exposed to 100 ppm concentrations of chlorobenzene, benzene, and n-hexane. Only chlorobenzene caused a response. Of a series of compounds investigated, only HCl, and compounds containing carbon-chlorine and carbon-bromine bonds, gave a response (Table I). The response to concentration is essentially linear over at least four orders of magnitude.

Combined with the permeator device, the highly-selective organochlorine sensor was shown to respond rapidly to dissolved material. Figure 5 shows the response to chloroform in water at concentrations that dip below the part-per-million level. This sensor can be used to measure an organochlorine in groundwater, for example, without any sample preparation. Many sites, especially military bases, and areas such as Rockford, Illinois, where there is a large concentration of machine shops, have serious problems with chlorinated C2 compounds in the groundwater. In these cases, the nature of the compounds is generally known, and selectivity is not a concern. Nevertheless, the sampling procedure, sample preparation, and gas chromatography to determine these compounds is involved and expensive. The availability of a simple probe that can just be inserted into a groundwater sample will greatly reduce the number of laboratory analyses that need to be done. The silicone material is chemically resistant, and can be left in place for years. Particulates cannot enter the system. Lastly, and importantly, the permeator is very inexpensive.

Pyrolysis-EC: Grain Odors Only a few organic compounds will react directly with amperometric sensors under field conditions. On a typical, platinum-electrode sensor, we can detect alcohols, epoxides, and formaldehyde. We also detect many permanent gases, such as carbon monoxide and hydrogen sulfide. Among these gases that do react, there is no inherent selectivity. The use of different sensors and controlled pyrolysis, however, gives us extra degrees of freedom that can be used to achieve selectivity.

The grain odor problem is very instructive, even to an audience that is concerned with identifying individual hazardous compounds. Sensor-array-based methods, including the pattern-analysis methodologies used, treat mixtures no differently than single compounds; both give characteristic patterns which can be identified against a pattern made from the same mixture. The individual components of a mixture need not be identified.

Grains are presently classified by odor by a panel of trained inspectors. The results are necessarily subjective. More importantly, the subjective opinion is the **standard**; there is no point in telling a customer that a sample of grain is acceptable because a machine says so. If it smells bad, it smells bad. On the other hand, trained inspectors frequently disagree to a greater or lesser extent on both the category and degree of an odor (Table II). Attempts to identify specific compounds associated with the odors, using GC or GC/MS, have produced masses of data, but limited results (12, 13).

The data obtained on the CPS-100 was subjected to two different kinds of analysis. The first was an established method called **k-nearest neighbor** (KNN, ref. 5). The 16 data points acquired by the CPS-100 were treated as a vector in 16-dimensional space. Each known sample of grain produced a vector which could be associated with a particular odor category. The vectors from the unknown samples were tested against this library of known vectors by calculating the scalar distance between the unknown vector and each known vector in the library. All vectors were first normalized to constant length, to remove the concentration-dependent part of the information. The shortest distance is the identification (Figure 6).

The second method is the **neural network** (for general references, see 14, 15). This is a recently-developed method that has received so much "hype" that we were at first suspicious of it. However, its performance has been outstanding in this application, the moreso because we used a commercially-available packaged method (NeuroShell, Ward Systems Group, Frederick, MD), without really understanding the internal mechanics of the method. This is a very important feature of a method which may be used in the field by operatives with differing technical backgrounds.

Figure 7 shows the CPS-100 data, in histogram form, for "good" wheat samples. The patterns are very similar, in contrast with data showing some extreme samples (one "sour" (S3) and one "insect" (I3) odor) (Figure 8). A experiment using the older KNN method was run using a dataset derived from three grades of wheat samples. A library of vectors was prepared by averaging the signals for all runs on each sample of wheat. The scalar distances were calculated between all possible pairs of the original data set and each of the averaged vectors. A summary of the identifications is shown in Table III. We were very (pleasantly) surprised to find that those samples that are "misclassified" by the KNN

algorithm are also those that the human inspectors did not agree on! Sample 42, for example, was voted "good" by two inspectors and "musty" and "COFO" by the other two. (COFO means "commercially objectionable foreign odor".)

Although KNN has shown good performance in past applications (5, 6, 8-11), it has some serious practical disadvantages. The greatest is that, when the sensors become aged or drift for other reasons, the complete training set must be remeasured.

A larger data set had been gathered by the time the work was begun with the neural nets. This data set had a peculiarity built into it: one of the sensors in the array went bad halfway through the measurements and was replaced. The data taken after that point gave noticeably different histograms.

The data set was arbitrarily divided into two groups. One group was used to "train" the neural network, a process requiring up to 150 hours on a 386-type computer. The actual classification process took seconds. Two tests were run on the optimized neural net. First was a test to confirm that the optimization process was complete. This was done by using the training set itself as unknowns. The rate of correct classification was 100%. Second, random, linearly-distributed errors were added to the data, followed by classification. The net tolerated 5% error without missing a correct classification. Added error of 10% and 15% caused a small amount of degradation (Table IV).

Having confirmed the robustness of the neural net, it was challenged using the reserved dataset. The net had not seen these numbers before; nevertheless the rate of correct classification was 65% (Table IV). This is low, although substantially better than random. Because the test conditions had changed during the measurements, we added another element to the data vectors to differentiate the measurements made before and after the sensor was changed. The numbers were arbitrary, 100 for the old sensor and 200 for the new. Using these 17-element vectors, the neural net was retrained. Now, the rate of correct classification of the reserved dataset jumped to 83%.

Pyrolysis-EC: Simplified Version This work is the result of a project to determine whether a greatly-simplified form of pyrolysis-EC would be useful for situations requiring limited selectivity. Figure 9 is a diagram of the patterns obtained for representative compounds in a typical experiment. The temperature of the catalyst is programmed for two minutes at room temperature, two minutes each at temperatures of 500, 600, 700, and 800 °C, and finally two minutes at room temperature again. The patterns that are obtained are distinct for many compounds. If your field problem is simply confirming the identity of the contents of a number of similar barrels of an unknown chemical, the pyrolysis-EC approach may in itself be sufficient, although most practitioners would feel more comfortable if it supplemented other field screening methods.

A table of distances for this limited configuration is shown in Table V. The smaller the number, the more similar the two compounds will appear for a given configuration of the experimental apparatus. This configuration gives very good identification of ethylene oxide in the presence of all but alcohols.

The pyrolysis-EC method has several advantages that are especially conducive to field work. It is suitable for portable instrument use; the components are shock-resistant and will operate in any orientation. They compact and lightweight, and the power requirements are small. They are also inexpensive.

Conclusions

1. A sensor has been developed and characterized that can identify chlorinated or brominated compounds in the vapor phase or, with the use of a permeable membrane, in dissolved form.

2. A combination of catalytic pyrolysis and electrochemical detection (pyrolysis-EC) can be used to distinguish unknown compounds with a modest degree of selectivity that may be adequate for many field applications.

3. Pyrolysis-EC data, combined with k-nearest neighbor and neural network classification methods, has been used effectively for such varied tasks as the classification of stored grains by odor, or the classification of waste chemicals by functional group (11).

4. The neural net can be made to adapt dynamically to instrument drift. In effect, it learns from experience.

4. Errors made by the classification methods correspond in a general way to errors made by human experts faced with similar ambiguities in the data.

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Table I. Sensitivities of the organochlorine sensor to several halogenated compounds.

Vapors	Concentration (ppm)	Response (x 10^{-6} mho/ppm)
C_2H_3Cl	125	0.024
C_2H_3Br	125	0.016
C_2H_3I	125	0.003
C_2H_3F	62.5	0.005
$C_2H_2Cl_2$	62.5	0.029
$C_2H_2Br_2$	62.5	0.020
$C_2H_2I_2$	125	0.003
C_2ClF_3	12.5	0.022

Table II. Subjective odor characterization of the grain samples used in our study.

SAMPLE No.	GMRL INSPECTORS DS	LS	KF	HM	FGIS CONSENSUS	AVE INTENSITY
F41	C2	OK0	OK0	OK0	OK	0.5
F42	OK0	OK0	M1	C2	OK	0.7
F67	OK0	M1	OK0	OK0	OK	0.2
F78	OK0	OK0	M2	OK0	OK	0.5
F128	OK0	OK0	OK0	OK0	OK	0.0
F30	I3	I3	I3	I3	INSECT	3.0
F39	I2	C3	I2	C1	INSECT	2.0
F69	I1	I2	I2	M3	INSECT	2.0
F89	I3	I3	I2	S3	INSECT	2.7
N53	I2	S3	S2	S3	S3	2.8
N166	S3	S3	S3	S3	S3	2.9
N168	S2	S3	S2	S2	S3	2.6

Table III. KNN classification of the USDA grain samples.

"Unknown" Vectors	Average of Known Vectors: Good (128, 42, 67, 41)	Insect (30, 39, 89)	Sour (53, 166, 168)
Good	128, 128, 42, 67, 67, 41, 41, 41, 41	42	42
Insect	89	30, 30, 30, 39, 39, 89, 89, 89	30
Sour	168	168, 168	53, 166, 166, 166, 168, 168

Table IV. Summary of the accuracy of the neural network algorithm for identifying vapors drawn from the wheat samples.

Sorghum Data Set	Accuracy of Identification	Wheat Samples Data Set	Accuracy of Identification
1. Original Data	100%	1. Total Data	100%
2. 5% Error added	100%	2. Train on 55% of Data set	65%
3. 10% Error Added	98%		
4. 15% Error Added	92%	3. Add channel for Test Conditions	83%

Table V. Distance matrices for a series of organic compounds. Table V-A is several concentrations of ethylene oxide; the concentrations are shown as the numbers in the symbols, e.g., ETO100 = 100 ppm. Table V-B shows the distances among the series of thirteen compounds. The Abbreviations are:

CHX - cyclohexane
ETE - ether
CLO - chloroform
FORM - Formaldehyde
ETO - Ethylene Oxide
ISO - isopropanol
KER - kerosene
STY - styrene
ETG - ethylene glycol
ACE - acetone
XYL - xylene
HAL - halothane
ETA - ethanol

TABLE V-A
Distance for Ethylene Oxide

	ETO100	ETO40	ETO20	ETO5	ETO5	ETO1
ETO100	0.00	0.31	0.28	0.22	0.25	1.02
ETO40	0.31	0.00	0.07	0.21	0.18	0.80
ETO20	0.28	0.07	0.00	0.21	0.16	0.82
ETO5	0.22	0.21	0.21	0.00	0.09	0.85
ETO5	0.25	0.18	0.16	0.09	0.00	0.80
ETO1	1.02	0.80	0.82	0.85	0.80	0.00

TABLE V-B

	CHX	ISO	ACE	ETE	XYL	KER	CLO	STY	FORM	HAL	ETG	ETO	ETA
CHX	0	1.57	0.19	1.76	1.02	1.07	0.69	1.44	1.74	2.09	1.52	1.73	1.95
ISO	1.57	0	1.42	0.44	0.76	0.62	1.49	0.46	0.31	0.72	0.4	0.62	0.81
ACE	0.19	1.42	0	1.59	0.85	0.91	0.55	1.27	1.58	1.93	1.35	1.55	1.77
ETE	1.76	0.44	1.59	0	0.82	0.74	1.53	0.41	0.2	0.59	0.3	0.25	0.38
XYL	1.02	0.76	0.85	0.82	0	0.34	0.88	0.45	0.85	1.27	0.55	0.75	0.98
KER	1.07	0.62	0.91	0.74	0.34	0	1	0.49	0.76	1.08	0.54	0.75	0.95
CLO	0.69	1.49	0.55	1.53	0.88	1	0	1.26	1.55	1.93	1.33	1.44	1.62
STY	1.44	0.46	1.27	0.41	0.45	0.49	1.26	0	0.45	0.93	0.12	0.37	0.63
FORM	1.74	0.31	1.58	0.2	0.85	0.76	1.55	0.45	0	0.61	0.34	0.41	0.56
HAL	2.09	0.72	1.93	0.59	1.27	1.08	1.93	0.93	0.61	0	0.84	0.79	0.73
ETG	1.52	0.4	1.35	0.3	0.55	0.54	1.33	0.12	0.34	0.84	0	0.3	0.55
ETO	1.73	0.62	1.55	0.25	0.75	0.75	1.44	0.37	0.41	0.79	0.3	0	0.27
ETA	1.95	0.81	1.77	0.38	0.98	0.95	1.62	0.63	0.56	0.73	0.55	0.27	0

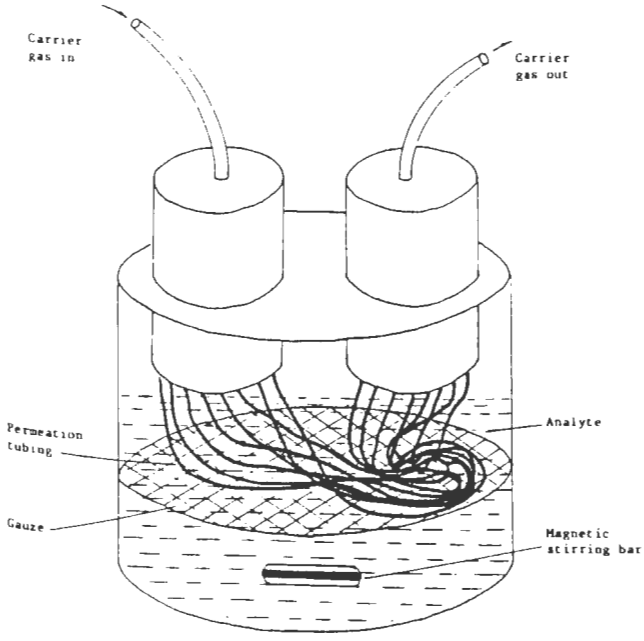

Figure 1. Permeation apparatus used to extract organochlorines from water.

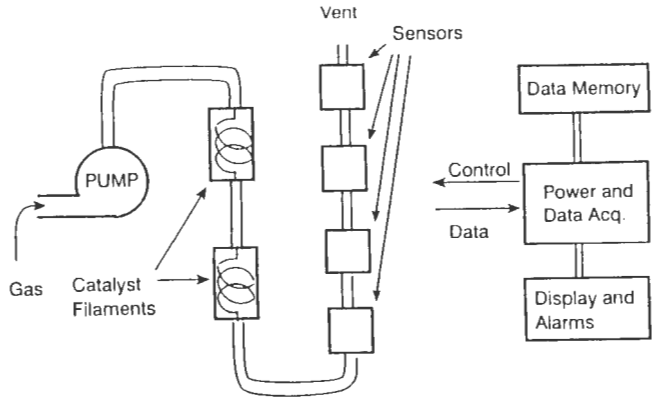

Figure 3. Configuration of the CPS-100 Toxic Gas Analyzer, fitted with four electrochemical sensors and two catalyst filaments.

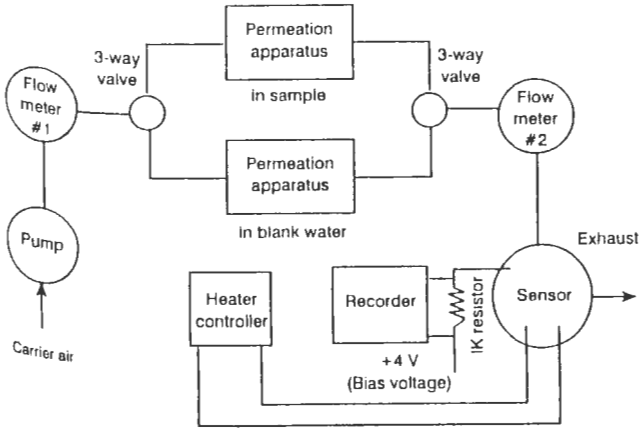

Figure 2. Experimental apparatus for selective analysis of aqueous chlorinated hydrocarbons using a separate reference permeator.

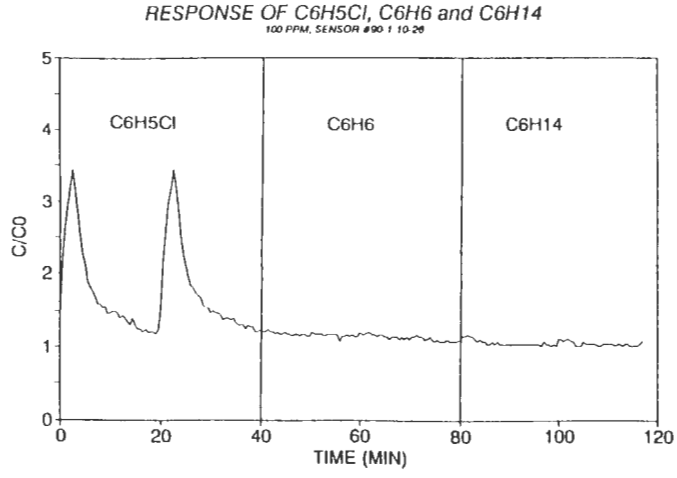

Figure 4. Response of the organochlorine sensor to chlorobenzene, benzene, and hexane.

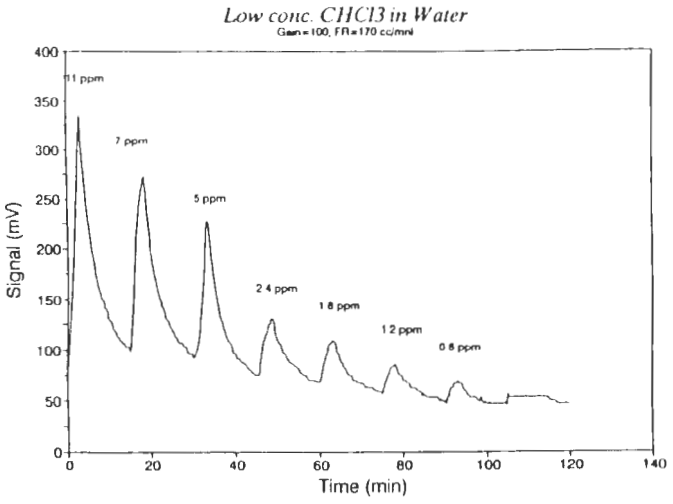

Figure 5. Response of the organochlorine sensor to decreasing concentrations of chloroform.

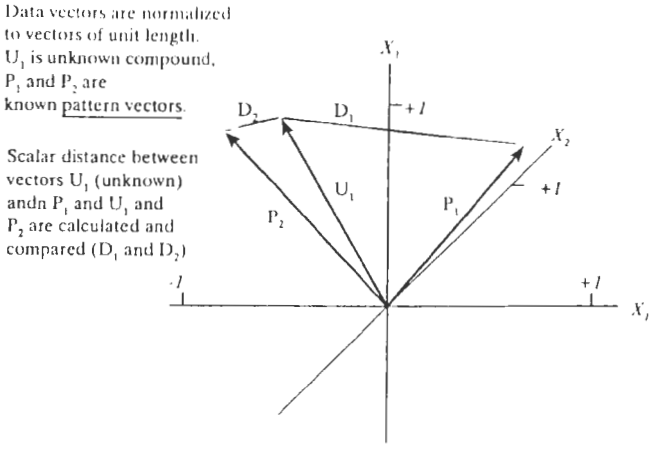

Figure 6. Schematic representation of the KNN pattern recognition method in 3-dimensional space. P1 and P2 are library patterns for known compounds, and U1 is the vector for an unknown. The distances from U1 to P1 and P2 are calculated and compared.

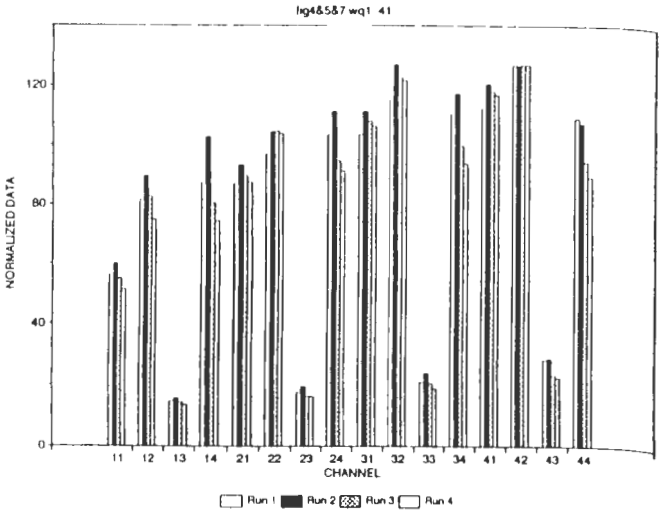

Figure 7. Histogram of normalized responses of the CPS-100 to four samples of "good" grain.

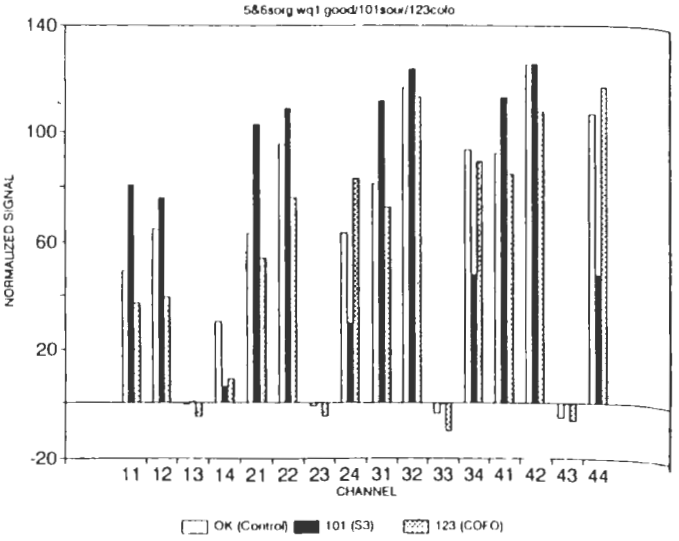

Figure 8. Normalized responses of the CPS-100 to "good" (OK), sour (S3), and COFO grain.

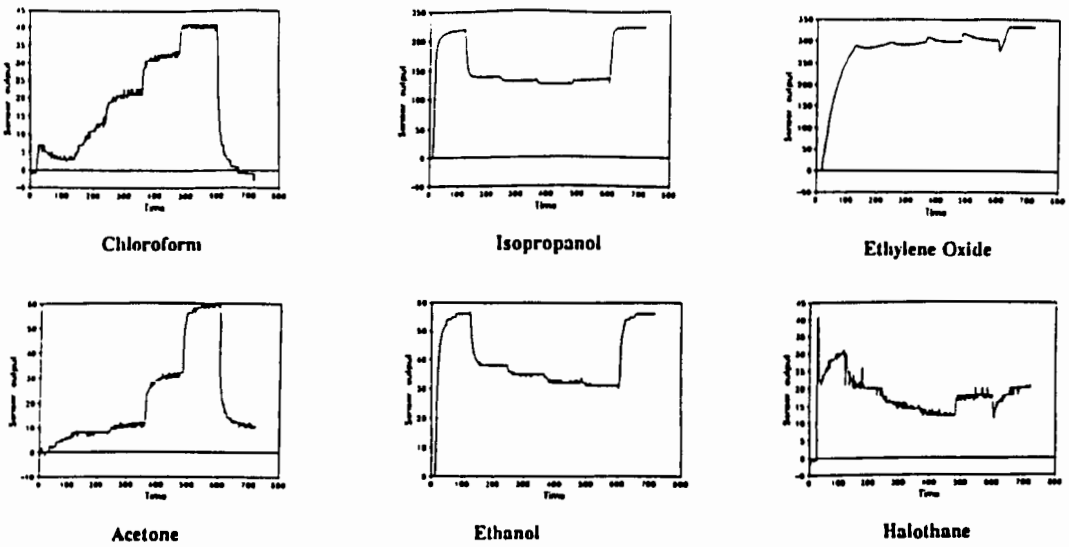

Figure 9. Responses of the simplified pyrolysis-EC apparatus to six different chemicals. In this experiment, the catalyst filament was programmed in 2 minute steps at room temperature, 500, 600, 700, and 800 degrees, and room temperature again.

DISCUSSION

GORMAN BAYKUT: My question is about the chemical analysis with these sensors. I'm not talking right now about the wheat vapor. But in terms of real chemical analysis, you must know the compounds you are going to analyze, otherwise you can't do the analysis because you need training. You can't analyze the unexpected compounds, am I right?

WILLIAM BUTTNER: The way the CPS 100 Program was originally envisioned, you had to install the library vectors of potential compounds. If you were going to look at TCE, there had to be a library vector associated with the TCE. On the other hand, these arrays are not totally selective in response. The response to TCE was similar to PCE, that is, tetrachloroethane. You could therefore identify classes of compounds. But you are right. You have to have some idea of the type of vapors present. A totally unknown situation will still give some ambiguity in your analyses.

GORMAN BAYKUT: But I think even though your software is powerful, you need a training period for every compound. How about the mixtures? If you analyze the mixtures will there be a problem?

WILLIAM BUTTNER: Mixtures are a problem for this type of system. Certain types of mixtures are well behaved. Gasoline, for example, is a mixture of many types of compounds, but it behaves as a single class.

GORMAN BAYKUT: I'm referring to the cracker. You have a thermal cracker in front of the electrochemical sensor areas. Sometimes you have a mixture of two or three compounds, or five, or seven and they react in the cracker. You get different answers, and the correlation is not linear.

WILLIAM BUTTNER: What you're referring to are the reaction products of the thermal catalysis that result from mixtures being exposed to the sensors. Yes, you are right. There is frequently a nonlinear response. The reaction products frequently do react with each other. That's a comment relevant to many field screening techniques. In some mixtures that factor is a little less significant. If you do generate very reactive compounds, for example from chlorinated compounds TCE, you do get a nonlinear response. That is a problem. This instrument was designed to look at single vapors, maybe not necessarily positively identified, but single vapors.

STEVEN KARR: I wondered if you've given any thought to applying fuzzy logic algorithms to this problem as opposed to neural networks?

WILLIAM BUTTNER: The neural network was a six-month program that we tried on the SBIR (we've just finished Phase I). To stay within the time constraints, we stuck to simple systems. We are investigating other neural network software packages and other identification algorithms. We will certainly consider fuzzy networks.

EDWARD POZIOMEK: Have you tried any real-world environmental samples with the system.

WILLIAM BUTTNER: I had a program through Savannah River to monitor for TCE emissions out of their stripping tower, as part of their groundwater clean up. Initially the results were very encouraging. The analyses that I measured were compared back to groundwater samples as measured at an independent laboratory. They were comparable in value. The unfortunate thing is that these amperometric sensors did not behave truly reversibly to chlorinated compounds, and that after a period of time their response factor, their sensitivity, would degrade and ultimately their response would die completely. For that reason it was determined that these types of sensor systems would not be applicable for the problems associated with Savannah River Laboratory. This was before this chlorine selective sensor was developed. It could potentially have application down there.

REAL-TIME DETECTION OF ANILINE IN HEXANE BY FLOW INJECTION ION MOBILITY SPECTROMETRY

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DISCLAIMER: Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ABSTRACT

Ion mobility spectrometry (IMS) with a conventional ^{63}Ni ion source exhibits chemical behavior that should be advantageous in detection of molecules with high proton affinity such as aromatic amines in common organic solvents. Since IMS instrumentation can be considered a continuous-sampling point sensor, IMS may be adapted for industrial process monitoring or area environmental monitoring. However, quantitative aspects of IMS are not well established and possible interferences may limit the usefulness of IMS. In order to characterize IMS behavior as an effluent sensor, a flow injection IMS device was evaluated in which an IMS was used as a detector for a heated injector port. An IMS drift tube was used with an acetone doped reaction region and a membrane inlet. Five microliter replicate samples were introduced and vaporized in the inlet at 15 - 90 second intervals and drawn into the IMS. Detection limits were ca. 0.5 mg L^{-1} for 5 ul aliquots (2 ng per sample). Sampling intervals could be reduced to 15 seconds for all concentrations below 40 mg L^{-1} above which however a working range could be considered to approximately 100 mg L^{-1}. Precision was 10 - 25% RSD and was largely concentration independent. Since the IMS alone in a vapor stream shows ca. 1 - 2% RSD, the bulk of variance was from the inlet and inlet-IMS interface. Four solvents (benzene, methylene chloride, ethyl acetate, and acetone) were evaluated as interferences. All solvents at some concentrations affected the peak area for aniline, although the causes arose through different mechanisms. The use of IMS as a flow sensor for aniline in organic solvents should presently be restricted to samples free of compounds with strong proton affinities and solvents which do not exhibit strong dipoles.

INTRODUCTION

Ion mobility spectrometry (IMS) with a conventional ^{63}Ni ion source exhibits chemical behavior that should be advantageous in detection of molecules with high proton affinity such as aromatic amines in common organic solvents. Since IMS instrumentation can be considered a continuous-sampling point sensor, IMS may be adapted for industrial process monitoring or area environmental monitoring. However, quantitative aspects of IMS are not well established and possible interferences may limit the usefulness of IMS. Among the attributes of an acceptable "field screening method for hazardous waste and toxic chemicals" are sensitivity, specificity, accuracy, precision, speed, and portability. Also, to be worthwhile, it should be applicable to the screening of analytes or classes of compounds which have a reasonably high toxicity. The optimum value of a real-time field technique would be in the screening of substances with acute toxicity, thereby assisting in the elimination of short term exposures. The purpose of this work is to investigate

such quantitative aspects of IMS as sensitivity, accuracy, and precision; interference is examined as a comparison of response to solvents of varying proton affinity; and speed of analysis is an additional experimental parameter.

In IMS, vapors are drawn into a reaction region where analyte is ionized through proton or electron transfers from a reservoir of charge, the reactant ions. The reactant ions originate in beta emission from a ^{63}Ni radioactive foil and the reactant ions exhibit near thermal energies. Consequently, product ions usually experience little fragmentation and exist principally as M^+, MH^+, or M_2H^+. Ionization in the reaction region is based on competitive charge exchange, and unequivocal response occurs when the target analyte has a proton affinity larger than that for any component in the sample matrix. When this is not assured, response can become confusing even for simple mixture (1). Thus, the primary basis for selectivity of IMS as a detector is based upon differences in proton affinities of constituents following vaporization into a flowing air stream. Product ions are injected into a drift region where ions acquire a constant velocity in a weak electric field. Differences in ion velocities are due to differences in cross-sectional areas, and this serves as a useful, second level of selectivity in IMS. However, response in IMS is fundamentally governed by the original step of product ion creation; thus, if a product ion is not formed in the ion source, regardless of cause, a peak corresponding to that substance will not be observed in the mobility spectrum.

Flow injection analysis (FIA) is a type of continuous analytical technique where discrete, reproducible aliquots of sample are introduced into a flux, allowed to interact with other components of that flux or with forces exerted on that flux, and are subsequently monitored by a detector having some inherent specificity for the resultant species. Reviews of flow injection analysis by Betteridge (2) and by Ranger (3) date the origins of this technique to the early to mid-1970's as an adaptation or subcategory of "continuous flow analysis" as described by Skeggs (4). This type of analysis has the advantages of being simple, accurate, reliable, reproducible, and can be accomplished with a small amount of simple equipment. All of these attributes are desirable in any real-time, field screening method. The disadvantages of FIA methods come from a dependence on detector selectivity in the absence of any separator techniques, as will be seen later.

Chemically, the high proton affinities of aniline and other aromatic amines suggest that ion mobility spectrometry may be a technically acceptable technique for monitoring of these substances by flow injection technique. Development of a field screening method for these compounds would be worthwhile based on toxicity, the primary toxic effects of this class of compounds on man including methemoglobin formation and cancer of the urniary tract (5). Environmentally, "aromatic amines constitute a family of serious pollutants due in part to a high degree of toxicity toward aquatic life (6). Particular attention has been given to the effects of aniline, aniline derivatives, and aromatic amines on fish (7,8), Daphnia magna (9,10) and microbes in estuarine water (11)." (Eiceman et al) Commercially, they are important as intermediates in the manufacture of dyestuffs and pigments, but are also used in the chemical, textile, rubber, dying, paper industries and other (5).

EXPERIMENTAL

Instrumentation

The introduction of a flow injection stream to an IMS detector was accomplished using the instrumentation and procedures described below. A block diagram of the flow injection IMS apparatus is shown in Figure 1 and was comprised of a heated injector taken from a gas chromatograph, an Airborne Vapor Monitor (Grasby Analytical, Ltd., Watford, UK) as the IMS detector, a pressurized source of air and supporting electronics to control injector temperature. Air flow through the injector port was ca. 5 ml/min and the injector temperature was 100°C. Both the injector block assembly and the IMS instrument were placed inside a laboratory hood, and there was a distance of less than 1 cm between the injector exhaust and the IMS inlet. Digital signal averaging was used to acquire mobility spectra with an Advanced Signal

Processor (ASP) (Grasby Analytical, Ltd.) into an IBM XT microcomputer. Also, signal was routed from an output voltage on the ASP to a Hewlett-Packard 3380A recording integrator so peak areas for the aniline product ion could be recorded versus time and integrated. The window of observation for drift times for the aniline peak was ca. 0.1 - 0.2 ms wide and was centered on the drift time for aniline, 8.74 ms. Other parameters for signal collection through the ASP board were: number of waveforms, 32; points per spectrum, 512; and scale expansion, 0.25. The integrator parameters were: attenuation and threshold, each 9; chart speed, 1 cm/min; area rejection, 10000; and peak width 0.5.

Reagents and materials

The following solvents were obtained in high commercial purity and used without further treatment: aniline (Aldrich Chemical Co., Milwaukee, WI, 99.5%+), hexane (Chromopure, Burdick & Jackson Co., Muskegon, MI), acetone (Chromopure, Burdick & Jackson Co.), benzene (B&J Brand, Chromopure, Burdick & Jackson Co.), ethyl acetate (Fisher Scientific, Pittsburgh, PA), and methylene chloride (Fisher Scientific).

Procedures

In general, 5 ul aliquots of liquid sample were delivered with a 10 ul syringe (Hamilton Co., Reno, NV) to the heated injection port during continuous signal processing with the IMS. An interval of 15 to 90 seconds was permitted for the air to sweep vapors from the inlet before another injection was made. Several parameters were examined to determine optimum operating conditions and access the reliability of IMS as a flow injection detector. The particular details of each of these studies were:

Clearance study and response curve - Five microliters of aniline in hexane at concentrations from 0 to 100 ppm (volume/volume liquid) were delivered in five replicates at different intervals from 15 to 90 seconds. Peak areas were determined for the aniline product ion in the preparation of a quantitative response curve. The effect of injection interval also permitted the determination of memory effects in the IMS under a range of concentrations.

Chemical interferences - In the study of chemical interferences in aniline determinations, 5 ul of 5 ppm aniline in hexane were co-injected with 0 to 4 ul of pure interfering solvent. These interfering solvents were methylene chloride, benzene, acetone, and ethyl acetate. Five replicate determinations were made at 60 second intervals.

RESULTS AND DISCUSSION

General

The reactant ion peak (RIP) with acetone reagent ion chemistry and the mobility spectrum for aniline in the hand-held IMS are shown in Figure 2. The mobility spectrum for aniline contained a single symmetrical peak at 8.74 ms drift time, consistent with previous findings for aniline with water-based chemistry in the ion source (12). Residual amounts of reactant ion at 6.97 ms in aniline mobility spectrum demonstrated that the ion source was not saturated and that comparable behavior may be anticipated at vapor levels lower than this. This mobility spectrum was generated using 5 ul of a 5 ppm solution (25 ng absolute mass) and the peak height relative to the RIP was reasonable considering the high proton affinities of aniline. Previously, aniline was shown with IMS/MS to yield a protonated molecule, MH^+ product ion (12) although the ambient temperature drift tube and alternate ion chemistry used here may favor the existence of a MH^+_xS ion where S is an acetone solvent molecule, but this has not been unequivocally established.

Clearance Behavior, Standard Deviation, and Response Curve

The hand-held IMS used in this work would be suited for field use due to its size (40cm x 15cm x 8cm), weight(2.6 kg), and ability to operate continuously in hostile environments unattended. The IMS itself is battery powered and could be interfaced with a battery powered lap top computer for data acquisition, providing a portable system. However, this IMS could be expected to exhibit memory effects from the ambient temperature drift cell and membrane-equipped inlet. At high concentrations of aniline, slow clearance from repetitive determinations might occur. In Table 1, peak areas and percent relative standard deviations (%RSD) from repetitive determinations are given for solutions between 0 and 100 ppm at injection intervals from 15 to 90 seconds. The %RSD ranged from 13 to 125, but showed a median of 21% Previous

experience with this IMS as a detector in FIA methods had yielded reproducibility of peak heights of 8 to 10 %RSD and this large variance was suspected to be due to the placement of the FI-IMS in the fume hood. Turbulence in a fume hood has been associated with position and movement of the user as well as amount and location of equipment in the hood (13). This turbulence likely affected yields in the interface between the inlet and IMS and this large RSD was suggestive that mechanical improvements in interface between the IMS and injection port are needed. A straightforward leak-tight connection was not employed in these studies due to the flow characteristics for this IMS and the eminent rupture of the membrane inlet if pressure differences developed between the inlet and ion source regions.

The anticipated memory effect from slow clearance of the aniline from the IMS was evident in the peak areas given in Table 1. In general, peak areas with 90 second injection intervals were the lowest for a given concentration level. Injection intervals less than 90 seconds caused an accumulation of aniline in the IMS and peak areas increased for example as much as 100% at 30 second intervals with the 100 ppm concentration. This was manifested in the signal for continuous monitoring as a rising baseline and in the mobility spectrum as a persistent product ion. Memory effects here were dependent upon concentrations, as expected, and at concentration below 20 ppm, injection intervals of 15 seconds could be employed with reasonable differences in absolute areas.

A plot of peak area versus concentration of aniline in hexane for 5 ul injections at 90 second intervals is shown in Figure 3 and resembled previous response or calibration curves in IMS (14). Such curves are comprised of narrow linear ranges (in this instance between 5 to 20 ppm), a shallow but mostly linear response at concentrations above the main linear region and a nearly linear plot with shallow slope below the linear region. This behavior is due to the nature of the kinetics of reactant ion formation from the beta emitting ion source and, thus, to the limited reservoir of charge available to analyte vapors.

Chemical Interferences

The existence of solvents with a range of proton affinities in industrial waste streams constitutes a potential compromise on the integrity of IMS response in flow injection determinations through two mechanisms. Conceivably, large levels of such solvents might compete for charge resulting in reduced peak areas for aniline at given vapor levels. Alternately, solvents may cause, at ambient cell temperatures, ion-solvent clusters which lead to shifts in drift times for product ions. This will cause a decline in certainty regarding peak identity or may cause the peak to fall outside a window of observation in the signal processing software.

Four solvents with low and medium proton affinities were selected for interference studies and mobility spectra for individual solvents are shown in Figure 4. Methylene chloride gave little response in positive polarity IMS as expected due to a low proton affinity. For the same reason, benzene showed a weak response with an acetone reactant ion chemistry and the product ion had a drift time shorter than that for the RIP. Acetone formed cluster ion, with drift times longer than that for the RIP, through ion-molecule interactions in the IMS drift region as described by Preston and Rajadhax (15). Only ethyl acetate (EtOAc) showed significant competition with the reactant ion, due to large proton affinities of EtOAc relative to acetone, with the obvious result of a product ion. Of these solvents, only benzene has been mass identified as M^+ (16) though acetates are known to form MH^+ and M_2H^+ product ions (17).

The influences of these solvents on IMS response to a 5 ul injection of 5 ppm aniline in hexane are shown in Figure 5 as a plot of peak height for aniline in various ratios of four solvents in a binary mixture with hexane. All solvents affected the peak area for aniline although the causes arose through different mechanisms. In Figure 6, mobility spectra are shown from equal mixtures of hexane and solvent for 5 ppm aniline and these can be compared directly to spectra for individual solvents (Figure 4) and for aniline (Figure 2). For EtOAc, the product ion dominated the ion chemistry when aniline

was present even though proton affinities favored aniline. Ethyl acetate at high concentrations relative to aniline appropriated virtually all the charge except that remaining with the RIP. The ion-molecule chemistry for acetone as an interference also followed this pattern and aniline was not detected with high levels of acetone. Thus, the rise in peak areas in Figure 5 represented a false positive by acetone for aniline since acetone product ion intensity intruded upon the drift time window used to monitor aniline. In such a situation, only inspection of the mobility spectrum could avert an error in monitoring on analyses. A product ion for aniline was evident with methylene chloride due to the low proton affinities of methylene chloride. However, the increase in response for aniline in positive polarities from addition of methylene chloride to hexane (Figure 5) was unprecedented in IMS and conclusions cannot be made pending IMS/MS studies. Benzene, with proton affinities between methylene chloride and acetone or EtOAc, exhibited a type of intermediate behavior. A product ion for aniline was observed in the presence of benzene, but the benzene was at a level sufficient to effectively compete for protons from the RIP and a benzene product ion was also observer (Figure 6). These spectra and trends suggest that an IMS will be sensitive to common solvents at low levels even with an alternate reactant ion chemistry, a membrane inlet, and low (<1%) levels of solvents other than hexane. However, if the solvent composition is known and reasonably constant, calibrations presumably could be prepared in that matrix. These findings for simple compositions argue for standard addition techniques with flow injection IMS determinations.

CONCLUSIONS

Ion mobility spectrometry has never been widely regarded as a quantitative instrument, but as a detector for flow injection determination, IMS exhibited suitable response curves, standard deviations, and response times. This was accomplished under the demanding situation of a fast transient vapor level in FIA methods. The linear range is a weak aspect to quantitative IMS and alternative configurations to conventional ^{63}Ni sources should be sought. Reactant ion chemistry based on acetone was not wholly successful in discriminating chemically against common organic solvents. Consequently, until improved source chemistry is found, standard addition should be considered the method of choice for quantitative FIA with IMS for aromatic amines.

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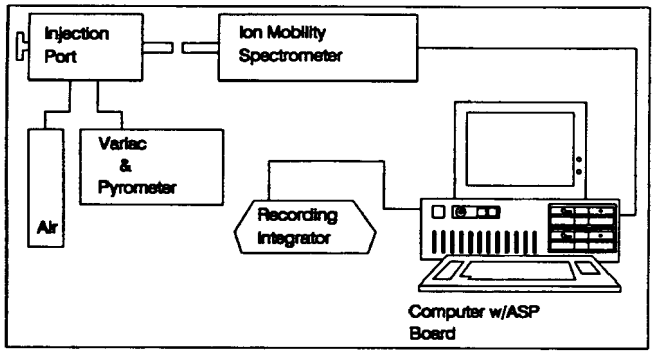
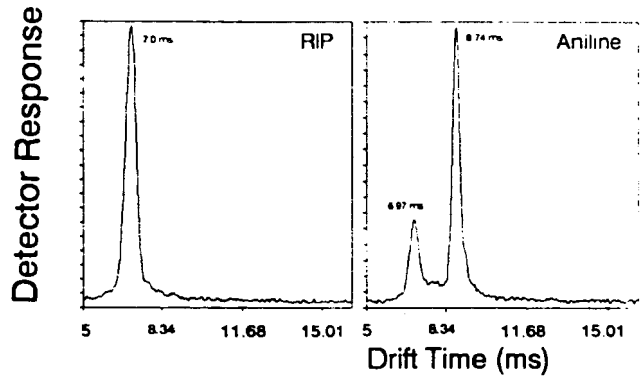
Table 1. Peak Areas from Plots of Aniline Product Ion Intensity versus Time in Flow Injection Ion Mobility Spectrometry

Aniline Concentration (ppm)	PEAK AREA ($X10^6$) (% RSD) Interval for injection (seconds) 15	30	60	90
0	0.83 (13)	1.6 (104)	0.84 (13)	1.1 (34)
0.4	2.8 (23)	5.4 (49)	2.5 (20)	2.0 (29)
1	6.8 (19)	5.2 (23)	4.6 (27)	1.6 (8.0)
5	19.6 (21)	14.9 (16)	16.0 (19)	10.9 (22)
10	32.6 (29)	32.9 (21)	30.4 (20)	26.1 (13)
20	•	35 (21)	41.9 (16)	46.6 (13)
40	•	49 (33)	40.4 (15)	37.6 (21)
100	•	95 (45)	62.7 (31)	42.5 (125)

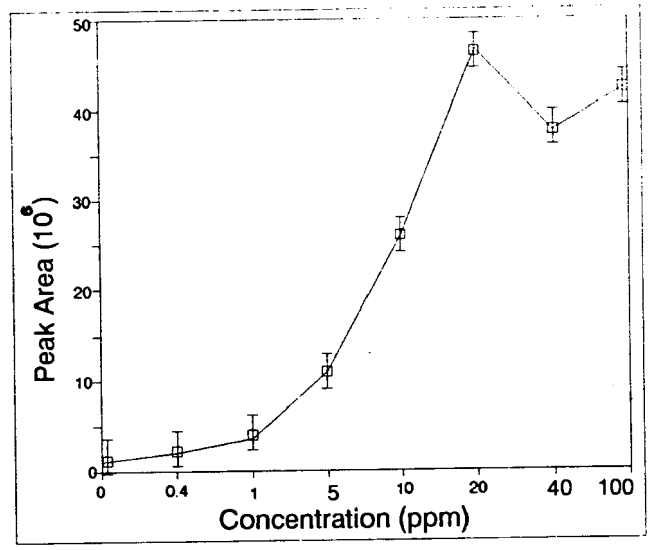
•Baseline drift due to residual aniline was too severe for integration or recognition of a peak in flow injection IMS.



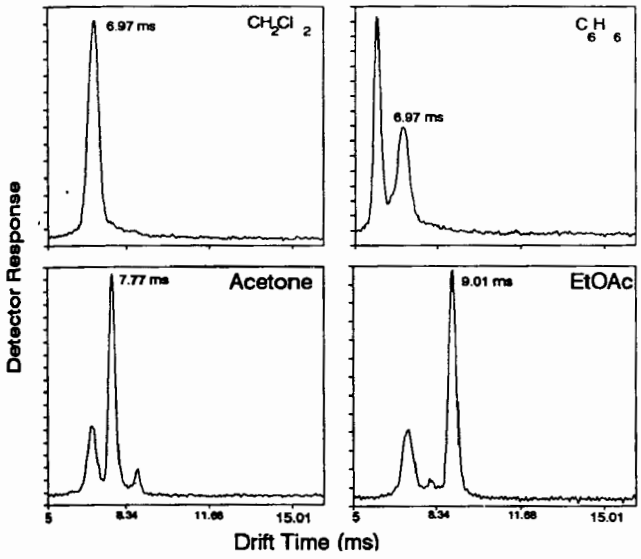
1. Block diagram of apparatus for quantitative flow injection ion mobility spectrometer (IMS) including continuously flowing air stream. Sample is deposited in the heated injection port, vaporized, and swept into the IMS detector. The mobility spectrometer was operated with digital signal averaging causing ca. 1 second intervals between display of successive IMS analyses.



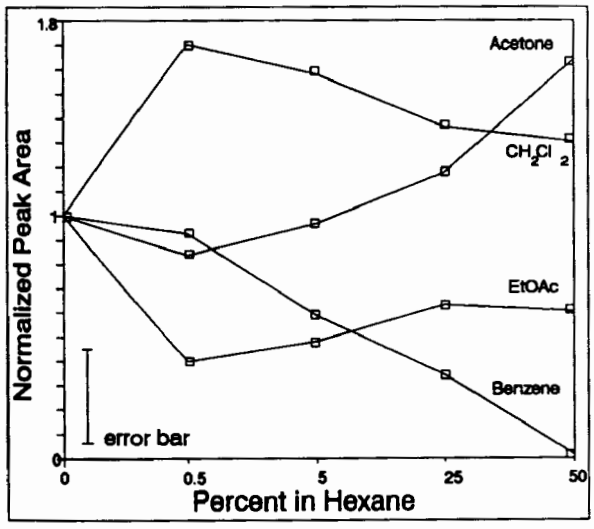
2. Ion mobility spectra for acetone reactant ion peak (RIP) alone and for aniline in hexane using a hand-held IMS. Spectra were obtained in positive polarity, and care was taken to keep the source from a saturated condition.



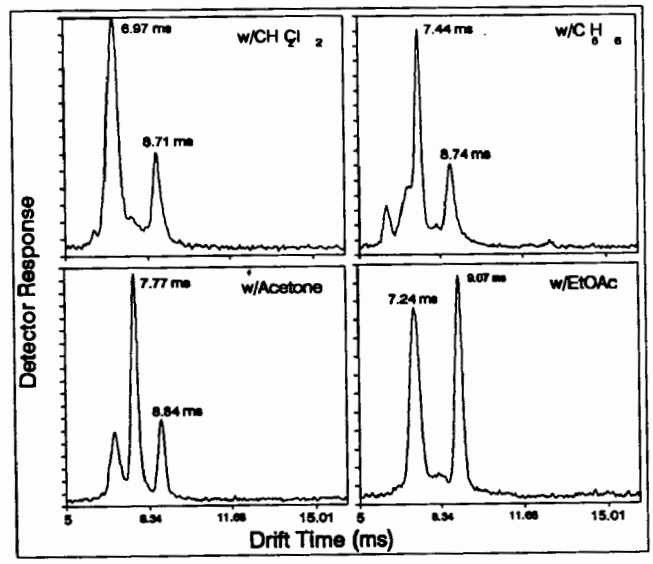
3. Response curve for quantitative determination of aniline in hexane using gaseous phase flow injection IMS. Error bars added at each point were twice (2X) the standard deviation taken as an average for all measurements.



4. Ion mobility spectra for solvents expected to be encountered in analysis of non-aqueous streams for aniline. Mobility spectra were obtained in positive polarity with acetone reagent ion chemistry. Spectra were obtained with solvent vapors permitted to deplete reactant ion intensity ca. 50% from background levels.



5. Effect on peak height for aniline at 5 ppm in binary solvent mixtures of hexane with other common solvents with vol/vol percentage from 0 - 50%. Curves were normalized to the peak height of aniline in hexane solution.



6. Mobility spectra for mixtures of 5 ppm aniline in 50 : 50 mixtures of individual solvents with hexane. Aniline in hexane exhibited a single product ion with drift time of 8.74 ms as shown in Figure 2.

DISCUSSION

STEVEN HARDEN: The question I have is with respect to orthonitrophenol and the sensitivity of the IMS system to that particular kind of material. Did you ever do a calibration run to determine what that sensitivity might be under various conditions?

PETER SNYDER: The answer to that question is no, we have not on pure orthonitrophenol. However, the signals — the amount of signal that we see from the other point of view, looking at it from the organism's point of view, and knowing how much organism we have. It seems like there is still plenty of analyte, given the relatively short time of detection, and knowing that the signal is still a bit spread out. The signal is not in one, or say two, or maybe three at the most, peaks. We see it at about seven, eight, nine 10 peaks, until it finally clears down.

So I'm not trying to skirt the question. It's just that no, we haven't done it to see how sensitive the CAM itself is, or the ion mobile spectrometer 20MP. However, I suspect that it has to be very sensitive, since 200, even 50 cells is a good response, and the response is spread out, so if we can find ways of compacting it, it'd be that much better.

MAHADEVA SINHA: What are the vapor pressures for the orthonitrophenol when it gets combined with the glucose. Do you get any response?

PETER SNYDER: Yes, we've done many, many blanks. We always do a blank before and after.

First of all, the vapor pressure of orthonitrophenol is 5.54 torr at ambient temperature. That doesn't should like much, but relatively speaking, that's a lot for the CAM. And the controls — we have done ONP by itself, with buffer, without buffer, and then just organisms themselves. Organisms do produce some peaks, but that's just right after the reactant ion peak. But it just happens to tail off, and there is no signal in the area that the ONP shows. So we have been pretty lucky in that respect.

The ONP has very negligible vapor pressure by itself. Even if you get a bottle of the dry powder, and just stick the CAM in the bottle, you see no response at all. That should be the most amount, the dry powder, and if anything's going on it would show. But even in the solution, there's no problem.

Orthonitrophenylacetate is a different story. There is hydrolysis going on and over a couple of hours, you can see orthonitrophenol being produced.

DETECTION OF MICROORGANISMS BY ION MOBILITY SPECTROMETRY

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ABSTRACT

A relatively new concept is explored where the potential for ion mobility spectrometry is investigated for the detection and determination of living microorganisms. The hand-held, NATO-fielded Chemical Agent Monitor (CAM) embodies the analytical device. Advantage is taken of the inherent enzymes found in microorganisms and an exogenous, tailored substrate was provided in order to initiate the desired biochemical reaction. The substrate was ortho-nitrophenyl-beta-D-galactopyranoside, and the product, ortho-nitrophenol, can be detected in the negative ion mode of the CAM and signals the presence of bacteria. Detection limits of approximately 10E4 E. coli bacterial cells in 5 min. and 3300 E. coli cells in 15 minutes were realized. The results suggest a new application of the CAM in the screening of bacterial contamination in community water and wastewater testing situations.

KEYWORDS: ion mobility spectrometry; microorganisms; E. coli; enzymes; ortho-nitrophenol; Chemical Agent Monitor; ortho-nitrophenyl-galacto-pyranoside; fecal coliforms.

INTRODUCTION

Detection and identification of microorganisms is a challenge in view of the required sensitivity, selectivity, and time of response of the detection technique. Table 1 lists these requirements for a number of methods. It appears that analytical instrumentation techniques broadly fall in the detection limit range of 10E6 bacterial cells with an instrumental response time of approximately 1.5 hr. The colorimetric and fluorometric enzyme assay procedures fare better and can be characterized by 10E3-10E5 bacterial cell limits of detection in a 0.25-4 hr response time domain.

Ion mobility spectrometry (IMS) is a straightforward, analytical vapor detection technique. Neutral analyte vapors enter the device and are ionized, usually by a ^{63}Ni ring. The ions are electrically gated and "drift" through an antiparallel flow of buffer gas (air or nitrogen). The ions are focussed by an electrical field about the heated, cylindrical drift region and are registered by a Faraday cup detector. The entire process, from vapor sampling to the detection event, takes place at ambient or near-ambient pressure, and thereby atmospheric pressure ionization chemistry characterizes the ion formation process. Ions are partitioned primarily according to their mass and shape and are characterized by their corrected drift times (typically in msec) or ion mobilities. In the negative mode, IMS is very similar with respect to an electron

capture detector in terms of the detection event and sensitivity.

The detection of bacteria by IMS originated from the concept of augmenting the hand-held Chemical Agent Monitor (CAM) with capabilities for biological detection, more specifically, that of viable microorganisms. The hypothesis was that the ion-molecule chemistry that characterizes the atmospheric pressure-based IMS technique, embodied by the CAM device, could be used to detect a targeted volatile product of the biochemical reaction between an *in vivo* bacterial enzyme and a tailored organic substrate. This proved to be an interesting challenge because parallels could be drawn with that of standard, well-established microbiological and clinical bacterial evaluation procedures in the process of devising the CAM detection of microorganisms.

EXPERIMENTAL

Ortho-nitrophenol (ONP) and ortho-nitrophenyl-beta-D-galactopyranoside (ONPG) were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI and Sigma Chemical Co., St. Louis, MO, respectively. The beta-galactosidase enzyme and ONP-acetate were obtained from Sigma Chemical Co., St. Louis, MO. Pure *E. coli* suspensions (ATCC 11303) or *Bacillus globigii* (ATCC 9372) were prepared by growth in a nutrient broth solution for 48 hr which was supplemented with 0.5% lactose sugar for induction of the beta-galactosidase enzyme. The bacterial growth was centrifuged and the pellet was washed three times with a sterile 0.1M phosphate-buffered saline solution (0.7% NaCl) at pH 7.4 (PBS). Approximately 1g of human fecal matter was suspended in 10 ml of distilled water. Strips of Whatman #5 filter paper (Whatman International, Ltd., Maidstone, England) were baked at 150°C overnight in glass vials and used for bacterial determination experiments. Two microliters of the *E. coli* or fecal matter suspensions were used for filter paper experiments and 0.1 ml was used for bulk volume liquid experiments. Two microliters of a 2.0 mg/ml ONPG solution in PBS were used for the filter paper experiments and 1.9 ml of the same ONPG solution was used for bulk volume microbial determinations. The fecal bacterial experiments were conducted at room temperature (25°C) while the pure *E. coli* experiments were carried out at 38°C.

After selected incubation periods at the given temperatures, the headspace of the bottle was sampled with the hand-held CAM by removing the cap and immediately placing the vial opening at the inlet of the CAM unit.

The hand-held CAM (Graseby Ionics, Ltd., Watford, England) device was used as the analytical detection technique which was designed specifically for air sensing in military field applications (15). Signals from the CAM were processed by using a Graseby Ionics, Ltd., advanced signal processing (ASP) board and software with an IBM-PC/AT. Details of the CAM unit are as follows: drift gas, nitrogen or air; ion source, 10-mCi ^{63}Ni; drift region length, 7 cm; drift field, 230 V/cm; drift gas flow, 300 mL/min; reaction region length, 3 cm; drift tube temperature, ambient; shutter width, 0.1 msec (16). A schematic and details of the operation of the hand-held CAM ion mobility spectrometry unit can be found elsewhere (17). For the fecal bacteria experiments the data were captured and displayed by the ASP software while for the pure *E. coli* determinations, the ion mobility signals were captured and displayed by a Nicolet 4094A oscilloscope and Hewlett/Packard 7470A plotter.

RESULTS AND DISCUSSION

A number of constraints were realized in that for a system such as the CAM to be a realistic analytical method for biological detection, only minimal logistic burdens to the collection, processing and introduction of the sample to the hand-held IMS unit would be tolerated. Therefore the question was posed: How can the CAM be used as it is intended (i.e. - a vapor detector) in the detection and possible identification of extremely complex entities such as microorganisms? The microbiological

literature provided constructive insights into this problem in the form of constitutive enzymes (enzymes that are always present in a bacterium) that are secreted at significantly different quantitative levels depending on the organisms. This is a property of living active cells and not of dead or dormant microorganisms. Conventional clinical procedures used in the detection and identification of organisms rely on tailored substrates (i.e. - compounds that mimic the enzyme's natural substrate) to interact selectively with the secreted enzymes of bacteria. The enzyme-catalyzed products of natural substrates are usually spectroscopically-silent and as such, tailored compounds substitute a portion of the natural substrate with a compound such that when it is released, it becomes spectroscopically active (e.g. - colorimetric or fluorimetric properties). This concept was then related to the proposed CAM detection of bacteria, except that the product would have to display a relatively high vapor pressure and the CAM must respond to the product.

Enzyme Substrate and Product

Previous investigations in this laboratory (13) have shown that bacteria such as Bacillus subtilis (BG), the yeast Saccharomyces cerevisiae, Serratia marcescens (SM) and E. coli produced at various rates the 3-hydroxyindole (indoxyl) as a highly fluorescent and blue colorimetric product from the reaction of indoxylacetate, indoxylglucoside and indoxylphosphate with their respective esterase, glucosidase and phosphatase enzymes. 4-methyl-umbelliferyl-beta-D-galactoside reacted with the beta-D-galactosidase enzyme in E. coli and SM to produce the fluorescent 4-methylumbelliferone product (13). The indoxylacetate probe (13) was the most sensitive where as little as 500 BG cells/ml could be detected in under 15 minutes. Modification of these substrates, with extensive biochemical IMS experimentation underscored the role of the organic substrate as the heart of the project. A number of important requirements concerning the substrate must be satisfied in order to ensure a successful approach. Requirements of the substrate include that it (a) is water soluble, (b) is recognized by a targeted enzyme, (c) displays rapid enzyme-substrate kinetics (i.e. - favorable association constant), (d) has minimal/negligible spontaneous hydrolysis and (e) that it gives a minimal/negligible response to the CAM. Requirements for the product include (a) a low association constant with biological material, (b) a relatively low water solubility, (c) favoring the gaseous phase, and (d) being "CAM-active". Alternate compounds were sought. Instead of ester compounds, established microbiological colorimetric indicators were analyzed. ONPG displays an acetal functional group that joins ONP and the beta-D-galactopyranoside sugar monomer (Figure 1) and is a standard microbiological indicator for the detection of all (total) fecal coliform bacteria (18, 19). Fecal coliform bacteria belong to the Enterobacteriaceae and are comprised of E. coli (4x10E8 cells/g feces), Klebsiella sp. (5x10E4 cells/g), Enterobacter (10E5 cells/g) and Citrobacter (10E6 cells/g) (20). These bacteria, with E. coli as the predominate species, are found in fecal matter, and the latter three genera are also associated with plants and soils. E. coli, however, can only be found in the environment through fecal contamination (21).

Figures 1 and 2 pictorially display the enzyme-substrate biochemical and detection events of the ONP product by the CAM. Figure 3 shows a CAM response of a phosphate-buffered saline solution of ONP in the negative ion mode. The main peak at 6.2 msec consists largely of $O_2^-(H_2O)_x$ clusters and the shoulder to the left of the peak is characteristic of the chloride ion. The peaks at 9.1 msec represent the ONP monomer at different concentrations and the low intensity peak at 11.7 msec represents the dimer ion (22). Thus, a favorable analytical situation has been established in that a compound has been found that not only has established roots in the microbiological detection and identification arsenal as a colorimetric indicator but also

responds to ion mobility spectrometry through well established ion-molecule, gas-phase reaction chemistry.

CAM-Bacterial Trials

A buffered solution of the ONPG substrate produced no response from the CAM unit. When an aliquot of pure beta-D-galactosidase enzyme was added to the ONPG solution, a yellow color appeared within seconds and the CAM ASP registered this event in the negative ion mode in a fashion similar to that in Figure 3. Bacterial tests followed. One was from a pure culture of E. coli and the other bacterial source was of fecal origin. Microliter volumes of bacterial sample and buffered ONPG were spotted on a strip of sterile filter paper and the latter was inserted into a vial. The vial was secured with a screw cap in order to contain any ONP product that was released into the vial headspace. For the fecal suspension, 2 microliters of a 1g feces/10 ml distilled water was used. Since an approximate concentration of E. coli in human fecal matter (20) is about 4x10E8 cells/g, the actual applied amount of bacteria was approximately 8x10E4 cells. Figure 4 portrays the results of this study. Position A in Figure 4 represents a background CAM response of the bacterial inoculation without ONPG substrate. The bacterium does provide distinct ion mobility peaks which are most likely due to inherent bacterial volatile compounds. A blank consisting of the buffered ONPG solution produced only the negative background ion mobility signal (Position B in Figure 4). Position C in Figure 4 represents the CAM response of the vial headspace after the buffered ONPG substrate was added to the bacterial spot on the filter paper and was acquired 40 min. after substrate addition. Note that in addition to the background ion mobility signal and the three peaks representing the bacterial volatile products, a new peak appeared at 9.1 msec which matched that of ONP (Figure 3). Figure 5 shows a replicate experiment where frame A represents the ONP response 15 min. after an ONPG solution was added to a fecal inoculation on a filter paper strip. Frame B shows that at 45 min, the ONP signal grew considerably.

An inoculated dose of 10E4 E. coli cells from a pure suspension on a filter paper strip produced a peak in five minutes (Figure 6). At the same E. coli inoculation, Figure 6 also shows the CAM response to the production of ONP after 10, 15 and 20 minutes. The background shows essentially no peak in the 9.1 msec time window and the reaction consisted of 2 ul of phosphate buffer added to 2 ul of ONPG. This indicates that the spontaneous hydrolysis of ONPG at 38°C is minimal and intense ONP signals can be observed over a relatively short period of time resulting from the bacterial enzymatic reaction at the relatively low amount of 10E4 E. coli cells. Figure 7 shows similar data except that the amount of inoculated E. coli was 3.3x10E3 cells. Indeed, within 20 min., a clear ONP signal was observed at 9.1 msec. This experiment was repeated (Figure 8) and in 15 min. a discernible ONP peak was observed. A bulk 2.0 ml volume suspension consisting of ONPG and fecal matter (a total of 4x10E6 fecal bacterial cells) took 2 hr for a response from CAM while the yellow ONP color in the suspension was observed prior to the CAM detection event. The longer dwell time is to be expected because the relatively large volume of water had a small surface area for the ONP to partition into the gas phase as opposed to microliter amounts which rapidly diffuse across a strip of filter paper.

Other Enzyme/Substrate Complexes

ONP-acetate can be cleaved by an esterase and this compound was used in the determination of the lipase enzyme in Bacillus globigii. Table 2 presents the amount of bacteria used to generate an ONP ion mobility peak after a 15 min. incubation time. One thousand cells of B. globigii produced an ONP signal comparable to that of Figure 6E. However, with the ONPG substrate, no signal was observed with 10E5 cells. The absence of an ONP signal is due to

the fact that B. globigii, as well as most other bacilli, do not contain the beta-galactosidase enzyme and as such ONP is not produced. The opposite situation occurs with E. coli. As Table 2 indicates, E. coli provides a positive biochemical reaction with ONPG, but not with ONP-acetate.

Comparison to Other Techniques

For the E. coli fecal coliform ONPG test, the CAM unit was observed to provide an ONP signal in 15 min. with approximately 3.3x10E3 E. coli bacterial cells. It is of interest to compare these response time/inoculation figures of merit with that of established and potential microbiological, clinical and analytical instrumentation techniques. Table 1 provides a list of a number of these methods including total number of bacteria and the time needed for a reliable analysis of bacterial presence. The CAM concept of bacterial detection via inherent enzyme biochemical reactions which yield tailored volatile products appears to be a competitive technique in the determination of microbial presence.

CONCLUSIONS

A major step in the chemical detection and identification of viable (i.e. - living) microorganisms was presented in terms of analytical techniques. The ion-molecule chemistry associated with IMS was shown to be a promising avenue for the monitoring of bacterial presence by taking advantage of available substrate-induced accessible enzymes. The hand-held ion mobility spectrometer CAM unit displayed detection sensitivity levels for E. coli fecal coliforms and response times similar or better than that of most commercially-available methodologies and analytical instrumentation techniques. This suggests a potential application of IMS for screening of bacterial presence in community/local water and wastewater testing protocols.

ACKNOWLEDGEMENT

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TABLE 1. COMPARISON OF MICROORGANISM DETECTION BY IMS TO OTHER TECHNIQUES

Total number of bacteria	Time (hr)	Technique	Response	Reference
80	8.5	gas chromatography	ethanol metabolite	1
10^5	1	radiometry	$^{14}CO_2$ metabolite	2
10^6	1.5	electrochemical	H_2 metabolte	3
10^7	0.5	organism growth	electrical impedance	4
10^7	0.25	polarized light scattering	Mueller matrix	5
10^3	0.4	light-addressable potentiometric sensor	redox potential	6
10^{11}	1	excitation-emission matrix	fluorescence	7
1	0.5	3-laser flowthrough cytometry	fluorescence	8
2.7×10^4	3	enzyme-linked lectinosorbent assay	lectin-conjugate	9
10^4	9	H_2/CO_2 evolution	visual, gas bubbles	10
10^4	4	glucuronidase enzyme	fluorescence	10
10^5	4.25	extracellular enzyme	colorimetric	11
5×10^7	0.5	aminopeptidase enzymes	fluorescence	12
10^5	0.25	extracellular enzymes	fluorescence	13
10^3	0.25	extracellular enzymes, nutrients	fluorescence	14
3.3×10^3	0.25	CAM	vapor metabolite	this study

TABLE 2. ENZYME/SUBSTRATE BIOCHEMICAL REACTIONS PROBED IN MICROORGANISMS

ORGANISM	ENZYME PROBED	SUBSTRATE	PRESENT LIMIT OF DETECTION (Bacterial Cells)*
E. coli	β-galactosidase	ONPG	3.3×10^3
E. coli	Lipase	ONP acetate	$6 \times 10^{5**}$
Bacillus subtilis	β-galactosidase	ONPG	10^{5**}
B. subtilis	Lipase	ONP acetate	10^3

*Within 15 minutes

**No signal observed at the given concentration

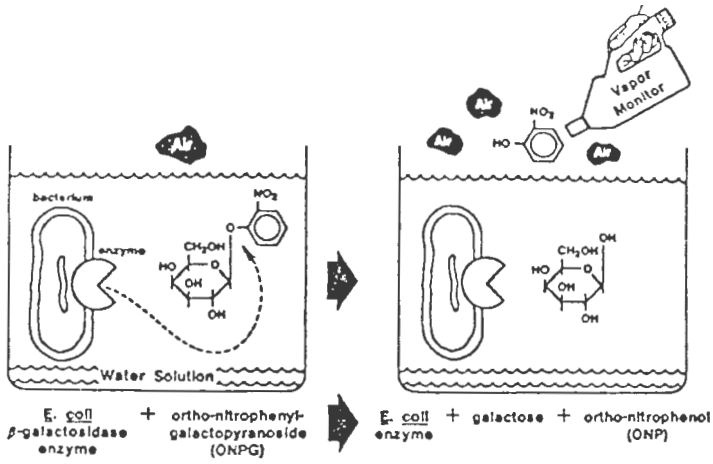

FIGURE 1. PICTORIAL REPRESENTATION OF THE E. COLI/BETA-GALACTOSIDASE BIOCHEMICAL REACTION WITH THE ONPG SUBSTRATE.

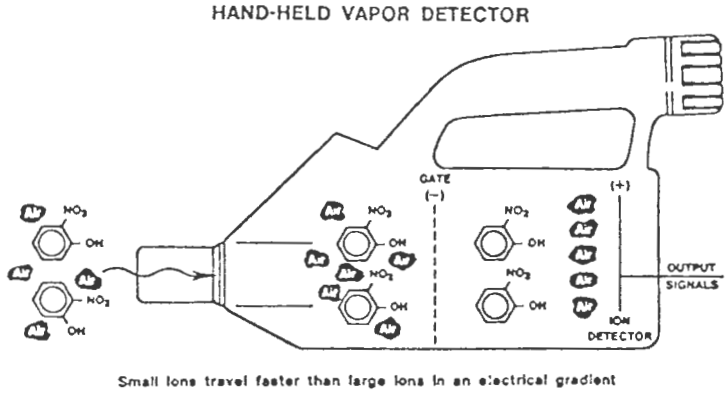

FIGURE 2. PICTORIAL REPRESENTATION OF THE ONP DETECTION EVENT WITH THE CAM HAND-HELD MONITOR. REFERENCE 17 PROVIDES DETAILS OF THE OPERATION OF THE CAM.

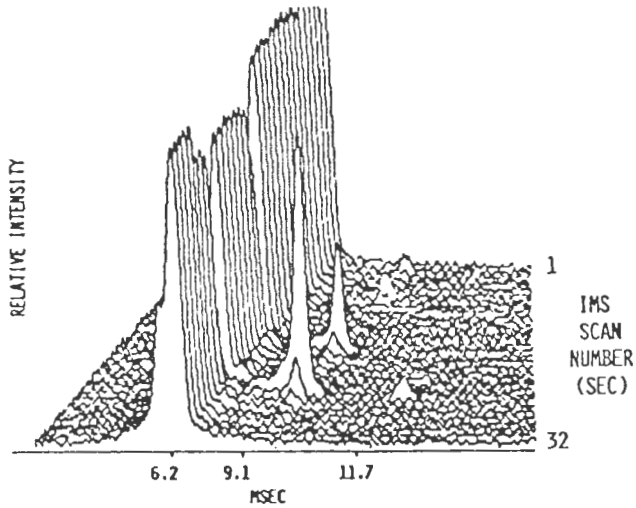

FIGURE 3. ION MOBILITY SPECTRUM OF ONP IN THE NEGATIVE MODE. THE PEAK AT 6.2 MSEC REPRESENTS THE BACKGROUND ION SIGNAL AND THE PEAKS THAT LIE AT 9.1 MSEC REPRESENT ONP AT DIFFERENT RELATIVE CONCENTRATIONS.

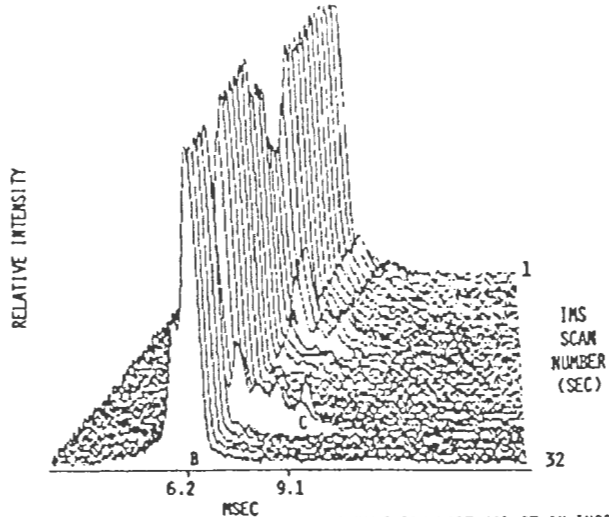

FIGURE 4. ION MOBILITY SPECTRUM IN THE NEGATIVE ION MODE (A) OF AN INOCULATION OF $8x10^4$ FECAL BACTERIAL CELLS ON A FILTER PAPER STRIP, (B) OF ONPG SOLUTION ON A FILTER PAPER, (C) AFTER 40 MIN. FROM AN ONPG SOLUTION ADDED TO AN INOCULATION OF $8x10^4$ FECAL BACTERIAL CELLS ON A STRIP OF FILTER PAPER. A PEAK AT 9.1 MSEC, DUE TO ONP, ONLY APPEARS WHEN BOTH ONPG AND BACTERIAL CELLS ARE PRESENT.

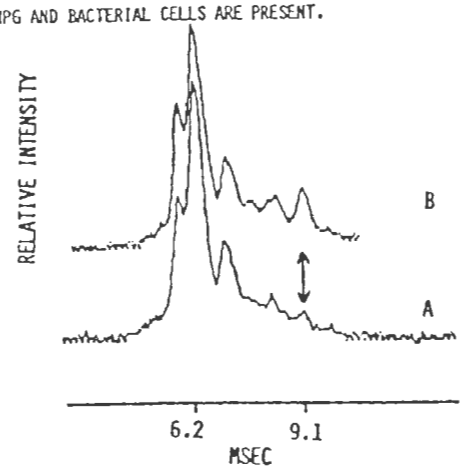

FIGURE 5. (A) 15 MIN. AND (B) 45 MIN. ION MOBILITY SPECTRA OF A REPLICATE FECAL BACTERIA EXPERIMENT (REFER TO FIGURE 4C FOR DETAILS).

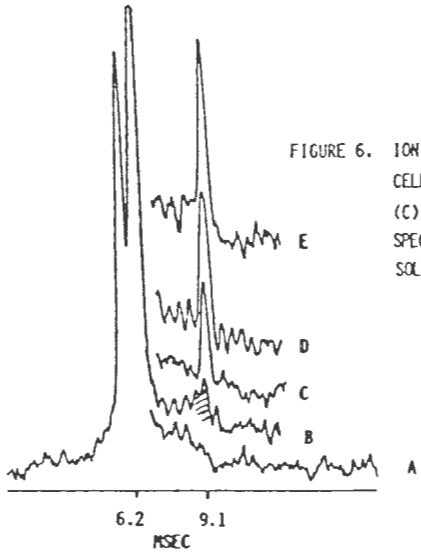

FIGURE 6. ION MOBILITY SPECTRA OF ONP LIBERATED FROM THE REACTION OF 10^4 E. COLI CELLS AND ONPG WITH AN INCUBATION AT 38°C FOR (B) 5 MIN (SHADED AREA), (C) 10 MIN, (D) 15 MIN, (E) 20 MIN. FRAME A REPRESENTS THE ION MOBILITY SPECTRUM OF A BLANK CONSISTING OF TWO MICROLITERS OF BUFFER AND ONPG SOLUTIONS ON A PIECE OF FILTER PAPER.

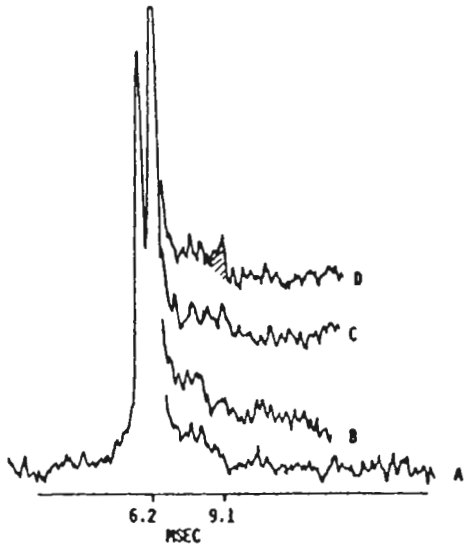

FIGURE 7. ION MOBILITY SPECTRA OF ONP LIBERATED FROM THE REACTION OF 3.3×10^3 E. COLI CELLS AND ONPG WITH AN INCUBATION AT 38°C FOR (B) 5 MIN, (C) 10 MIN, (D) 20 MIN. FRAME A REPRESENTS THE ONPG BLANK. NOTE THAT ONLY FRAME D SHOWS A CLEAR ONP RESPONSE OVER BACKGROUND.

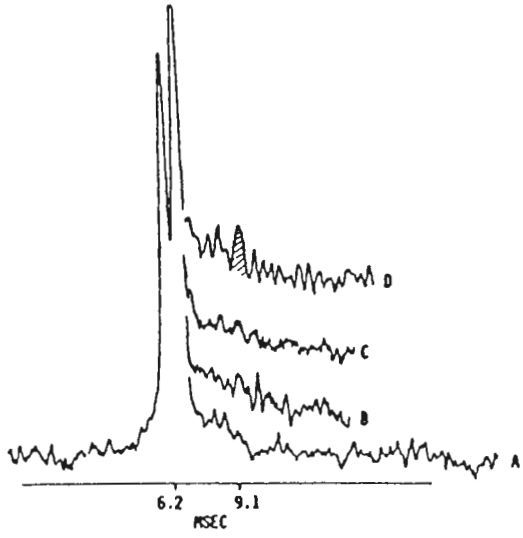

FIGURE 8. REPLICATE EXPERIMENT OF FIGURE 7 EXCEPT THAT SPECTRUM D WAS TAKEN AT 15 MINUTES. NOTE THAT ONLY FRAME D SHOWS A CLEAR ONP RESPONSE OVER BACKGROUND.

DATA ANALYSIS TECHNIQUES FOR ION MOBILITY SPECTROMETRY

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ABSTRACT

The past several years have seen the advance of ion mobility spectrometry (IMS) as an analytical technique. Most of these advances have been made in the hardware development end of the problem, the result being that portable IMS devices have begun to appear in the marketplace. The other end of the problem, the signal processing and data analysis techniques, has not been addressed to the same degree. Recent attempts at applying data analysis techniques to IMS data have been made, and the results are encouraging. Data processing algorithms ranging from those which perform simple tasks to those performing more difficult tasks have been developed. Among the algorithms which will be discussed are algorithms for measuring the peak areas of selected peaks of interest in biological studies, and linear discriminant analysis for detecting and identifying industrial chemicals at, or near their maximum exposure limits.

INTRODUCTION

When dealing with environmental issues, there are two points of emphasis that must be considered. These two points of emphasis are the protection of individuals in the workplace, a task regulated by the Occupational Safety and Health administration (OSHA), and the protection of the environment in which we live, a task regulated by the Environmental Protection Agency (EPA). These two points of emphasis, while dealing with the same general problem, are typically at different ends of the concentration range of chemical or biological contamination or exposure. The concentration ranges for which one must monitor an individuals exposure to chemical and biological contaminants is usually in the low parts-per-million, ppm, range to tens of thousands of ppm [1-3], and is set by Federal law [3]. The concentration range which is monitored for environmental compliance is usually parts-per-billion, ppb, to low ppm. A useful method for the monitoring both concentration ranges at the same time is ion mobility spectrometry, IMS.

Ion mobility spectrometry is based upon the flow, or drift, of molecular ions through a gas of uniform temperature and pressure. A weak electric field is uniformly applied to the gas in the drift region of the IMS, causing the ions to move along the field lines. These ions continue to drift until their movement is impeded by collisions with neutral gas molecules. Since the electric field is still being applied to the gas,

the ions are accelerated once again and the process of acceleration and collision is repeated until the ions strike the detector. IMS is similar to Time of Flight mass spectrometry in that the electric field causes the ions to drift, but it differs in that Time of Flight mass spectrometry is performed under vacuum and there are few, if any collisions to retard the ions. The average velocity, v_d, of the ions is determined by millions of the accelerations and energy-losing collisions. The time required for an ion to traverse a known distance in the drift region of the spectrometer is the drift time, t_d.

The average velocity of the ions, also called the drift velocity, is related to the strength of the applied electric field through the equation

$$v_d = l_d / t_d = KE \qquad (1)$$

where v_d is the drift velocity, l_d is the length of the drift region of the spectrometer, t_d is the drift time of the ion, E is the electric field strength, and K is a constant of proportionality. This constant K is also called the "mobility" of the ion. The mobility of the ion is directly dependent upon both the molecular ion being studied, and the neutral gas through which the ion must drift. A more useful constant which is used in IMS work is the "reduced mobility" of the ion. The reduced mobility of the ion, the mobility of an ion through a gas at standard temperature and pressure, is related to the measured mobility of the ion through the equation

$$K_o = K\ (273.15/T)\ (P/760) \qquad (2)$$

where T is the absolute temperature of the gas in the drift region, P is the total pressure of the gas and the ions in the drift region, and K_o is the reduced mobility of the ion. Because it is often difficult to measure the temperature and pressure within the drift region of the spectrometer, a common practice which is used in determining the identity of ions is to measure the ratio of the reduced mobility of the ion of interest to that of a known species. This known species is usually the reactant ion for the study. If the neutral gas is air, the reactant ions are H_3O^+ when dealing with positive ions, and O_2^- when dealing with negative ions. The ratio of the reduced mobilities are related to measurable quantities through the equation

$$(K_{o1}/K_{o2}) = (K_1/K_2) = (t_{d2}/t_{d1}) \qquad (4).$$

The only parameters which are needed in the analysis is the ratio of the drift times for the ions.

The equation for calculating the mobility of an ion through a gas has been shown to dependent on the first-order collision integral [4,5], which is proportional to the transport cross section. This implies that the mobility of an ion is dependent on the size of the ions, the shape of the ion, and the distribution of charge on the ion; this results in the possibility of more than one ion having the same mobility.

In an ion mobility spectrometer, Figure 1, the sample is introduced through a sample inlet probe. This inlet probe contains a semi-permeable membrane, which allows only a portion of the sample to enter the ionization chamber. The portion of the sample which does not enter the ionization chamber is vented through the exhaust. The carrier flow gas, which is input directly into the ionization chamber and the sample are then exposed to the ionizing source, a ^{63}Ni source in this work. The ions and the gas molecules are then allowed to mix and react in the ionizing chamber. Typical ion reaction schemes which take place in the ionization chamber are shown in Table A. A driving pulse of known shape and duration is then applied to the bipolar gating grid, allowing the mixture to enter the drift region of the spectrometer. While in the drift region, the ions are subjected to an applied electric field (200 V/cm in our studies), which causes the ions to begin their acceleration and collision process. After the ions have traversed the drift region,

TABLE A

TYPICAL ION REACTION SCHEMES

Typical Positive Ion Reactions

$$H^+(H_2O)_n + X \rightarrow H^+X(H_2O)_m + (n-m)H_2O$$
$$H+X(H_2O)_m + X \rightarrow H^+X_2 + m\ H_2O$$

(X is the species to be detected)

Typical Negative Ion Reactions

$$O_2^- + AB \rightarrow O_2 + AB^-$$
$$O_2^- + AB \rightarrow O_2 + A + B^-$$
$$O_2^- + AB \rightarrow (AB \cdot O_2)^-$$

(AB is the species to be detected)

they strike the collector electrode. The signal is then processed to produce the ion mobility spectrum. For those who wish, a more detailed description of ion mobility spectrometry can be found elsewhere [6].

The past several years have seen the advance of ion mobility spectrometry as an analytical technique, with the utility of IMS as an analytical tool for the rapid detection of airborne vapors in the atmosphere being previously demonstrated [7-10], and computer techniques for pre-processing IMS signals have also been presented [11-12].

EXPERIMENTAL

Equipment

Data were collected on an IMS spectrometer [Airborne Vapor Monitor (AVM) from Graseby Analytical, Watford, Great Britain] and stored on an IBM Personal Computer. The data transfer is accomplished using a Graseby Analytical Advanced Signal Processing (ASP) board and its associated software. Each spectrum consisted of 640 data points, which was collected at a sampling frequency of 30 kHz. The other operational parameters of the AVM are shown in Table B.

Vapor Generation

The vapors being used in the linear discriminant data set are generated with a Q5 vapor generator, shown in Figure 2. The Q5 generator has 16 component parts. These parts are: (1) an equilibrator assembly, (2) an air supply (or nitrogen supply) stopcock, (3) a constant pressure regulator (stabilizer) for the air supply, (4) two sampling bubblers filled with solvent (the bubbler is not shown Figure 2), (5) a flowmeter (manometer) for the air supply, (6) a constant pressure regulator (stabilizer) for the diluent air supply, (7) stopcocks for the stabilizers, (8) a stopcock shut off the flow of air from the equilibrator to the mixing chamber, (9) a flowmeter (manometer) for the diluent air supply, (10) a mixing chamber, (11) a reservoir, (12,13) sampling stopcocks, (14) a reservoir exhaust stopcock, (15) a charcoal trap on the exhaust of the reservoir (not shown in Figure 2), and (16) a charcoal canister on the sampling line after the SAW device (not shown in Figure 2).

The equilibrator assembly is the liquid test reagent container of the dilution apparatus. Dry air, under a constant controlled pressure, flows into the equilibrator. This air stream passes over the surface of the test reagent, and becomes

TABLE B

OPERATIONAL PARAMETERS FOR THE AVM

Number Of Waveforms To Be Summed	-	32
Number Of Samples Per Waveform	-	640
Gating Pulse Repetition Rate	-	40 Hz
Gating Pulse Width	-	180 uS
Delay To Start Of Sampling	-	0 uS
Sampling Frequency	-	30 KHz
Gating Pulse Source Is	**	External **

saturated with the reagent vapor. The equilibrator is maintained at a constant temperature of 25 ^{o}C by partial immersion in a constant temperature water bath. Included in the equilibrator is a porous alumina cylinder (from Thomas Scientific, Swedesboro, N.J.) to produce a greater surface area for the liquid-vapor equilibration. The dry air-test vapor mixture flows from the equilibrator assembly to the mixing chamber where it is diluted with dry air to the required concentration of milligrams test vapor per liter of dry air.

The flow of air through the equilibrator is controlled by an in-line stopcock, a constant pressure regulator, and a flowmeter. The stopcock is located at the inlet of the equilibrator, and acts as the shutoff valve for the air supply, from the flowmeter to the equilibrator. The constant pressure for the air supply is maintained by bubbling the dry air through a constant level of fluid, e.g. water, in the stabilizer. By raising or lowering the level of the fluid in the stabilizer, the air pressure controlled. The level of the fluid is raised by adding fluid to the stabilizer, and lowered by draining fluid through the stabilizer stopcock located on the bottom of the stabilizer. Changing the pressure of the air supply in this way increases or decreases the flow of the test vapor through the dilution apparatus. Excess air passing through the stabilizer is vented to the laboratory hood. The flowmeter, or manometer, consists of an inner glass tube, which is graduated in millimeters, and outer glass tube through which the air flows, a glass capillary tube of predetermined bore size, a cover to seal the capillary, and a bulb type bottom filled with colored water, which is connected to the constant pressure regulator. The capillary is calibrated such that the flowrate through the capillary is known for any water height. Thus, the flowrate is determined by the height of the water in the inner tube, and the capillary calibration data. The flowmeter measures the flow rate of the dry air-test vapor mixture in milliliters per minute. The flow rate of the diluent air is controlled in the same fashion as the equilibrator air supply with a larger inside diameter capillary tube. The flowmeter for the diluent air is measured in liters per minute. The nominal concentration of the test vapor can be calculated using the equation

$$C = \{(f * p)/([F + f]*P)\} \quad (5)$$

where C is the nominal concentration of the test vapor in parts-per-million by volume, f is flow rate of air through the equilibrator, F is the flow rate of the diluent air, p is the vapor pressure of the test reagent at the temperature of the experiment, and P is atmospheric pressure. Thus, the concentration

of the test vapor may be easily changed by varying either the flow rate of air through the equilibrator, or by changing the flow rate of the diluent air. In practice, it works best to change the flow rate of the diluent air, when possible, because the efficiency of the vapor generation in the equilibrator decreases at higher flow rates.

The dry air-test vapor mixture from the equilibrator and the diluent air are passed into the mixing chamber located at the entrance of the reservoir. The dilute test vapor is thoroughly mixed by a swirling circular motion of the air in the mixing chamber before entering the reservoir. The reservoir is the container for the diluted test vapor, from which samples are taken for concentration analysis and for testing purposes. There is a charcoal canister located on the exhaust of the reservoir. This canister serves as a scrubber to remove test vapors passing from the reservoir to the atmosphere in the laboratory hood.

Pre-Processing of Spectra for Linear Discriminant Analysis

The pre-processing and data processing procedure used in the linear discriminant analysis is shown in Figure 3. The first pre-processing step is to determine if the spectrum has been collected in the positive (+) or negative (-) mode. This knowledge is important since the Graseby ASP board does not differentiate between the two types of spectra, i.e. the ASP board converts all spectra to positive values. The determination of the operating mode under which the spectrum was collected is made by reading the data file header which includes a single character which is used to designate mode. A preliminary discrimination is made based on the mode; a spectrum collected in the negative mode has no chemical semblance to a spectrum collected in the positive mode. Once the mode has been determined, it is necessary to determine the time at which the reactant ion peak (RIP) appears. The reactant ion for the AVM, O_2^- in the negative mode and H_3O^+ in the positive mode, is the species which transfers the charge to the chemical species being analyzed. The location of the RIP must be determined for each spectrum, if possible, because the location is affected by changes in temperature, pressure, and relative humidity. If no RIP is found, then one must assume the RIP is located at the same time as the RIP for the previous spectrum. After determining the time at which the RIP appears, the spectrum is normalized to create a dimensionless X-axis. To do this, each value on the X-axis was divided by the value position of the reactant ion peak. For negative ion spectra collected at, or near, sea level, the peak position with the maximum intensity between 6.0 and 7.0 milliseconds drift time was used for the identification of the reference ion peak. For positive ion data, a value between 6.5 and 7.5 millisecond drift time was used as a window in which to find the reference ion peak. This reference window is easily adjusted for spectra collected at other altitudes or pressures by multiplying the window values by the ratio of the operating pressure to atmospheric pressure at sea level. This new spectrum also appears as a pseudo-"Reduced Mobility" spectrum which has a dimensionless X-axis corresponding to a Ratio of Drift Times, T_R. Only the data in the range 0.5 to 3.0 along the T_R axis are used. A cubic spline is then applied to the spectra such that every spectrum has the same data spacing with respect to the Ratio of Drift Times axis. The IMS data files used in this study have data points every 0.005 T_R.

LINEAR DISCRIMINANT ANALYSIS

Traditionally, much of the effort associated with the analysis of the IMS spectra has been left to the chemist. In an effort to aid in the preliminary identification, a

personal computer (PC) based spectrum identification package has been developed. This package, written in Microsoft Fortran, uses a linear discriminant function for its identification, and consists of three separate programs. These programs are: IMSDISC, a program which reads selected data files from the PC and builds a discrimination data set; TRAIN, a program which analyzes the discrimination set and calculates the linear discriminant function that best isolates the data of interest from the interferant data; and IMSIDENT, a program which reads the data to be analyzed and identified and calculates its linear discriminant value.

Linear discriminant analysis, one of the most basic forms of pattern recognition used by scientists, is used as a supervised learning technique. In supervised learning techniques, the computer learns to classify the samples being analyzed based on knowledge about the samples; in this study, the samples either belong to the class of chemicals you wish to identify, or they do not. The goal of the learning is to develop a classification rule, the linear discriminant function, which allows the validity of the classification to be tested and ultimately to properly classify unknowns.

The linear discriminant function has the general form

$$g(x) = w_o + \sum_{i=1}^{n} w_i x_i \qquad (6)$$

where w_o is the threshold vector, w_i is the weight vector, x_i is the response vector, and $g(x)$ is the response function. The discriminant function, $g(x)$ is determined by choosing those variables x_i with characteristics which differ between the groups being classified. These variables are then linearly combined and weighted such that the groups are as statistically different as possible. This linear combination of variables is calculated using the perceptron convergence criteria.

The perceptron [13-15] is a pattern recognition procedure which consists updating the weight vector by considering only those patterns, or spectra in this work, which have been misclassified in the training set. Each misclassified pattern is considered in turn, with a fraction of each misclassified spectrum being added to the weight vector. This procedure is continued until all of the spectra are classified correctly, or until it is determined that the procedure fails to converge to a satisfactory solution.

In this software package, the three programs are run separately, but are still inter-related. The first program, IMSDISC, uses a file called NAMES. NAMES is simply the file that contains the names of the individual data files to read, and a value that tells the program whether the file is to be treated as the sample or as an interferant. The data from the individual data files is then treated such that all the files are compatible with respect to time spacing between data points, delay to start of data sampling, and number of data points. To accomplish this, IMSDISC uses a spline function to interpolate and fit the data. After the data has been treated to fill the compatibility requirement, the discriminant threshold is set to zero by multiplying all interferant spectra by negative 1, (-1). The sample spectra are left unaltered. The data is then stored in a discriminant data file.

The second program, TRAIN, develops a linear discriminant based on the perceptron convergence criteria. TRAIN prompts the operator for the name of the input discriminant file that was created with the program IMSDISC. It reads the data from the discriminant data set, accepts input for the values of a scaling factor, between 0.000000001 and 0.1, and the number of iterations to perform using this scaling factor. In practice, it is generally necessary to use a series of decreasing scaling factors and iterations to calculate the linear discriminant function which best differentiates the samples and the interferants. After the linear

discriminant function has been calculated, the linear coefficients are written to a file on the computer disk for use by the last program. These first two programs, IMSDISC and TRAIN, are the time consuming programs and are run only when a new compound is to be added to the database.

The third program in this package, IMSIDENT, uses the linear discriminant values created with the program TRAIN. Thus, it is dependent on the first two programs in the package. IMSIDENT can be used in one of two possible configurations; the first configuration is as a stand-alone program, and the second is that it can be incorporated into a data collection program for real time identification of an unknown environment. In the stand-alone configuration, the program prompts the operator for the name of the data to analyze. The program reads the data, and performs a spline interpolation to make the data compatible with the discriminant data sets. Next, the program reads a file named COEF.FIL that contains the names of the coefficient files. The linear discriminant value is then calculated. If the linear discriminant value is positive, an alarm message is generated which notifies the operator that the spectrum has been identified. No message is generated if the discriminant value is negative. The results of the identification process are then written to a file named ALARM.RPT for later use, and the program then prepares to read the next data file to be analyzed.

In the second configuration, the program functions as a real time monitor. The name of the data file to be analyzed is passed from the data collection program to the IMSIDENT package rather than prompting the operator for the name of the data file to analyze. The spline interpolation is then performed on the data, and the linear discriminant value is calculated. If the discriminant value is positive, the alarm message is generated; no message is generated if the discriminant value is negative. The results of the identification process are written to a file named ALARM.RPT for later use.

DISCUSSION

The program package was developed for use with the Graseby Ionics Advanced Signal Processing (ASP) board, the Graseby Airborne Vapor Monitor (AVM), and a Zenith 286 PC. Using this hardware and the linear discrimination package, it has been possible to identify and semi-quantitate the presence of 15 common chemical vapors in air. These compounds, most of which are of industrial importance, and the levels at which the Occupational Safety and Health Administration (OSHA) have determined them to be hazardous are shown in Table C, with the ion mobility spectra of these compounds shown in Figures 4 through 21. When the software is used in the stand-alone configuration (i.e., separate from the data collection routines) and using the Zenith 286 PC, the presence of these compounds can be determined and the compound identified in less than ten seconds. This includes the time necessary to perform the spline interpolation and the calculation of the discriminant value for the data; however, this does not include the time required to create the discriminant functions.

The results shown in Table D are from the evaluation of a series of files used to determine the presence of N-Methyl Formamide. The "All Clear" report indicates that the IMSIDENT program does not find any similarities between the N-methyl formamide test spectrum and the spectra of the fifteen compounds stored in the database. The report of an alarm indicates that the program did find similarities in the spectra, and the magnitude of the discriminant is a measure of the amount of similarity.

It is not really surprising that there are a number of false positive alarms indicating the presence of diethyl ether. Older

versions of the AVM used an acetone dopant within its detection system, whereas newer versions of the AVM use water vapor in the atmosphere as the dopant. This dopant in the older AVM's results in the presence of an acetone reactant ion. This reactant ion is the ionic species which is responsible for transferring the ionic charge to the chemical compound being studied. All of the spectra used in the discrimination functions were recorded using water as the reactant ion. Thus, the discriminant functions have not been trained to eliminate the possibility of alarming on a spectrum which has an acetone reactant ion peak, and an alarm is reported. Examination of two representative spectra for which an alarm was reported, shows the similarity of the IMS spectrum for the diethyl ether, the lower trace in Figure 22 (ETHER in Table D) and N-methyl formamide background spectrum, the upper trace in Figure 22 (\AVM\DATA\nmfo0000.ACQ in Table D). The location of the reactant ion peak does not appear at the same time as does the diethyl ether peak, however the band shapes are similar. If the discriminant function is trained to ignore the acetone reactant ion peak, one does not get an alarm. Results of identification procedure with the acetone reactant ion peak being ignored is shown in Table E.

TABLE E

File "ALARM.RPT" for
N-Methyl Formamide Analysis
with Acetone Reactant ion Ignored

```
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0000.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0001.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0002.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0003.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0004.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0005.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0006.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0007.ACQ
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ALL CLEAR FOR FILE  \AVM\DATA\nmfo0011.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0012.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0013.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0014.ACQ
ALL CLEAR FOR FILE  \AVM\DATA\nmfo0015.ACQ
```

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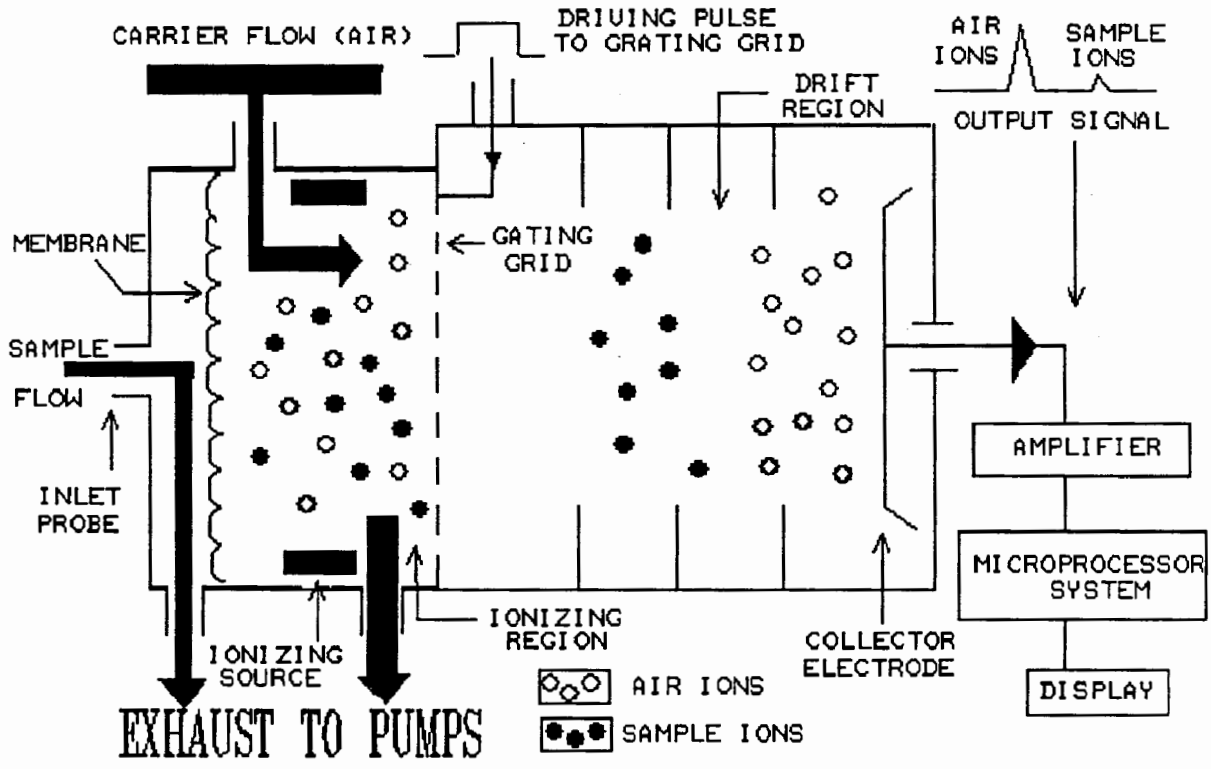

Figure 1. Schematic diagram of an ion mobility spectrometer.

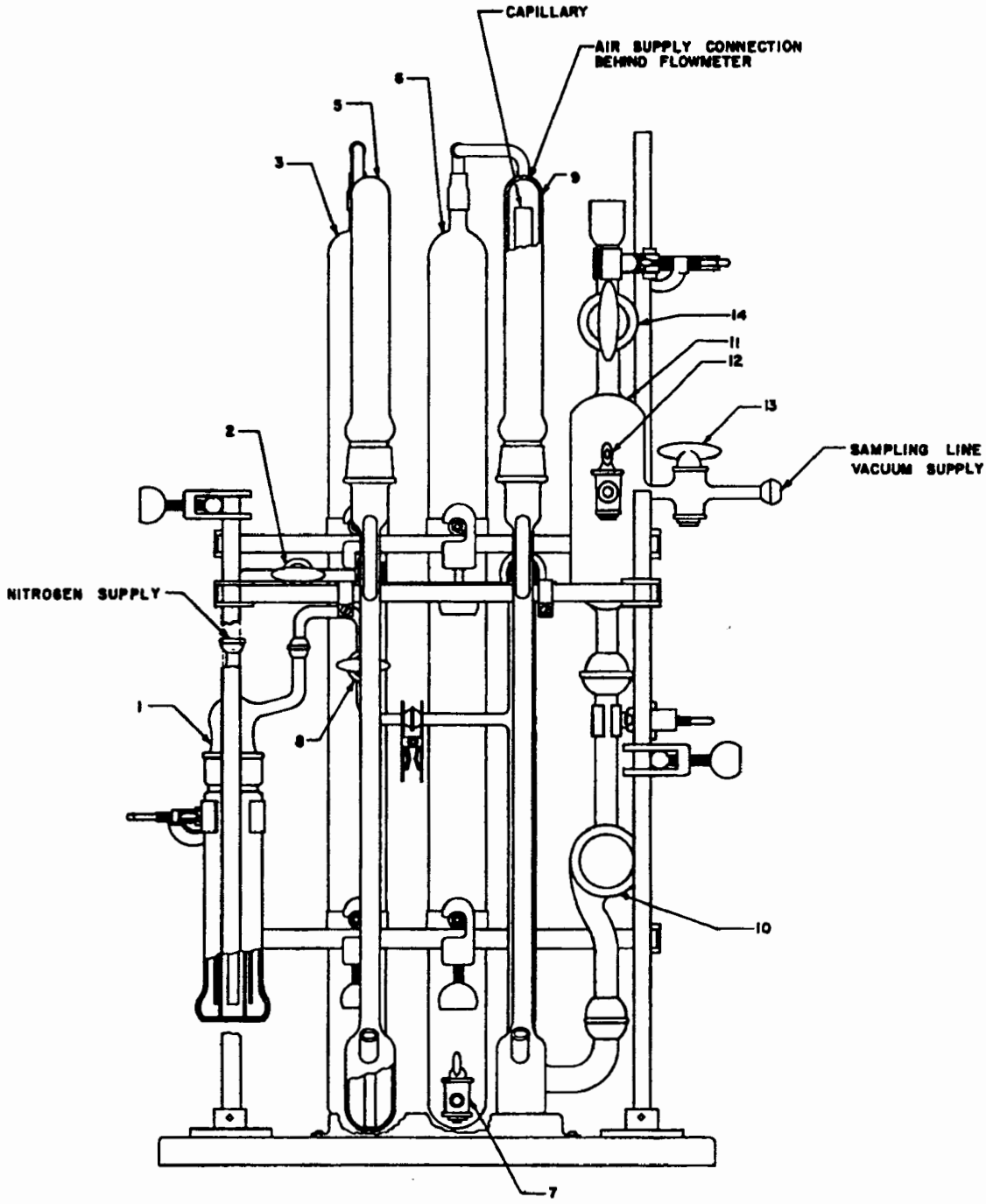

Figure 2. Schematic diagram of the Q5 vapor generator.

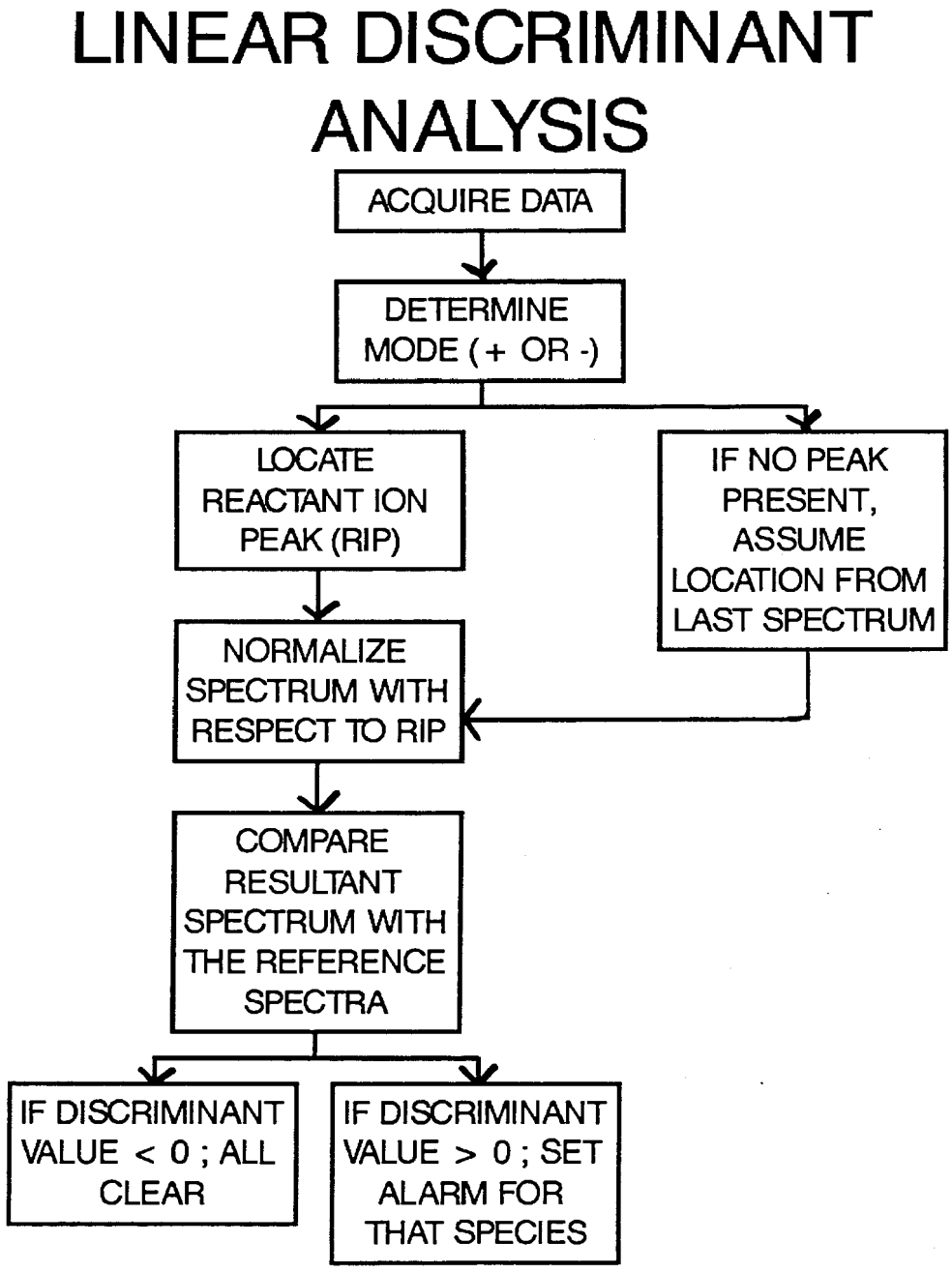

Figure 3. Block diagram showing the steps taken when performing a linear discriminant analysis on an ion mobility spectrum.

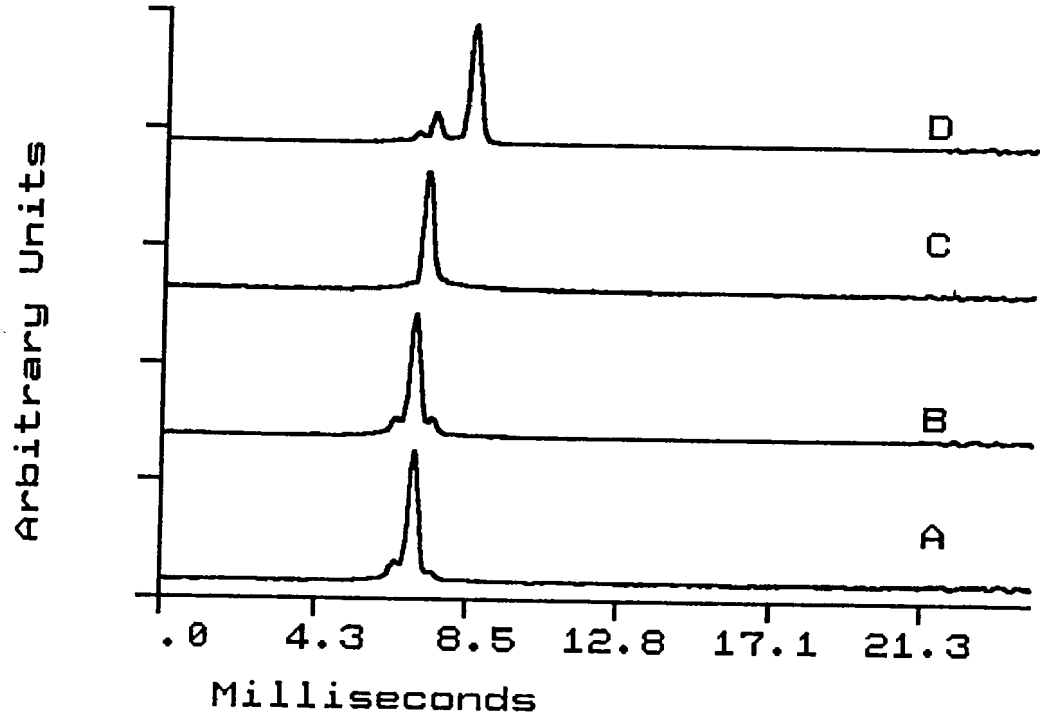

Figure 4. Typical ion mobility spectra of iodine taken in the negative ion mode as a function of concentration. Spectrum A is 2.5 parts-per-billion (ppb) iodine, B is 10 ppb iodine, C is 100 ppb iodine, and D is 1.0 parts-per-million (ppm) iodine.

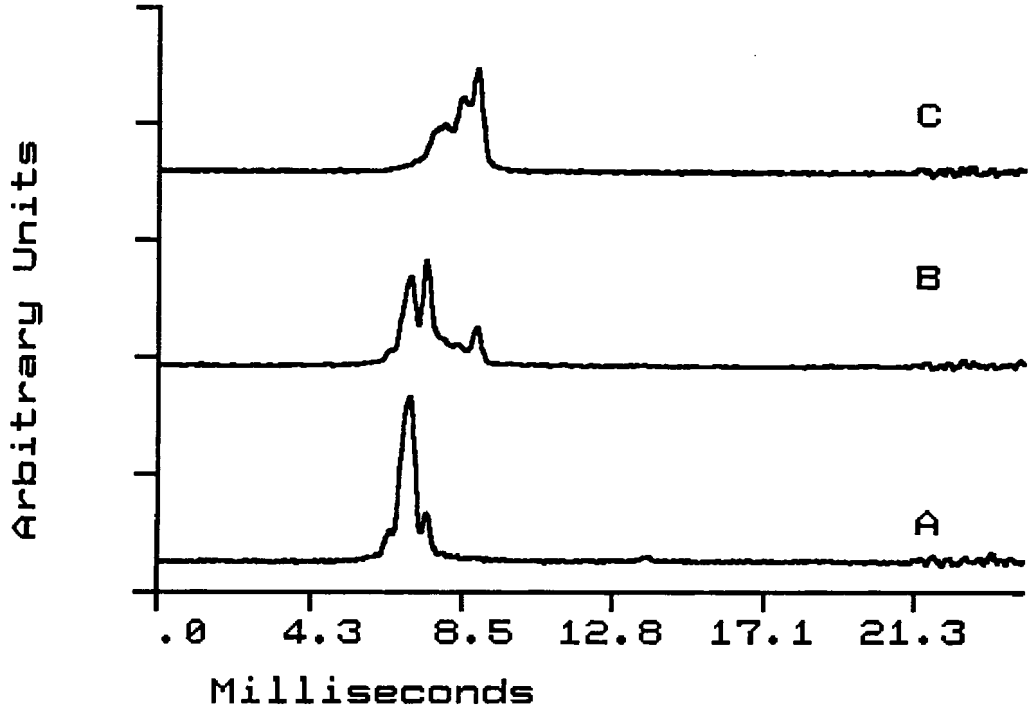

Figure 5. Typical ion mobility spectra of acetic acid taken in the negative ion mode as a function of concentration. Spectrum A is 100 ppb acetic acid, B is 1.00 ppm acetic acid, and C is 10.0 ppm acetic acid.

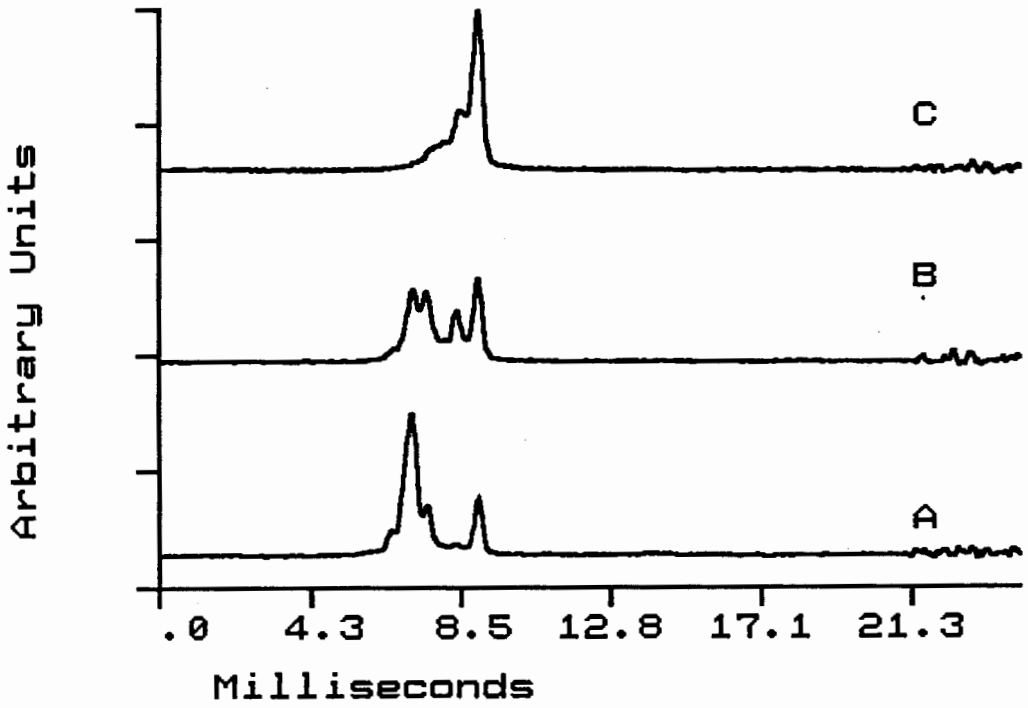

Figure 6. Typical ion mobility spectra of acetic anhydride taken in the negative ion mode as a function of concentration. Spectrum A is 50 ppb acetic anhydride, B is 500 ppb acetic anhydride, and C is 5.0 ppm acetic anhydride.

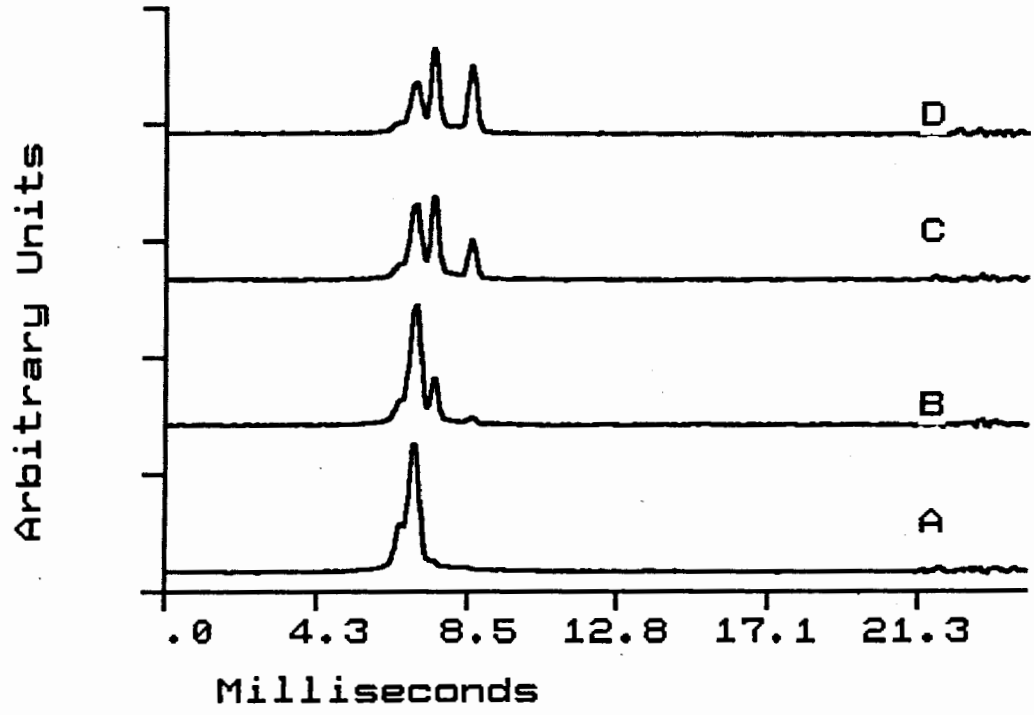

Figure 7. Typical ion mobility spectra of hydriodic acid (HI) taken in the negative ion mode as a function of concentration. HI vapor is generated from a 55% solution of HI in water. Spectra A through D represent increasing concentrations of HI. Actual concentrations of HI have not been determined.

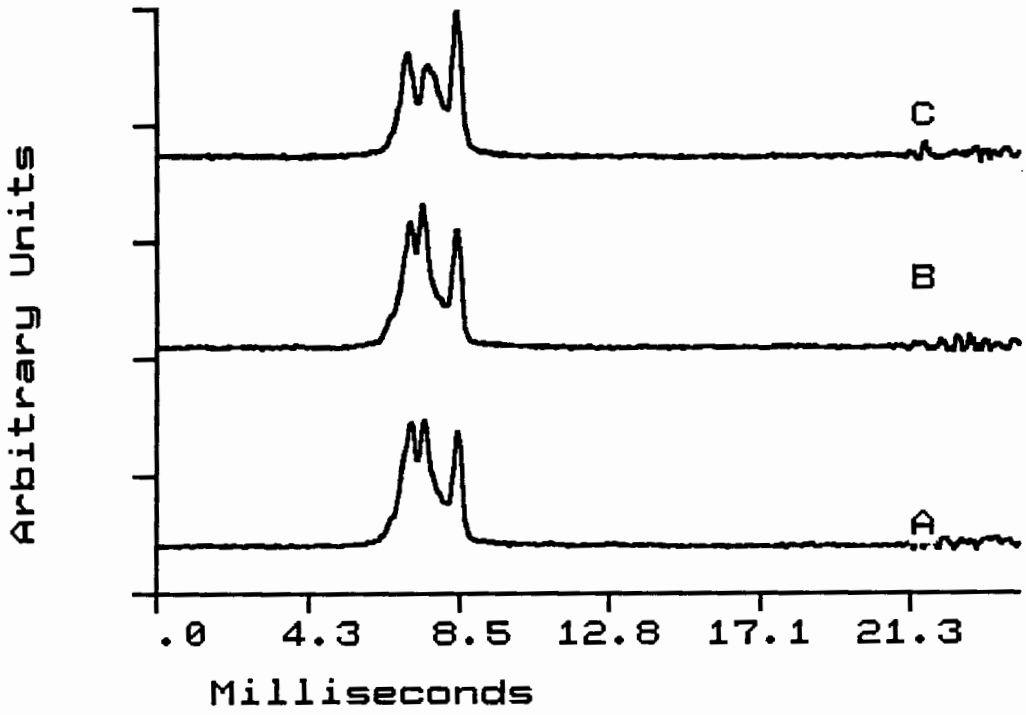

Figure 8. Typical ion mobility spectra of formamide taken in the negative ion mode as a function of concentration. Spectrum A is 300 ppb formamide, B is 3.0 ppm formamide, and C is 30.0 ppm formamide.

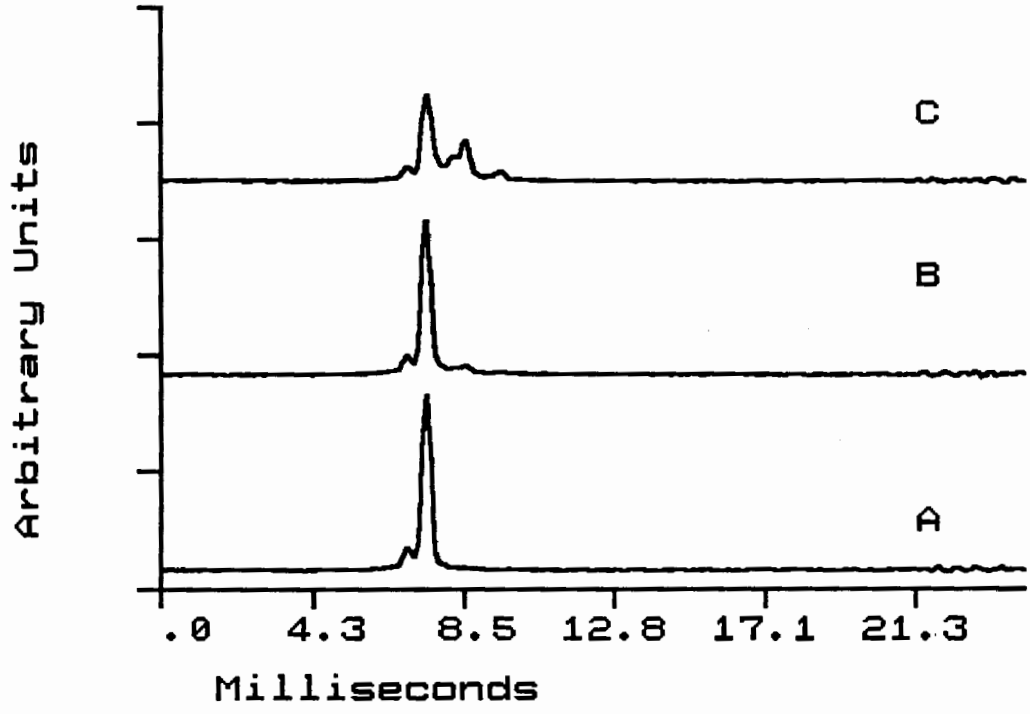

Figure 9. Typical ion mobility spectra of isooctane taken in the positive ion mode as a function of concentration. Spectrum A is 3.5 ppm isooctane, B is 35 ppm isooctane, and C is 350 ppm isooctane.

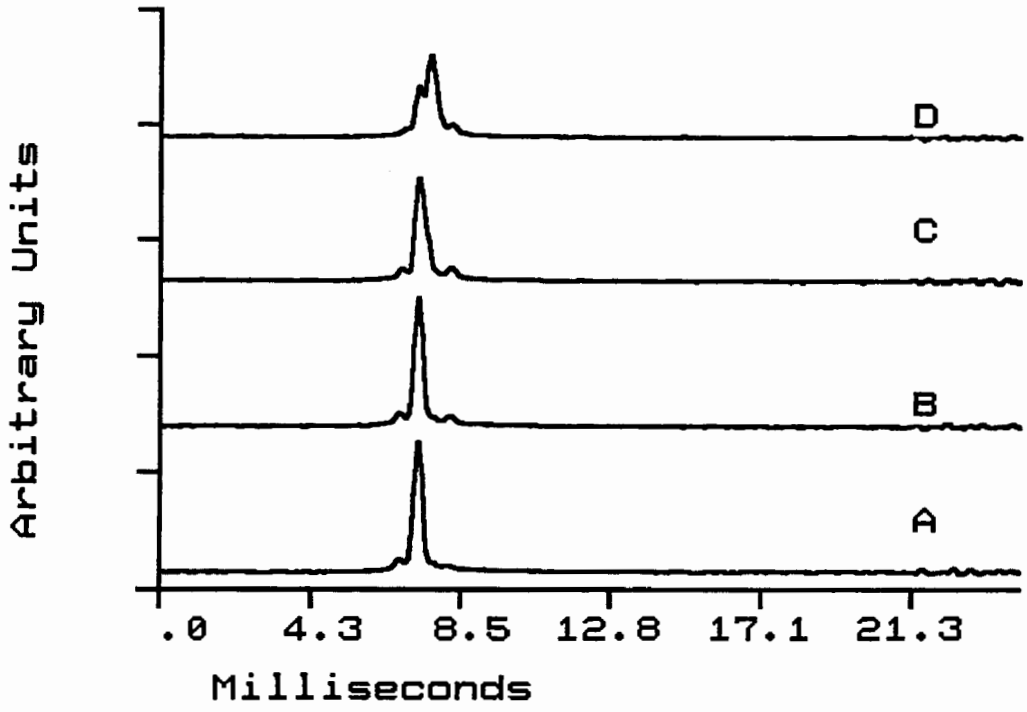

Figure 10. Typical ion mobility spectra of toluene taken in the positive ion mode as a function of concentration. Spectrum A is 15 ppb toluene, B is 250 ppb toluene, C is 1.7 ppm toluene, and D is 10.0 ppm toluene.

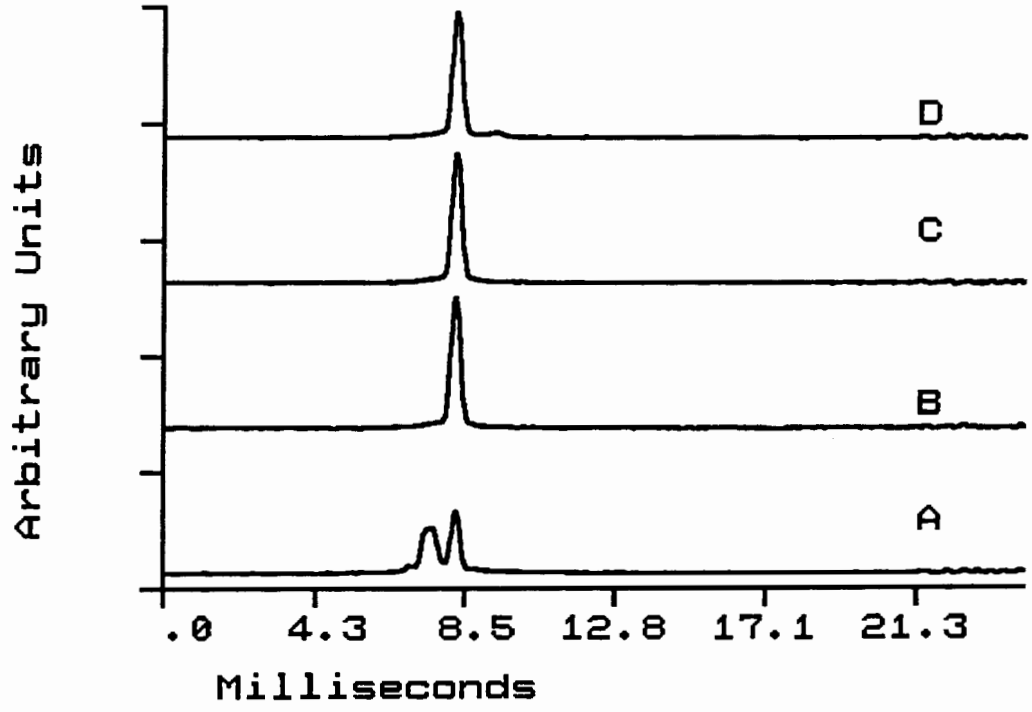

Figure 11. Typical ion mobility spectra of acetone taken in the positive ion mode as a function of concentration. Spectrum A is 1.0 ppm acetone, B is 10.0 ppm acetone, C is 100.0 ppm acetone, and D is 1000 ppm acetone.

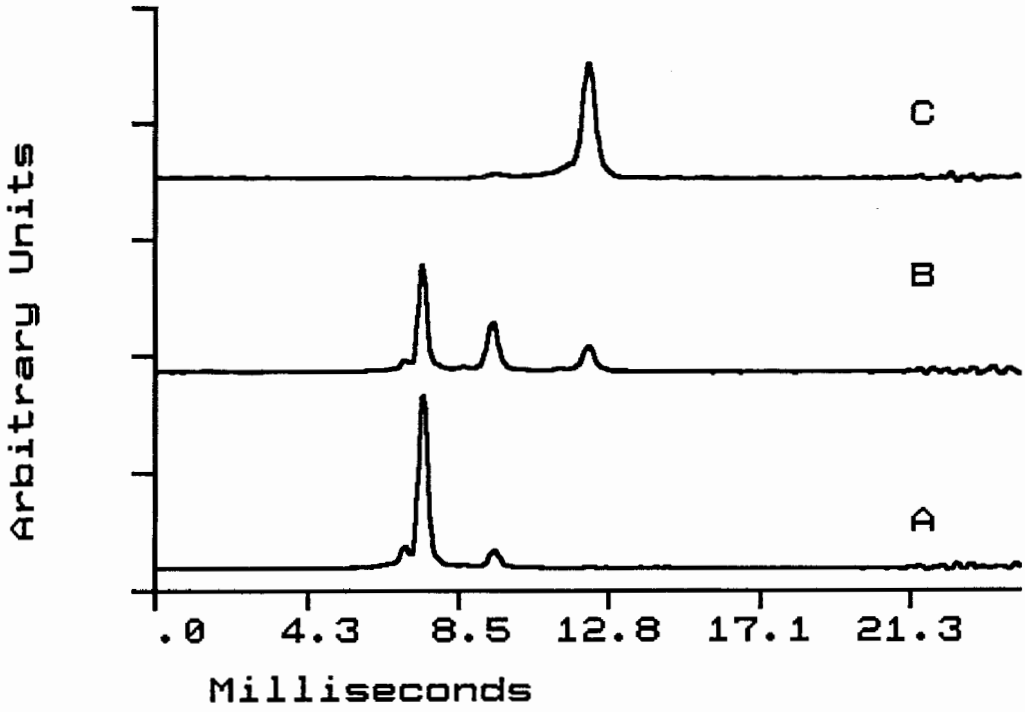

Figure 12. Typical ion mobility spectra of phenyl-2-propanone (P2P) taken in the positive ion mode as a function of concentration. Spectrum A is 10 ppb P2P, B is 100 ppb P2P, and C is 1.0 ppm P2P.

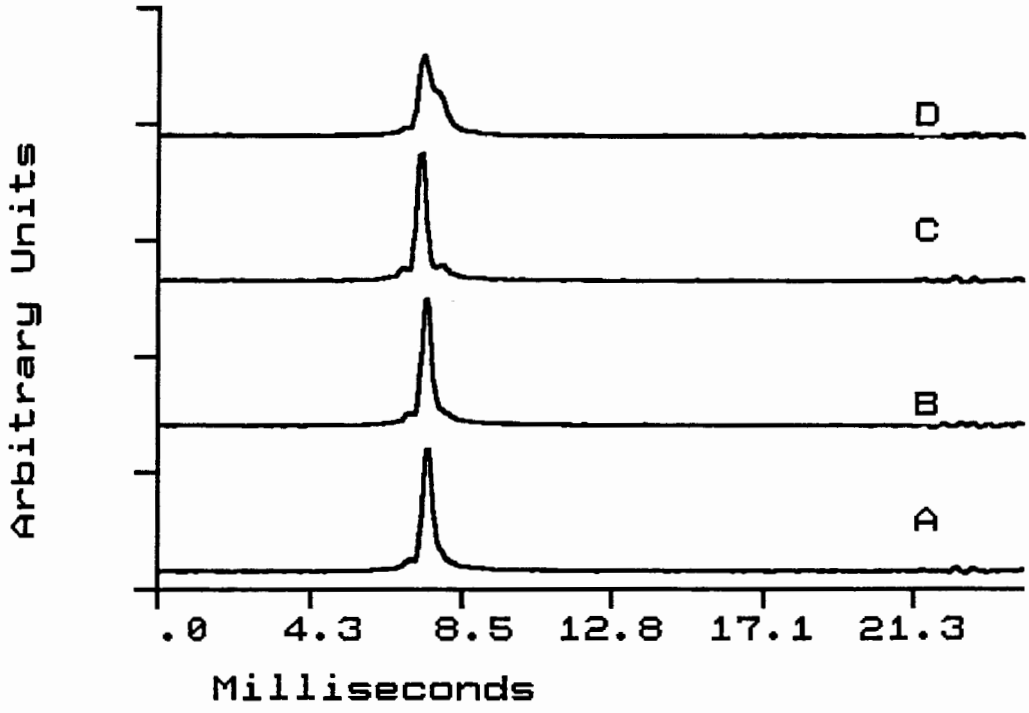

Figure 13. Typical ion mobility spectra of benzene taken in the positive ion mode as a function of concentration. Spectrum A is 250 ppb benzene, B is 1.0 ppm benzene, C is 10.0 ppm benzene, and D is 100 ppm benzene.

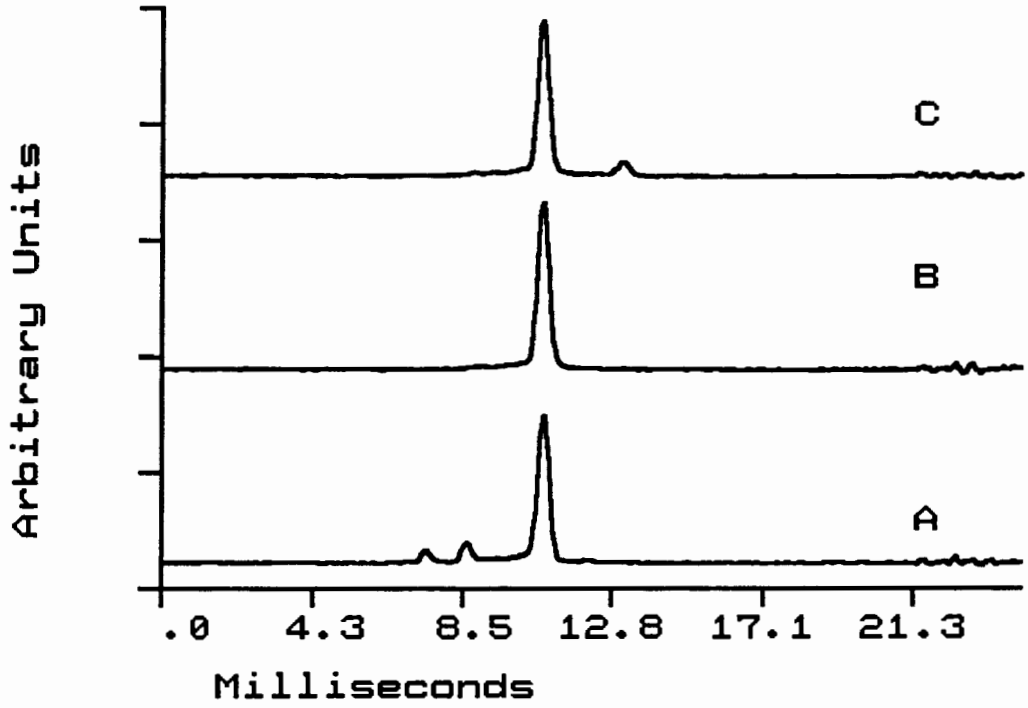

Figure 14. Typical ion mobility spectra of cyclohexanone taken in the positive ion mode as a function of concentration. Spectrum A is 500 ppb cyclohexanone, B is 5.0 ppm cyclohexanone, and C is 50 ppm cyclohexanone.

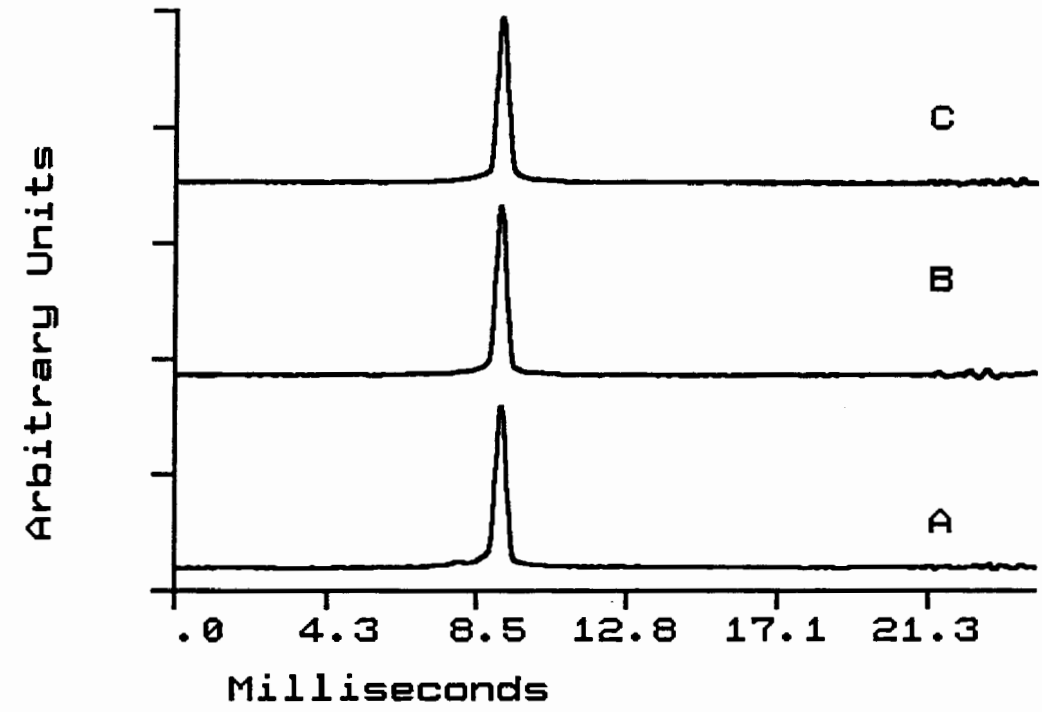

Figure 15. Typical ion mobility spectra of methyl ethyl ketone (MEK) taken in the positive ion mode as a function of concentration. Spectrum A is 3.0 ppm MEK, B is 30 ppm MEK, C is 300 ppm MEK.

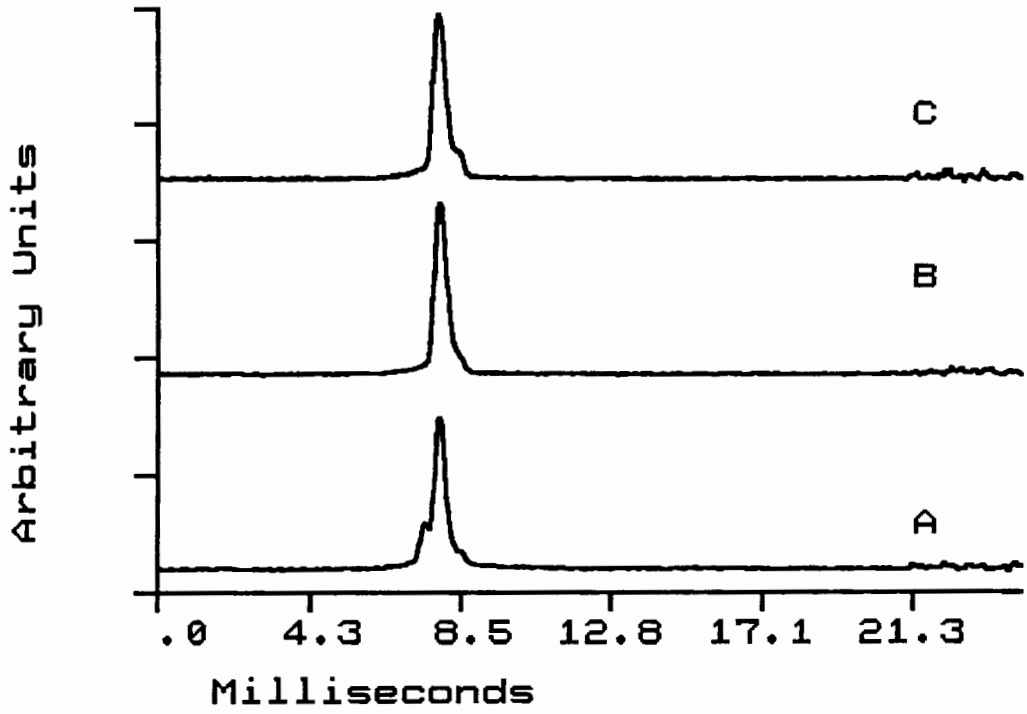

Figure 16. Typical ion mobility spectra of formamide taken in the positive ion mode as a function of concentration. Spectrum A is 300 ppb formamide, B is 3.0 ppm formamide, C is 30.0 ppm formamide.

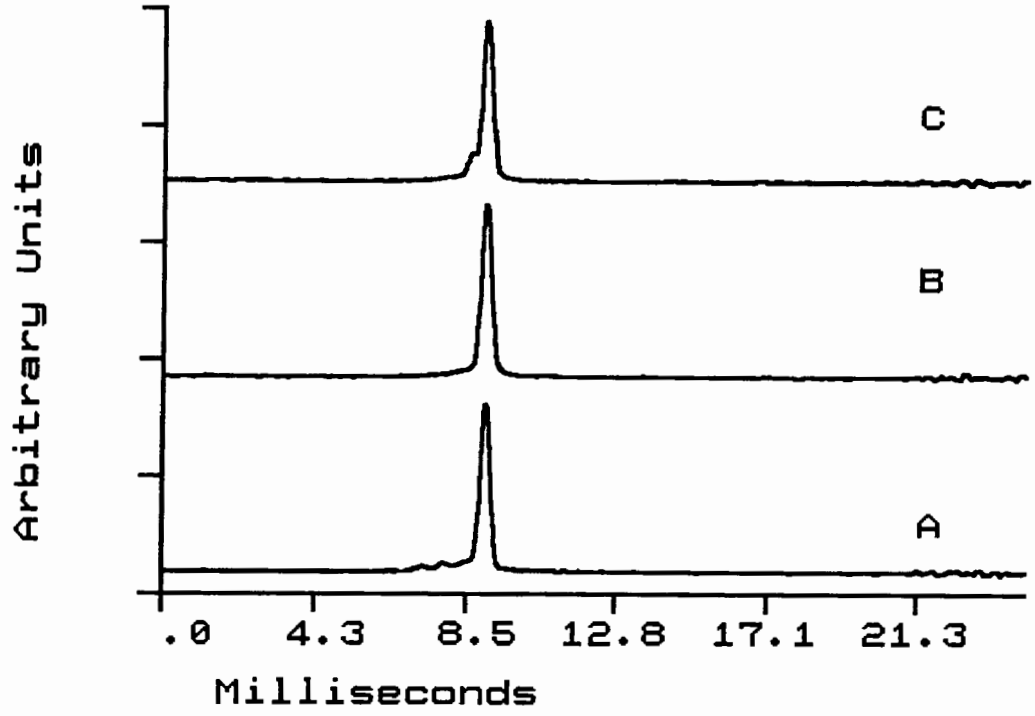

Figure 17. Typical ion mobility spectra of diethyl ether taken in the positive ion mode as a function of concentration. Spectrum A is 4.0 ppm diethyl ether, B is 40 ppm diethyl ether, and C is 400 ppm diethyl ether.

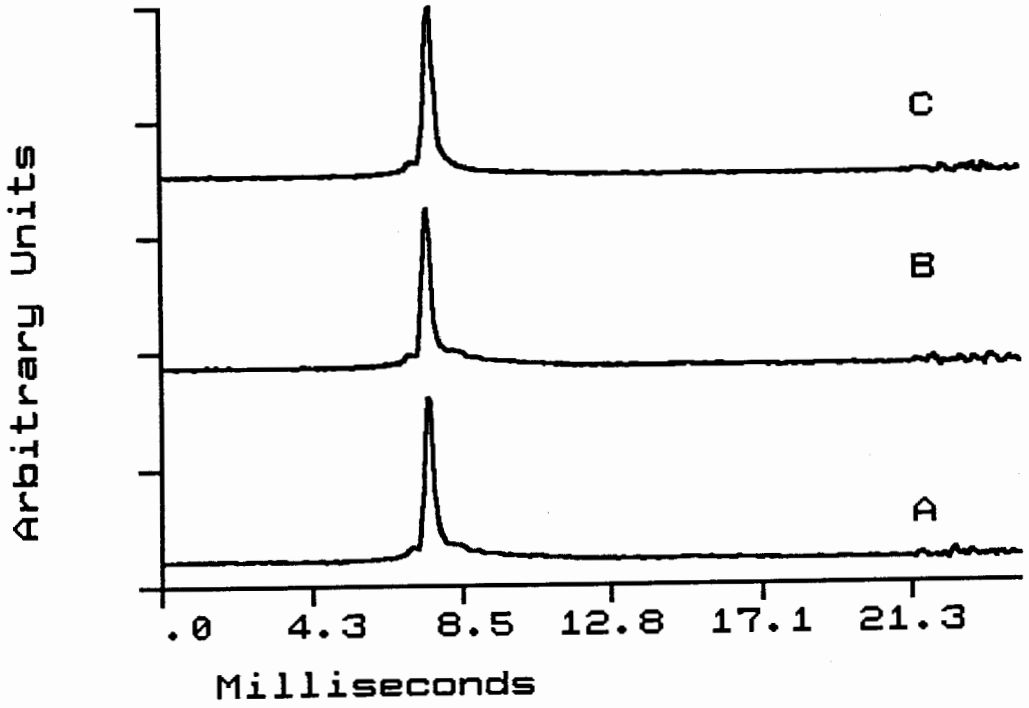

Figure 18. Typical ion mobility spectra of methanol taken in the positive ion mode as a function of concentration. Spectrum A is 8.0 ppm methanol, B is 80 ppm methanol, and C is 800 ppm methanol.

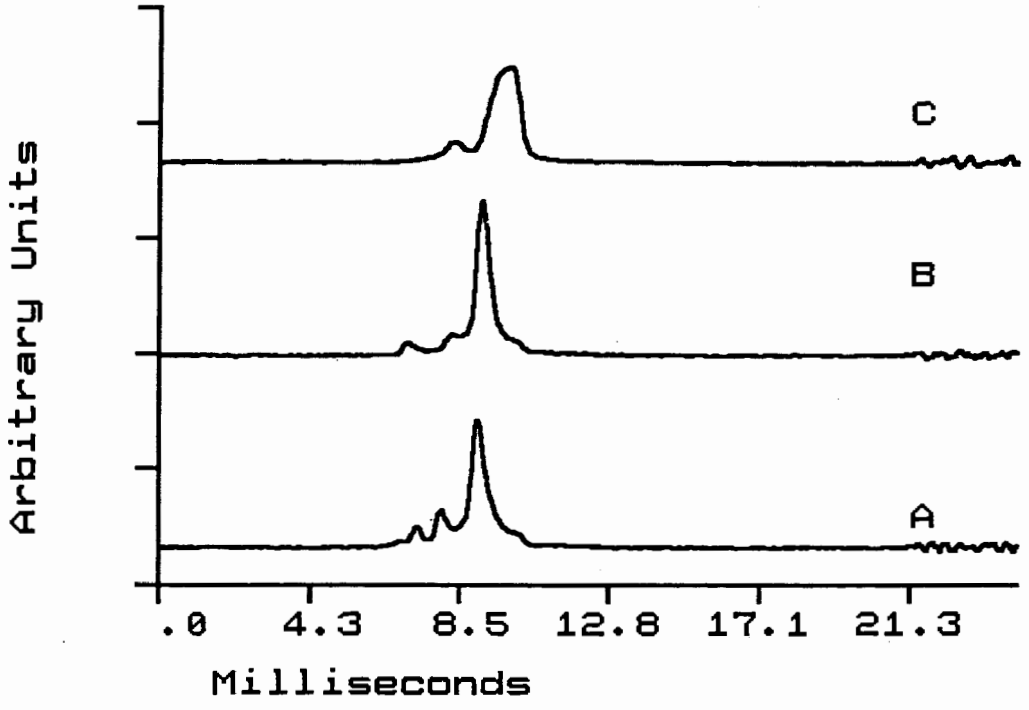

Figure 19. Typical ion mobility spectra of isopropanol taken in the positive ion mode as a function of concentration. Spectrum A is 4.0 ppm isopropanol, B is 40 ppm isopropanol, C is 400 ppm isopropanol.

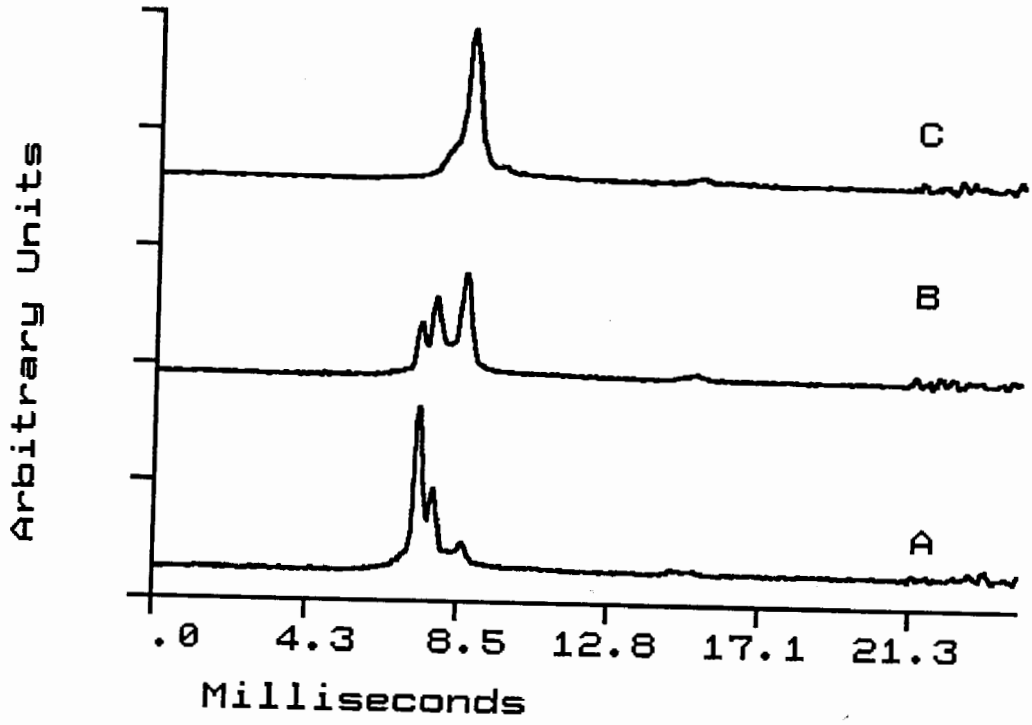

Figure 20. Typical ion mobility spectra of acetic acid taken in the positive ion mode as a function of concentration. Spectrum A is 100 ppb acetic acid, B is 1.0 ppm acetic acid, and C is 10 ppm acetic acid.

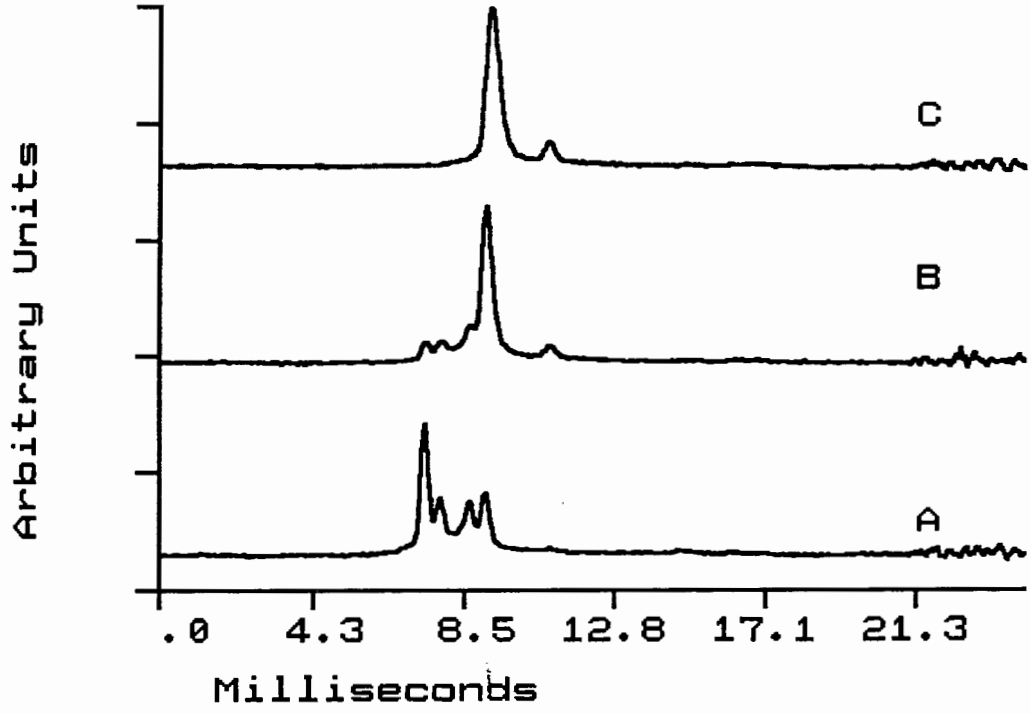

Figure 21. Typical ion mobility spectra of acetic anhydride taken in the positive ion mode as a function of concentration. Spectrum A is 50 ppb acetic anhydride, B is 500 ppb acetic anhydride, and C is 5.0 ppm acetic anhydride.

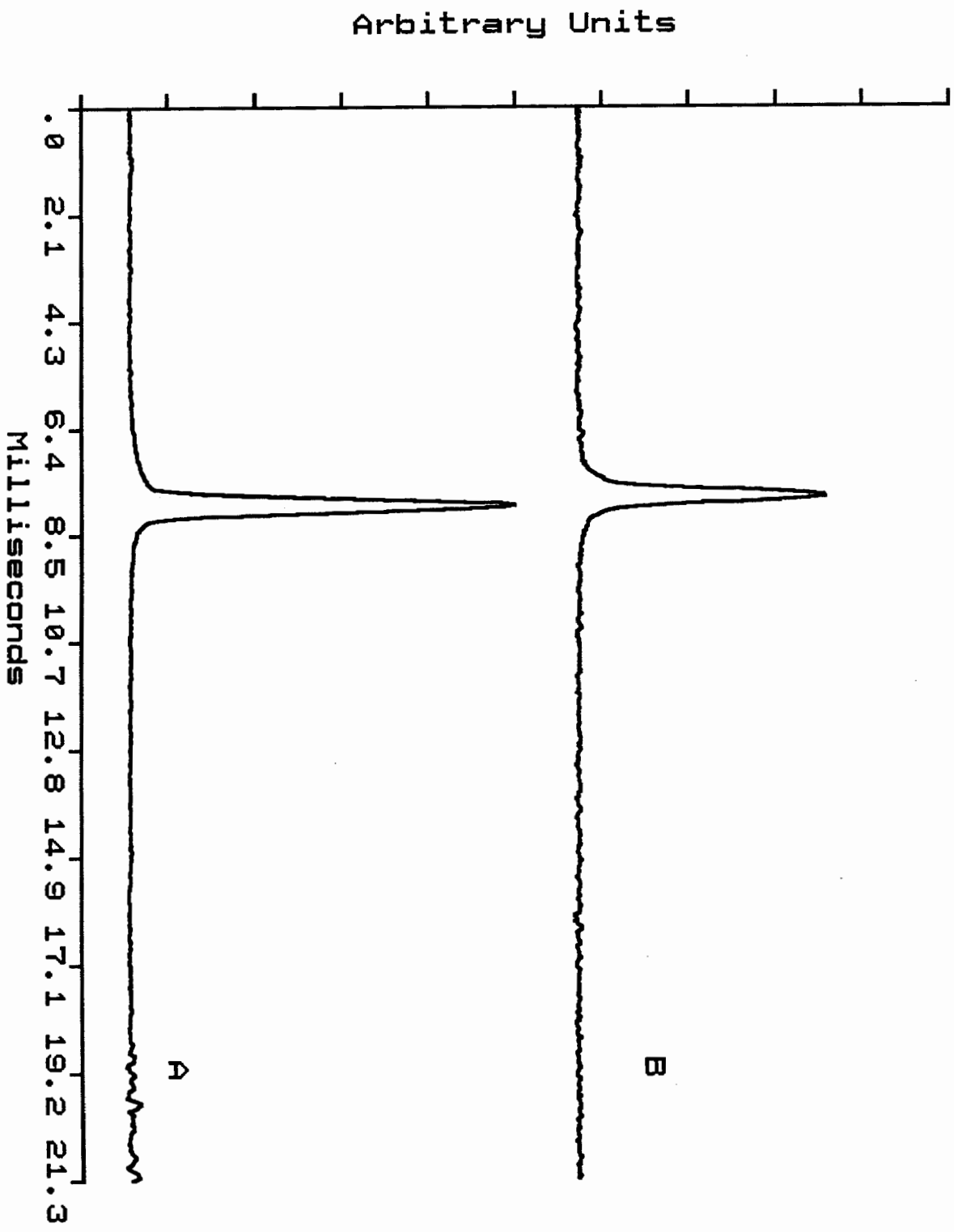

Figure 22. Typical IMS spectra analyzed using linear discriminant analysis. Spectra show the similarities often encountered in IMS spectra. Spectrum A is diethyl ether, and spectrum B is an acetone reactant ion spectrum.

DISCUSSION

DREW SAUTER: Perhaps you could explain certain aspects that have hindered adoption of ion trap mass spectroscopy, basically ion molecule reactions. One of the things I've run into, and others have, is that in certain limited scenarios, you can probably define your ion molecule chemistry.

PETER SNYDER: Yes.

DREW SAUTER: But the truth of the matter, and correct me if I'm wrong, is that you can have unknown reacting ions in the sample. In an unknown situation, it would seem that you could actually get spectra that were sample dependent. Basically, would you see IMS being more useful as a sort of screening tool on relatively limited scenarios, as opposed to a tool that could offer more general analysis capabilities?

PETER SNYDER: Well, I can't disagree with that when you just talk about IMS by itself. Because of the potential complicating responses that can occur if your environment is not controlled, anything can happen.

DREW SAUTER: What I mean though is in the real environmental world, a lot of samples have a lot more than one compound, and not only that do they have a lot more than one compound, recognizing that you can separate things by GC's, they tend to have different concentrations.

PETER SNYDER: Yes.

DREW SAUTER: Hence if they have different concentrations, and there's ion molecule reactions going on, you have them going on with some rate constant. They're producing different populations of ions, and hence a different sample dependent spectra. That strikes me as a significant drawback, despite all the grand things that you've shown.

PETER SNYDER: You have to consider what IMS is based on? IMS is based on ion molecule reactions, and that can be broken down into proton affinity and electron affinity by and large. So then you have to look at what kind of compounds are responding.

DREW SAUTER: But there's also a concentration term that you showed in your graph.

PETER SNYDER: Yes, absolutely. Concentration is very important. I guess the difficulty in response comes then when you get to phosphonate compounds or phosphoryl compounds that are very sensitive to proton affinity. They get that proton very nicely, and by and large to the exclusion of many other compounds, even in their presence, or at relatively high concentrations. Ammonia, probably would take exception too. That might be a complicating factor.

But in most cases, phosphoryl compounds really come through, and that's one of the strengths of the chemical agent monitor, in terms of looking for phosphoryl-based nerve agents.

As you go down to amines, esters, ketones and alcohols, the relative proton affinities are not as wide.

STEVE HARDEN: I'd like to just comment on that before we get on to the next question, and say that yes, you have indeed hit upon one of the problems with ion mobility spectrometry for analyzing real-world mixtures.

The reason the Army has developed it for their purposes is that the compounds they're interested in either have such extreme proton affinities, or extreme electronegativities, and that the sensitivity is very high for those compounds. So it works for our purposes, and it may not work for some environmental purposes that you mentioned, because of this mixture problem.

It also points out one of the needs and requirements in this unknown analysis, or analysis of unknowns, for preparation of sample you mentioned the GC/MS system. We'll hear some more about that in our next paper.

But one can also point out that in some of the data (in this paper) for some compounds that do have a high electronegativity, can be picked out using these techniques that we were talking about, and we can then point out the fact that yes, indeed, that material was present.

That little bump on the side of that peak was, I think, the mustard, which is an Army compound of interest. The bump was on the side of a peak of phenol, phenol being in much greater concentration.

In previous sensitivities and single processing techniques, we can bring it even more if we used preparation of samples. However, you do separate samples at the expense of complexity of instrumentation, and that's one reason why the Army hasn't pursued that to this particular point. So we have.

HERB HILL: For a long time now we have been using ion mobility spectrometers as a chromatographic detector, basically because we feel that there really are problems with interferences, except for very specific cases.

I'm really excited to see us beginning to talk about the use of, what I call chromatographic filters on the front end of IMS, for field monitoring. We've done studies, for example, treating IMS as a chromatographic detector, and you can see that the interferences under conditions like that are no worse than you would have with a flame ionization detector, an electron capture detector. The quantitative value of IMS is acceptable in any range. It's as good as any of the standard chromatographic detectors that we have. We've published papers in which we've put interfering species in, compared them to an FID, and ECD, an IMS, and you see that the quantitative value of the data is fine, it's good in IMS. When you add the chromatograph controls on the front end, you can do dioxins. We do ligands in blood analysis, we do a variety of very small, minute trace compounds in very, very complex mixtures, as well or better, than you can be a lot of techniques.

And it should apply very well to field analysis for portable, if you put a portable GC on the front end of that.

PETER SNYDER: Yes, you're absolutely right. And the literature that you have published over the past decade and a half, attests to that. There's many different sample matrices that Professor Hill has looked at with very good resolution, depending upon the column characteristics. There has been a lot of good information coming out of that, using an IMS as a detector.

So basically the newer innovative topic we're looking at here, is using the hand-held version of the IMS, to see how far we can go with that.

ION MOBILITY SPECTROMETRY AS A FIELD SCREENING TECHNIQUE

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1. INTRODUCTION

Ion Mobility Spectrometry (IMS), also called Plasma Chromatography, is used to detect trace quantities of organic vapors in gaseous mixtures. Several researchers over the past 15 years have demonstrated the utility of mobility detection for a variety of organic compounds.[1-11] Quantities as low as 10^{-10} grams of nitrosamines have been reported[12].

IMS is a conceptually simple technique that relies on the drift time, or time of flight, of molecular, or cluster, ions through a host gas as a means of differentiation. This differs from classical mass spectrometry in that there is little, if any, fragmentation and the ions are not mass analyzed. Detailed theory can be found elsewhere.[13-15] The ions are differentiated by charge and by mobility. The reduced mobility K_0 (corrected for standard pressure and temperature) is expressed as

$$K_0 = 42.51\ D$$

where D is the scaler diffusion coefficient of Fick's law. This reduced mobility K_0 is catalogued and identified for each ionic species present.

2. EXPERIMENTAL

The work was performed on a MMS-290 Ion Mobility Mass Spectrometer (PCP, Inc.). shown in figure 1 and an Air Vapor Monitor made by Graseby Ltd.

The PCP, Inc. MMS-290 spectrometer used in these experiments consists of an ion mobility spectrometer followed by a quadrapole mass spectrometer coupled to a Nicolet signal averager with a computer interface for storage, data manipulation and display.

There are four modes of operation for the MMS-290. In the total ion mode the MMS-290 acts as an ion mobility spectrometer. Ions are gated into the drift region and detected by the electrometer. All ions detected are averaged, stored and displayed. In the integral ion mode the mass spectrometer is the detector instead of the electrometer. Again, all ions are detected, averaged, stored and displayed. There is no mass analysis in this mode. It is used to check that the ion distribution is not changed by traveling the extra distance through the mass spectrometer. The third mode is the mass spectrum. The shutter grid is held open to allow a continuous stream of ions into the mass spectrometer which is mass analyzing the ions. This provides a mass spectral scan of the total ion flux. The last mode of operation is the tuned ion mode where the MMS-290 is operated as in the integral ion mode but the mass spectrometer is only detecting one mass ion at a time. This shows which mass ions are associated with each mobility peak.

The Airborne Vapor Monitor (AVM) used in these experiments consists of an IMS described above with a membrane inlet and internal electronics for signal processing and alarm. It operates in both positive and negative ion mode, has

no internal display but can be interfaced to a personal computer for display and storage of the IMS spectra. The AVM has only an electrometer, it has no mass spectrometer to mass analyze the ions, and it operates as the total ion mode of the MMS-290.

Air, or the sample gas, is drawn into the ionizing region and is ionized by 60 keV Beta rays from a radioactive Ni63 source. A potential exists between the ionizer and the collector forcing the ions in the direction of the shutter grid. The closed shutter grid neutralizes all ions reaching it. The shutter is pulsed open for approximately 0.1 millisecond (msec) and a cross section of the ions flow into the drift region. The shutter closes again isolating a short pulse of ions that travel down the drift region propelled against the drift gas flow by the potential on the collector. The ions are differentiated by their charge in the electric field and their mobility in the drift gas (velocity V_d)

$$V_d = K E.$$

The IMS differentiates the ions because by the time that they reach the shutter grid the ion molecule reactions have equilibrated and in the drift region no more reactions take place.

As the separated ions reach the collector, they are detected by a fast electrometer, and a current is generated directly proportional to the number of ions. The resultant spectrum is depicted in figure 2 [16].

The highest K_0 ions (C+) are usually smaller or more compact followed by the slower ions B+ and A+, in time.

Both positive and negative ion formation of reactant and product ions are multistep processes. Good, Durden, and Keburle[17] have determined the mechanisms involved in positive reactant ion formation:

$$N_2 \xrightarrow{\beta^-} N_2^+ + e^-$$

$$N_2^+ + 2\,N_2 \longrightarrow N_4^+ + N_2$$

$$N_4^+ + H_2O \longrightarrow H_2O^+ + 2\,N_2$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$H_3O^+ + H_2O + \cdot N_2 \longrightarrow (H_2O)_2H^+ + N_2$$

The size of the resultant reactant ion water clusters depend upon the relative humidity but generally water chemistry dominates the positive ion mode. The water ion may cluster directly with the sample molecule M or, as is the case more often, the sample molecule abstracts the proton from the water cluster and then may attract more or less water molecules depending on the humidity. At high concentrations the sample molecules may form dimers with a proton. Whenever there is some other molecules present with a higher proton affinity than water they may replace the water in the above mechanisms i.e. Acetone or NH_3. So, in figure two peak C may be the reactant ion, B the hydrated monomer, and A the protonated dimer.

Negative reactant ion formation as summarized by Spangler and Collins[18] include the following:

$$e^-(\text{thermal}) + O_2 \longrightarrow O_2^-$$

$$O_2^- + CO_2 \longrightarrow CO_2\,O_2^-$$

$$O_2^- + nH_2O \longrightarrow (H_2O)_n\,O_2^-$$

where n = 1,2.

The sample molecule can cluster with the O_2^- or abstract the O_2^- from the CO_2. As can be easily seen, the chemistry can be quite involved before any products are formed.

The operating parameters for the MMS-290 were;

Cell length	15 cm
Operating voltage	3000 volts
Electric field	200 volts/cm
Carrier gas	200 ml/min
Drift gas	500 ml/min
Cell Temperature	40 °C
Pressure	Entered Daily
Drift distance	10 cm

The AVM was operated as received from Graseby Analytical, Ltd.(Watford, Herts, UK). Signals from this IMS were processed with a Graseby Analytical, Ltd., advanced signal averaging (ASP) board installed in an IBM PC/AT computer. Known or approximate operating conditions were;

inlet flow	500 ml/min.
Drift tube temperature	ambient
membrane temperature	70 °C
reaction region	2.2 cm
drift region	~3.8 cm
field gradient	~ 200 V/cm

The samples were generated using a Q-5 apparatus, (where a saturated vapor stream is mixed with a high volume diluent dry air stream). By varying the quantities of both streams the concentration of sample in the diluted vapor stream was controlled. The resulting diluted vapor stream was sampled by either the IMS/MS inlet or the AVM. All samples were used as received from the manufacturer. The concentration of the saturated vapor stream was calculated from vapor pressure data or from the Antoine equation.

3. RESULTS AND DISCUSSION

The data following are an example of the power of this detection system to high concentration vapors of acetic acid. The acetic acid was used "as is", and, as will be shown, was contaminated with acetic anhydride(as is often the case). The target concentration for acetic acid

detection with the AVM was the Time Weighted Average (TWA) of 10 ppm[19], the Short Term Exposure Limit (STEL) of 15 ppm[19], up to the Immediately Dangerous to Life or Health (IDLH) level of 1000 ppm[20]. Figures 3-6 show the response of the AVM for these three concentrations.

The identity of the peaks in the above data was determined with the IMS/MS in the following manner. First, the reduced mobility is calculated for each peak. Since the reduced mobility is a factor of pressure and temperature and these vary in the AVM and between the AVM and IMS/MS, a drift time ratio is calculated by dividing the specie mobility by the reactant ion mobility (both are under the same temperature and pressure). Then, the IMS/MS is operated in the total ion mode and the integral ion mode to check that there is no effect between the different inlets of the AVM and the IMS/MS and that the mass spectrometer entrance of the IMS/MS does not change the specie (figures 7 and 8). The first thing noticed is that the pinhole inlet of the IMS/MS is much more sensitive than the membrane of the AVM. The membrane is required, however, to keep too much water and contaminants from spoiling the sensitive IMS cell. So, allowing for the difference in sensitivity, the mobility spectrum of the IMS/MS is compared with the AVM to correlate the mobility peaks between the two instruments. Once confirmed, the mass spectrum is taken to determine what mass species are the major contributors to the ion mobility spectrum (figure 9). Then, each mass is scanned in the tuned ion mode to determine to what peak in the mobility spectrum each mass contributes (figure 10). As can be seen, in this low concentration, the masses 55,73,83,101,and 129 are all hydrates and "nydrates" of the H^+ "reactant ion" and the masses 79, 97, 125, and 153 are hydrates and "nydrates" of the H^+ acetic acid monomer. The concentration is then increased and the analysis series is repeated. As the concentration increases the mass spectrum becomes more complicated but assignments can be made bases upon past experience. Since, at this time, we do not have the capability there is no secondary mass fragmentation for confirmation of these species. Tables 1 indicates the assignments for each mass fragment in the mass spectrum. Table 2 is a list of the mobility ratios and the assignments for each mobility peak seen at the various concentrations.

CONCLUSION

This example of acetic acid illustrates the potential of this hand held ion mobility spectrometer to differentiate between regulated concentrations of hazardous chemicals. In support of another program this work has been extended to identification of these regulated concentrations (TWA, STEL, and IDLH) of 15 other solvent chemicals. Although limited in scope, by extending this data base the AVM could be used as a field screening device and as a safety device for field personnel.

TABLE 1

AMU	Specie	Comment
55	$H^+(H_2O)_3$	reactant ion
73	$H^+(H_2O)_4$	reactant ion
79	m $H^+(H_2O)$	monomer hydrate
83	$H^+(H_2O)_3+N_2$	reactant ion
97	m $H^+(H_2O)_2$	monomer hydrate
101	$H^+(H_2O)_4+N_2$	reactant ion
125	m $H^+(H_2O)_2+N_2$	monomer "nydrate"
129	$H^+(H_2O)_4+2N_2$	reactant ion
153	m $H^+(H_2O)_2+2N_2$	monomer "nydrate"

TABLE 2

Mobility Ratio	Assignment	
1.00	$H^+(H_2O)_x(N_2)_y$	Reactant Ion
1.08-1.09	m $H^+(H_2O)_x(N_2)_y$	Acid Monomer
1.18-1.24	m_2 $H^+(H_2O)_x(N_2)_y$	Acid Dimer
1.34-1.35	m n $H^+(H_2O)_x(N_2)_y$	Acid Anhydride
1.47-1.48	n_2 $H^+(H_2O)_x(N_2)_y$	Anhydride Dimer

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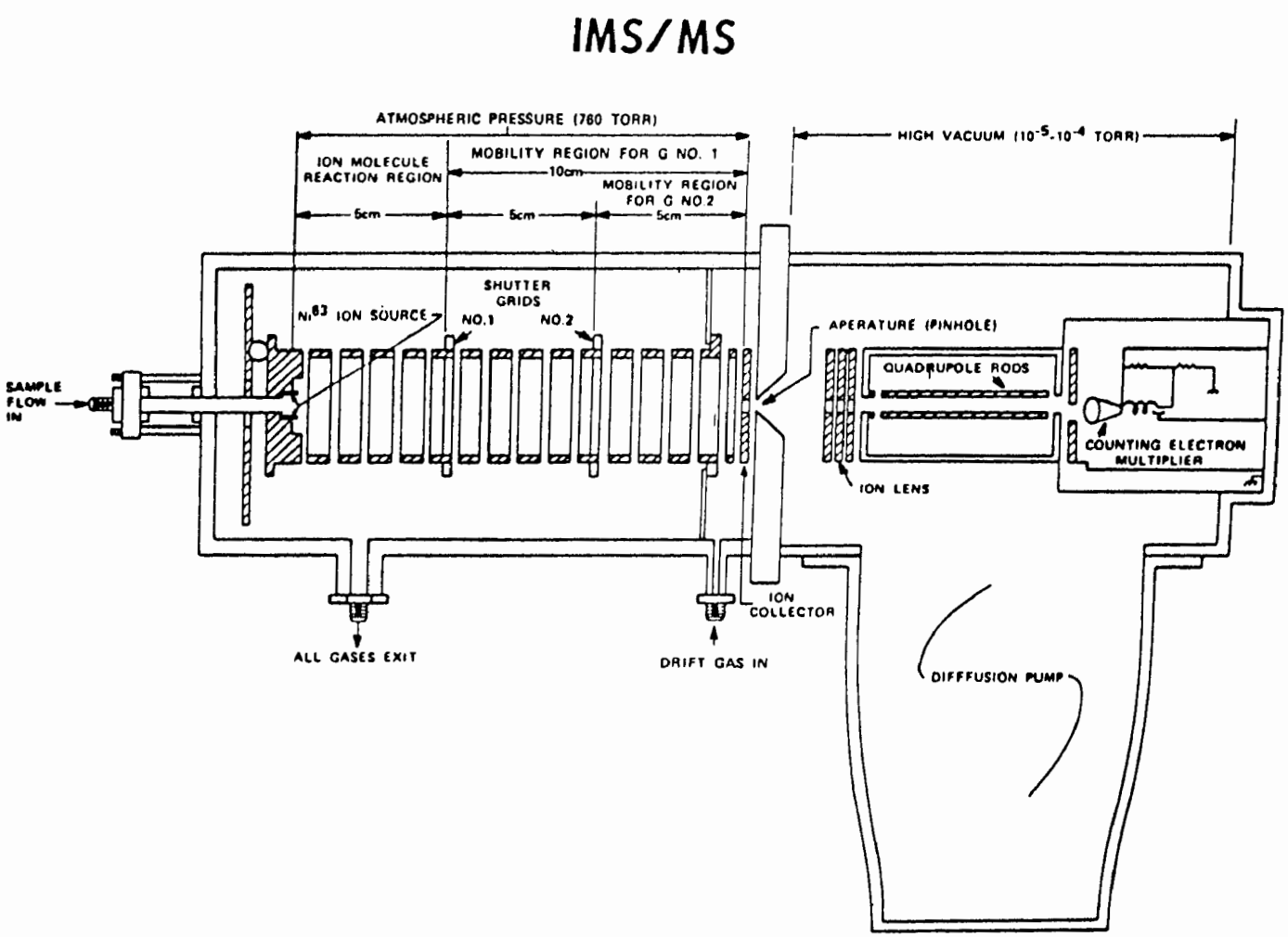
FIGURE 1


IMS/MS
ATMOSPHERIC PRESSURE (760 TORR)
HIGH VACUUM (10^{-5}-10^{-4} TORR)
ION MOLECULE REACTION REGION
MOBILITY REGION FOR G NO. 1
10cm
MOBILITY REGION FOR G NO.2
5cm
5cm
5cm
SHUTTER GRIDS
Ni^{63} ION SOURCE
NO.1
NO.2
APERATURE (PINHOLE)
QUADRUPOLE RODS
COUNTING ELECTRON MULTIPLIER
SAMPLE FLOW IN
ION LENS
ION COLLECTOR
ALL GASES EXIT
DRIFT GAS IN
DIFFFUSION PUMP

TYPICAL [ION ARRIVAL TIME SPECTRUM]

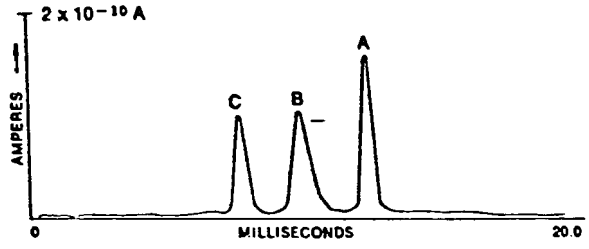


FIGURE 2

Figure 3: AVM Spectrum (Air)

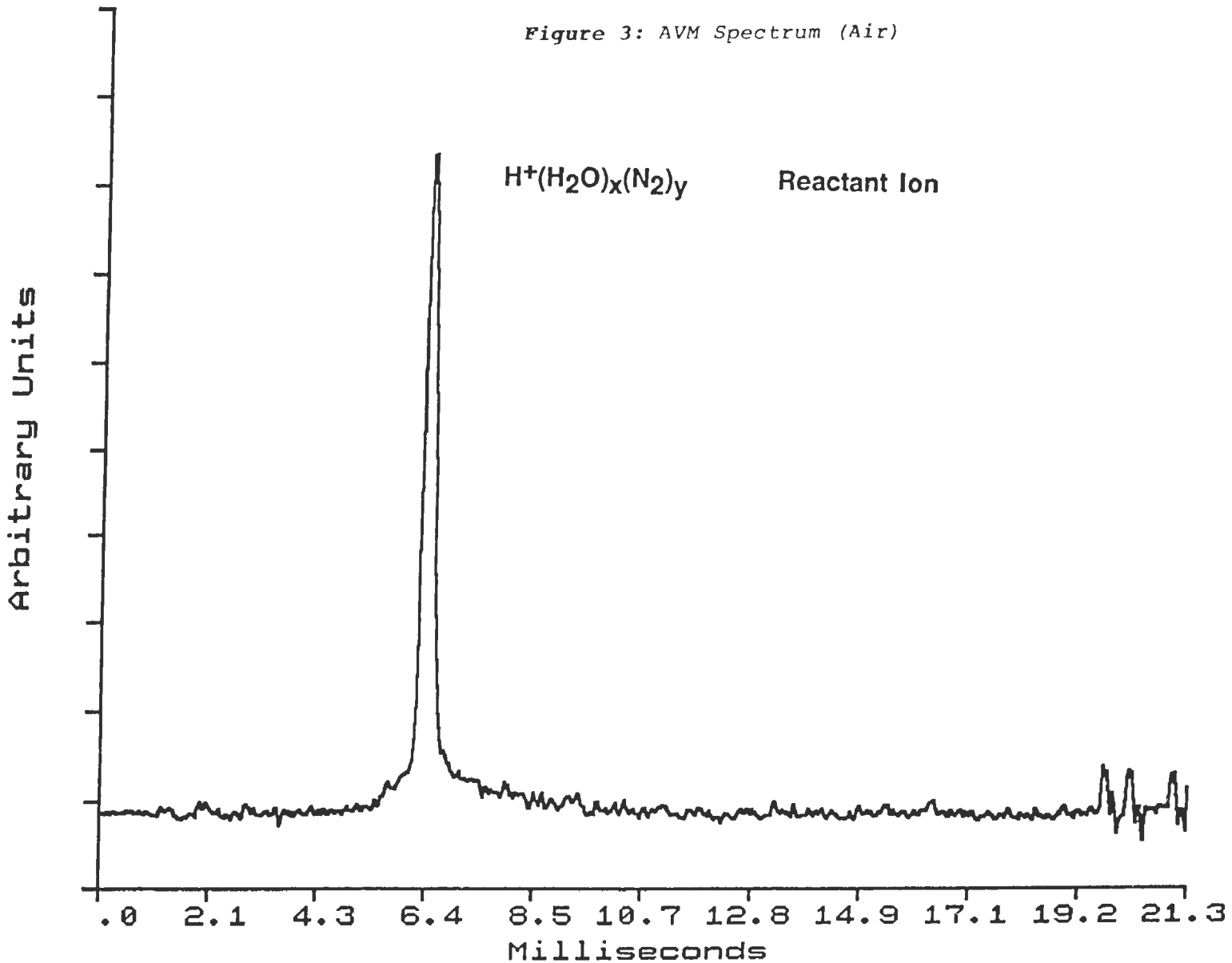


Figure 4: AVM Spectrum (Acetic Acid 10 ppm)

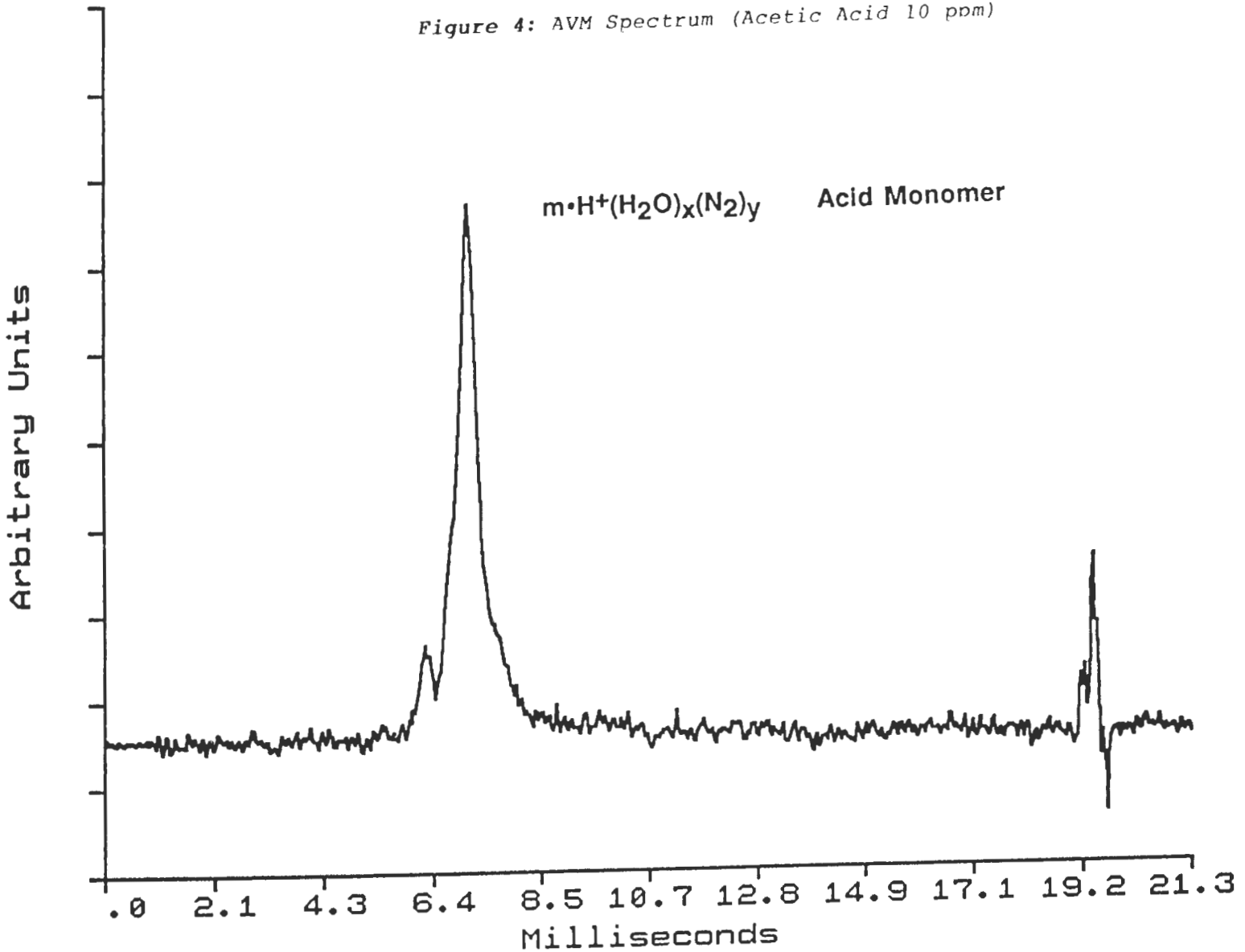


Figure 5:AVM Spectrum (Acetic Acid 15 ppm)

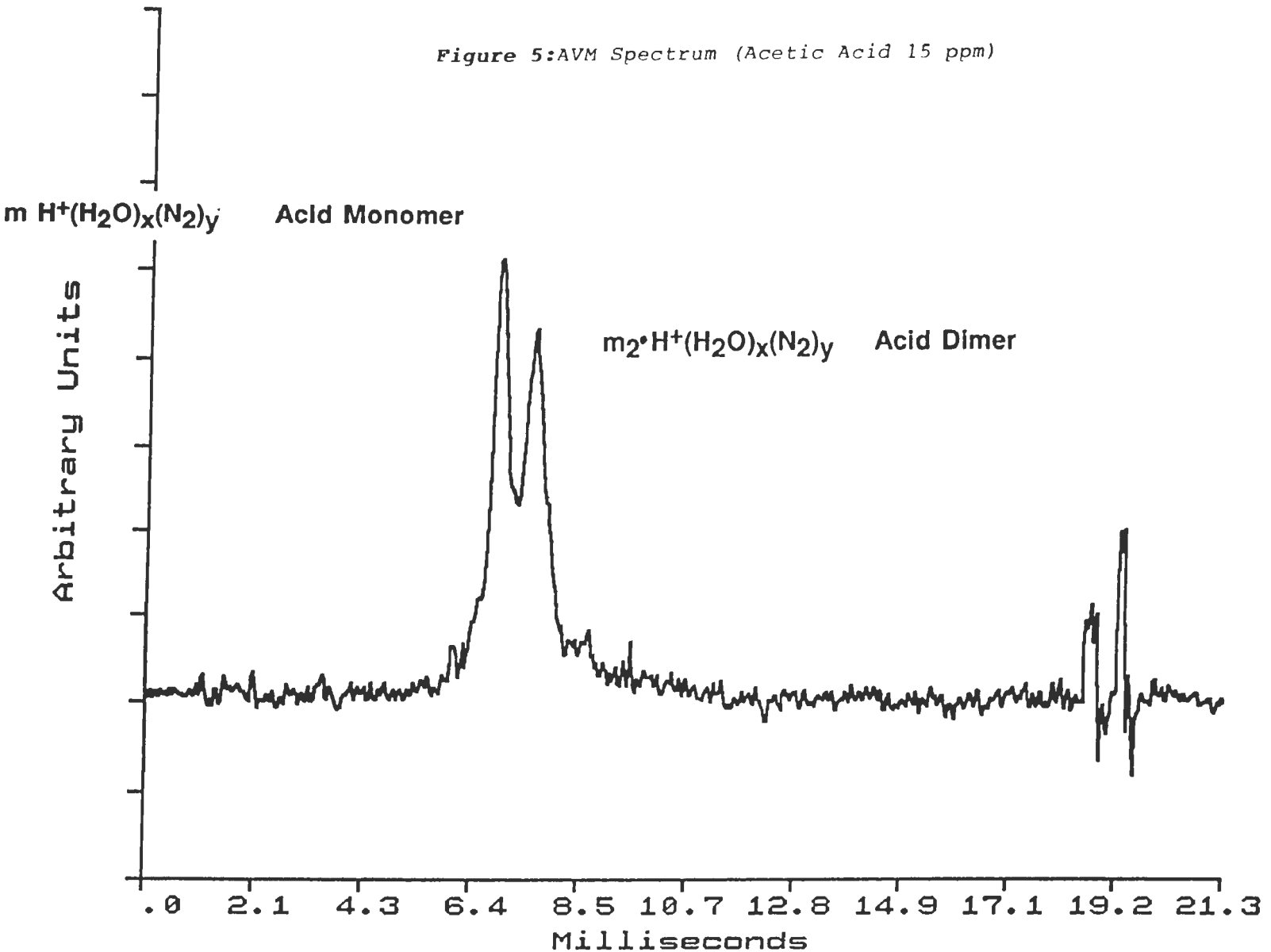
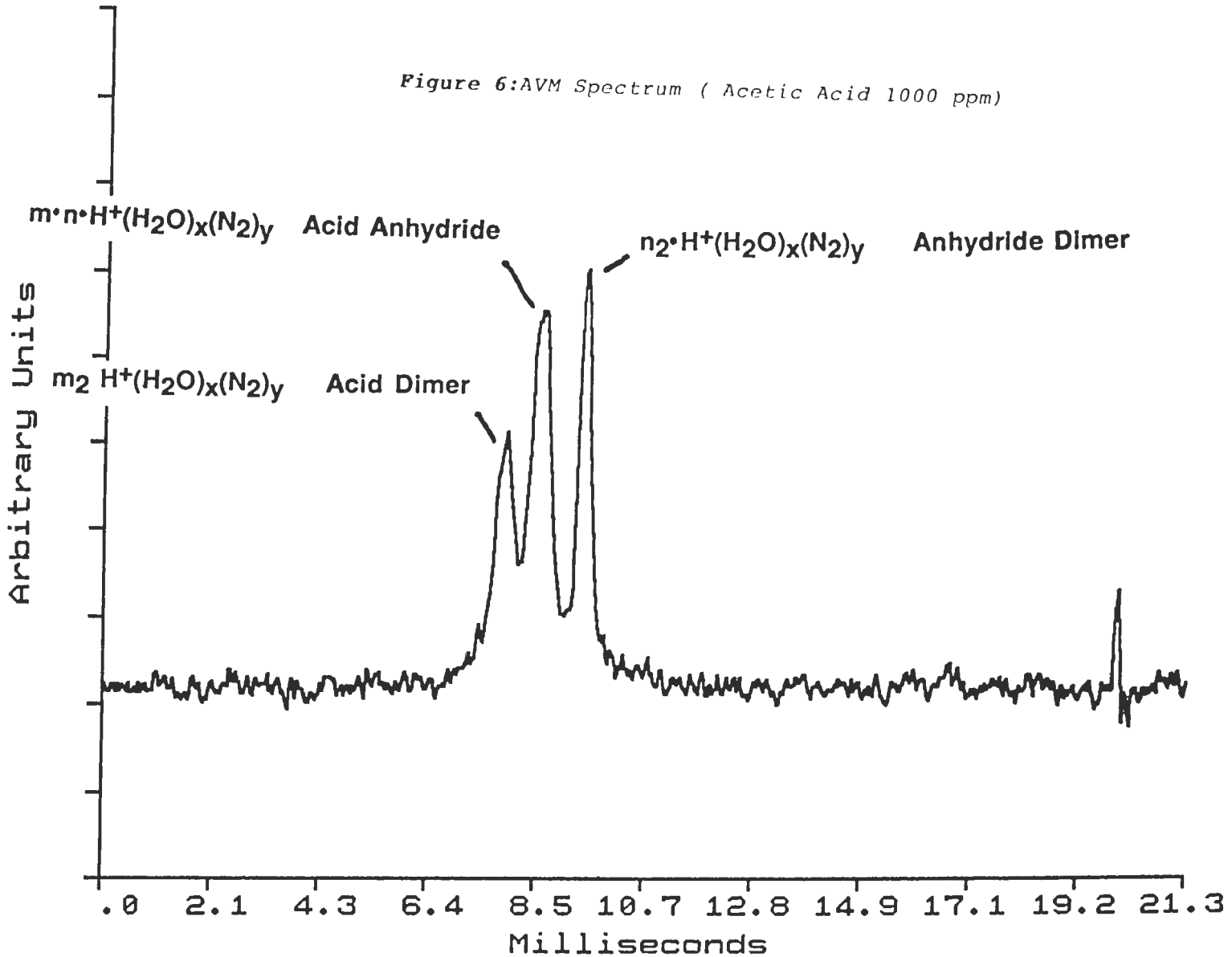


Figure 6:AVM Spectrum (Acetic Acid 1000 ppm)



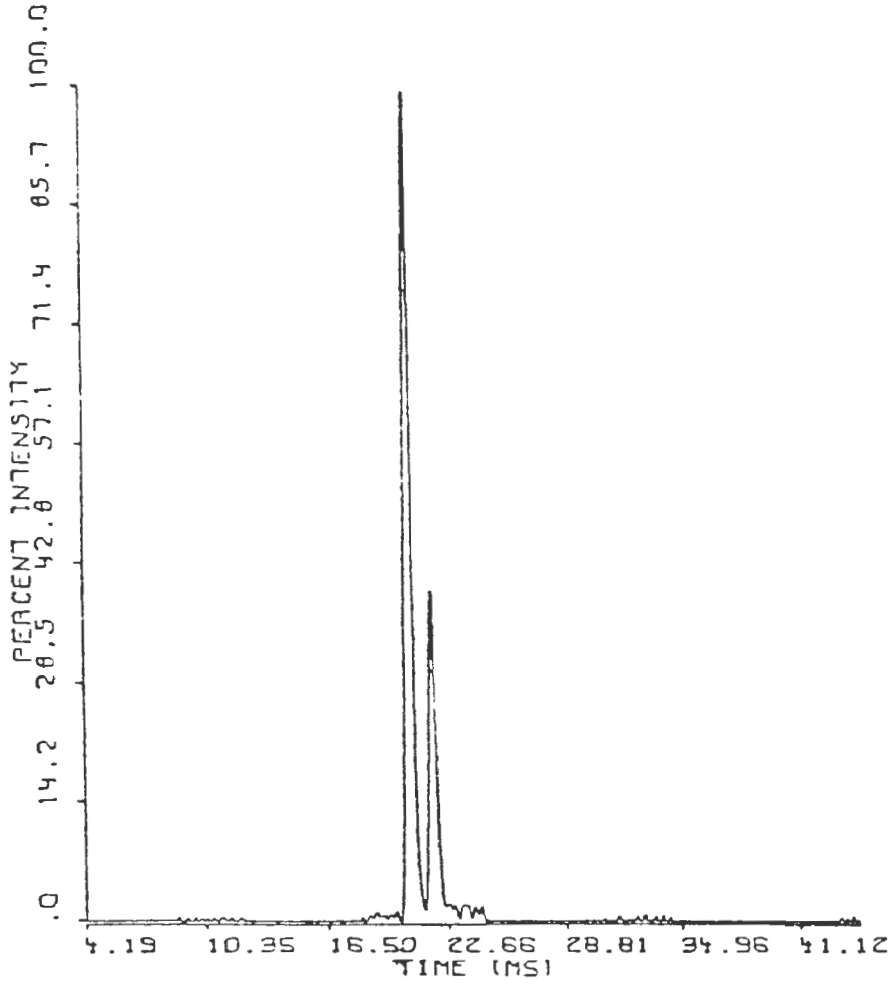


Figure 7: *IMS/MS Spectrum "Total Ion Mode" (Acetic Acid 80 ppb)*

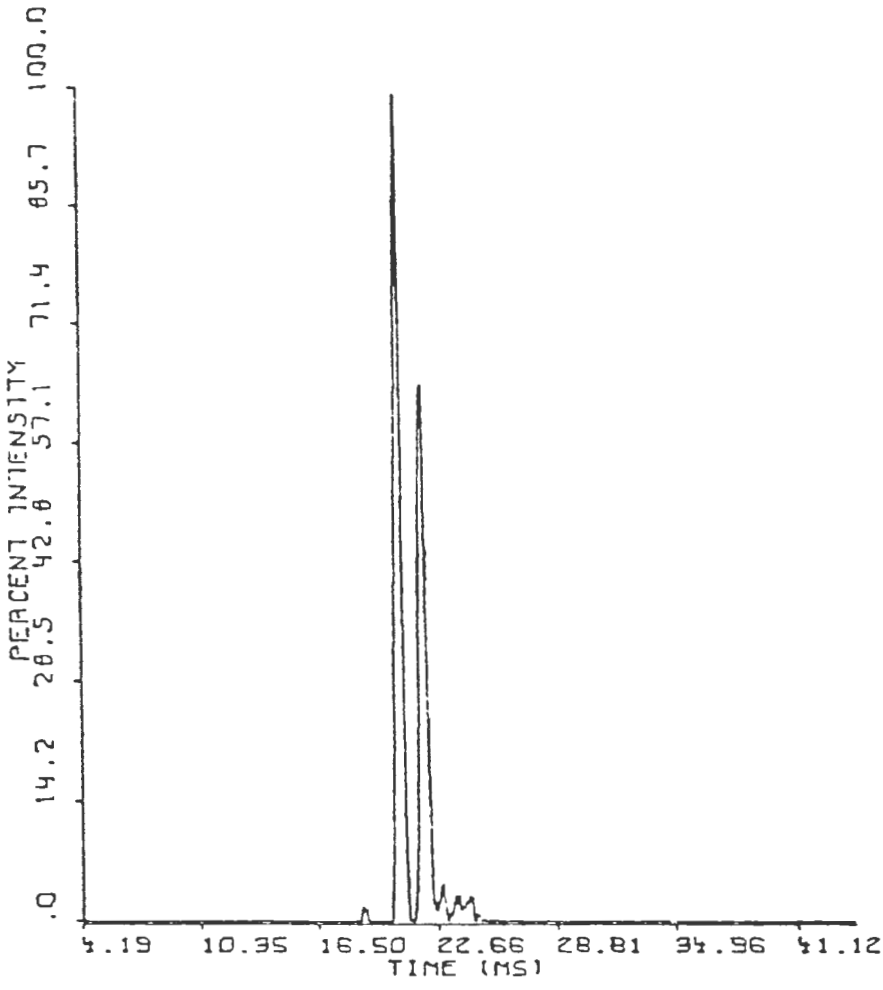


Figure 8: *IMS/MS Spectrum "Integral Ion Mode" (Acetic Acid 80 ppb)*

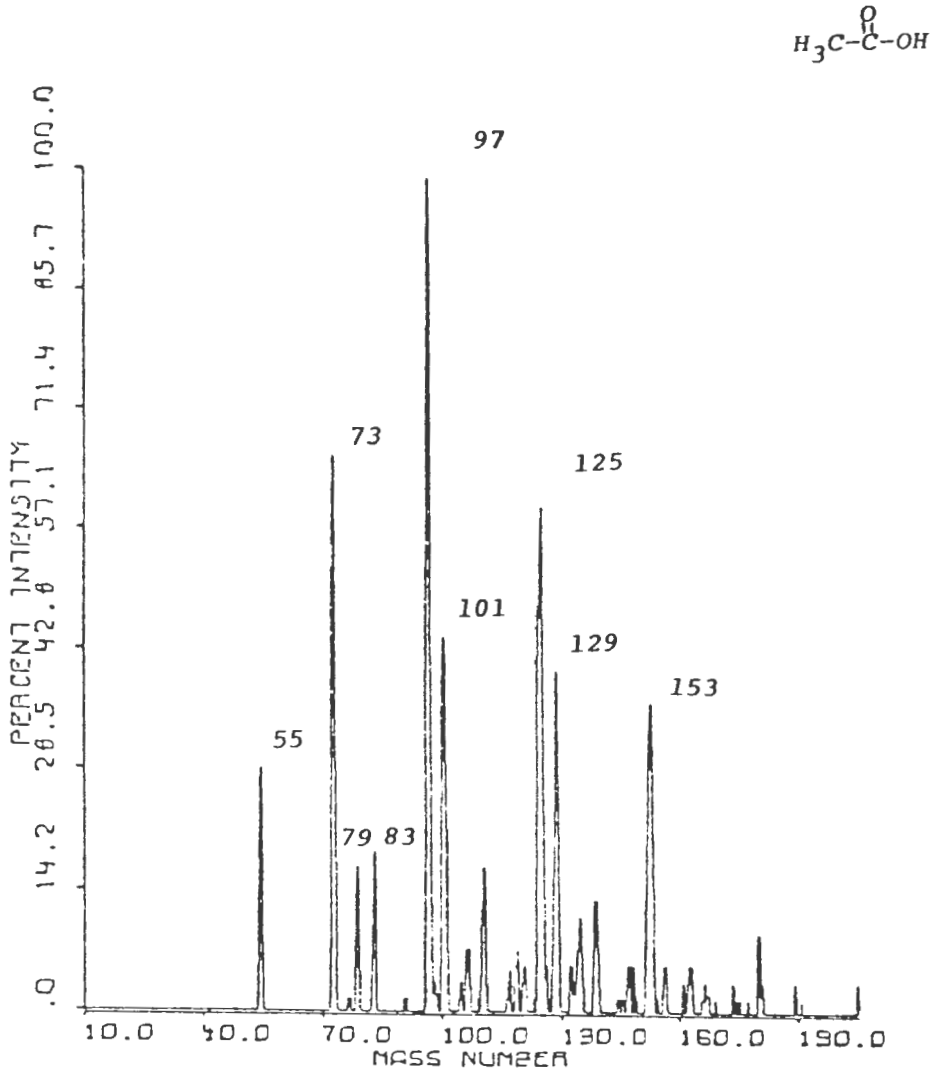


Figure 9: *IMS/MS Spectrum "mass spectrum mode" (Acetic Acid 80 ppb)*

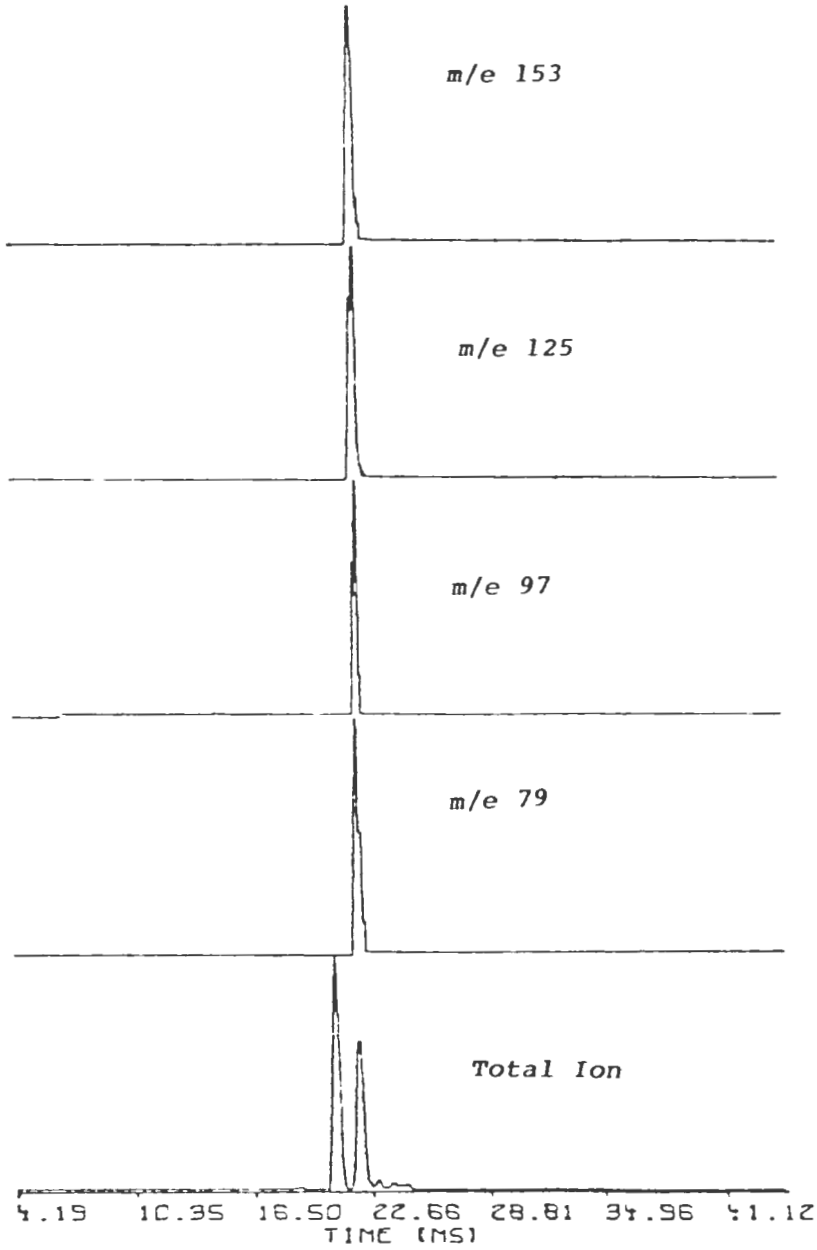


Figure 10: *IMS/MS Spectra "Tuned Ion Mode" (Acetic Acid 80 ppb)*

HAND-HELD GC-ION MOBILITY SPECTROMETRY FOR ON-SITE ANALYSIS OF COMPLEX ORGANIC MIXTURES IN AIR OR VAPORS OVER WASTE SITES

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ABSTRACT

Ion mobility spectrometry (IMS) was formally introduced approximately 21 years ago, and has been used as a detector for chemical warfare agents. IMS research and development outside the military has recently been the subject of renewed interest. Military IMS units are small, rugged, and portable which makes them ideal candidates for inclusion in portable airborne vapor monitoring systems. The strengths of IMS are low detection limits, a wide range of application, and simplicity of design and operation. The gentle ionization processes used in IMS impart a measure of selectivity to its response. However, atmospheric pressure chemical ionization with compounds of comparable proton affinities leads to mobility spectra for which interpretive and predictive models do not exist. An alternative approach for the analysis of complex mixtures with IMS is the use of a separation device such as a gas chromatograph (GC) as an inlet. The attractions of GC-IMS over GC-mass spectrometry (MS) for field use include the small size, low weight, and low power demands of GC-IMS.

Parameters in GC-IMS which required examination before further development or field application included three major concerns. The first was selection of an optimum temperature of the IMS detector and evaluation of the effect of IMS temperature on mobility spectra. The second was a study of the stability and reproducibility of chromatographic retention and mobility behavior. The final issue was the

development of suitable data reduction methods. Results suggest that an IMS cell temperature of ca. 150° to 175°C provided mobility spectra with suitable spectral detail without the complications of ion-molecule clusters or fragmentation. A commercially available, portable IMS unit was configured as a GC detector to evaluate the possibility of using the unmodified unit as the basis for a portable prototype. Significant fluctuation in peak heights were observed (ca. +/- 12%), but mobilities varied slightly (ca. 1 %) over a 30 day test period. Neural network pattern identification techniques were applied to data obtained at room temperature and at 150°C. Results showed that spectral variability within compound classes was insufficient to distinguish related compounds when mobility data was obtained using the commercial room temperature IMS cell. Similar but less severe difficulty was encountered using the 150°C data. Incorporation of retention indices as a referee parameter was useful in eliminating false positives.

INTRODUCTION

Background

The detection of trace levels of hazardous organic volatile compounds in complex mixtures represents an analytical and sampling challenge. Waste site sampling requires ppb detection limits in samples comprised of complex matrices and mixtures of from ten to hundreds of analytes. Other considerations include the time of sampling and time of analyses, delays in analysis, labor costs, labor training, and cost/sample ratio. The time and expense of complete laboratory analyses can force that fewer samples be taken with the attending risks. Technical aspects make the translation of widely accepted laboratory instrumentation (GC-MS and GC-FTIR) difficult or unsatisfactory due to cost and complexity. Certainly, gas chromatography with some advanced detector will be required for chemical resolution of complex mixtures of organic compounds over waste sites. Proven detectors such as mass spectrometry and infrared spectrometry allow necessary specificity of detection but represent cumbersome and intricate instrumentation not easily configured for field use. These instruments often require highly skilled operators as well. The high power consumption of portable GC/MS and GC/IR systems certainly limits their use in many field situations. Other detectors which have been

common to portable GC units lack specificity and necessitate a reversion to dual column or dual detector methods for confirmation of peak assignments. The development of a hand-held GC-IMS combines the separation power of GC in combination with a multidimensional detector. The release of the civilian counterpart of the military IMS units was a logical starting point for development of a portable GC-IMS.

Ion Mobility Spectrometry

Ion mobility spectrometry (Figure 1) is based on the ionization of vapors in air at atmospheric pressure. The differentiation of ions occurs by measurement of gaseous ionic mobilities (1). A typical IMS instrument is divided into two regions. The first is the reaction region containing an ion source (typically ^{63}Ni). Ion separation occurs in the second (drift) region of the spectrometer, where separation is based on the size-to-charge ratio of the ions. The ion shutter that separates the two regions injects ions from the reaction to the drift region using period pulses of the shutter field. The drifting ions are detected at the end of the drift tube by a detector plate.

In IMS, ionization occurs through collisional charge transfer between a reservoir of charge, i.e. the reactant ions, and neutral analytes, M. The most abundant reactant ions generated from a beta-emitting source in air are $(H_2O)_n*H^+$ and $(H_2O)_n*O_2^-$. These ionic clusters co-exist at near thermal energies in the reaction region. Product ions experience little or no fragmentation and exist commonly as M^+ and MH^+ or M^- and $M*O_2^-$ depending on proton or electron affinities of the neutral species. Ions formed in the reaction region are injected into the drift region by the ion shutter. In the drift region, ions move at particular drift times (t_d) through an electric field, E, of ca. 200 V/cm. For a drift region with a given length, L (cm), the drift time is related to velocity (v_d, cm/s) and ion mobility (K, $cm^2/V*s$)) through equations 1 and 2:

$$v_d = L / t_d \quad (1)$$

$$K = v_d / E \quad (2)$$

Ions strike a flat plate detector and a mobility spectrum or plot of detector current (in pA or nA) versus t_d (usually in ms) is produced. Consequently, the basis for selectivity in IMS is differences in drift times for ions governed by ion mobilities. Drift times are dependent on temperature and pressure and are normalized to reduced mobility constants, K_o, that are related to molecular

properties through the Mason-Shamp equation. In general, the equations for mobility constants are considered well-established for small spherical ions but extrapolations to large organic molecules may be tenuous. Practically speaking, direct quantitative predictions of K_o values for organic molecules are presently impossible. Mobilities are inversely proportional to collisional cross sections. Thus, IMS is an ion separator based on size/charge rather than mass/charge as found in mass spectrometers.

Ion mobility spectrometry offers advantages such as low power, simple and rugged construction, ppb detection limits, and mobility spectra representative of individual constituents. Disadvantages traditionally ascribed to IMS include significant memory effects, irreproducible behavior and complex response to mixtures (2). These difficulties can be circumvented with the addition of a GC as an inlet and with the reconfiguration of the drift tube (3,4). Furthermore, hand-held IMS instruments are currently available in military-hardened form with battery operation (5). The military IMS cells are attractive for use in portable GC units and were used as a starting point for the study of GC/IMS parameters.

Objectives

Several areas of GC-IMS have not been addressed and must be understood for practical advances in field applications of GC/IMS. The first area is optimization (or influence) of IMS temperature on GC/IMS performance and on the mobility spectra obtained from the IMS. Second is the evaluation of the effect of concentration on reduced mobility and mobility patterns. Third is the evaluation of a commercially available portable IMS as a GC detector, and the final area is the preparation of a suitable software peak identification program. Each of these has served as the basis for an objective in the work described below.

RESULTS AND DISCUSSION

Effects of Temperature on Ion Mobility

The successful development of a portable GC-IMS requires that the optimum IMS temperature be determined. This data had to be determined empirically, since little foundational theory was available. Typically, low temperature mobility behavior shows considerable ion clustering and complexity, while higher temperatures encourage ion

fragmentations. An intensive study was undertaken to determine the optimum operating temperature for the IMS since a wide variety of analytes are expected to be encountered. A representative set of 43 compounds was selected from seven different chemical classes, shown in Table 1. The temperature effect study was conducted on a Tandem Ion Mobility Spectrometer (TIMS, PCP Inc., West Palm Beach, Fla.) which allowed heating of the inlet and drift tube. Confirmational mass spectral studies were conducted on an MMS-160 IMS/MS (PCP, Inc., West Palm Beach, Fla).

There are four basic processes that can occur when a compound is introduced into the IMS. First, there may be no detectable reaction, such as when a species that is active only under positive polarity is introduced into an IMS operating in negative polarity. Second, clusters may form between the analyte and various ions such as H_3O^+, N_2^+, or NH_4^+. Such clusters appear as peaks in the spectrum. The third possibility is the formation of cluster ions which subsequently undergo equilibria reactions while in the drift tube. The magnitude of the equilibrium constant will determine the effect on the resulting mobility spectrum. If the equilibrium is slow relative to transit time, no significant effects will be seen. If the equilibrium is fast relative to the transit time, the ions arriving at the detector can differ significantly from the original ions produced, and peak broadening may result. Finally, fragmentation may occur, and the resulting spectra may exhibit such behaviors as a generalized increase in the baseline or a series or numerous small peaks. The exact manifestation will depend on the degree of fragmentation. The IMS portion of a portable GC/IMS should operate isothermally to reduce power consumption and complexity. It is thus essential to select the cell temperature such that clearly resolved, sharp, and reproducible peaks are produced. Peak broadening and fragmentation patterns will be difficult, if not impossible, for a data reduction system to classify. It is also desirable that the cell operating temperature be as low as possible to minimize power requirements. The other factor that must be considered for temperature selection is memory effect. Higher temperatures encourage rapid clearing of the cell and promote cleaner operation. Thus, 3 factors must be balanced in selecting the optimum IMS temperature: clearing time, mobility behavior, and power requirements.

The effect of IMS cell temperature on mobility behavior was studied by analyzing the 43 target compounds using nine different cell temperatures from 50 to 250°C. The results showed that while all compounds behaved differently, a general pattern was discernable. At the lower temperatures (ca. 50 to 150°C), many compounds experienced drift tube reactions, and peaks were either very broad or moved as the concentration in the drift tube changed. At the midrange temperatures (ca. 100-200°C), drift tube equilibria decreased, and stable ion/molecule clusters were observed. At the higher temperatures (ca. 200-250°C), fragmentation became prevalent. Figures 2 and 3 show two examples of compound classes and their behavior over the temperature range studied. The aromatics (figure 3) are not dramatically affected by temperature changes, although benzene and ethylbenzene do show evidence of drift tube reactions at 75 through 150°C. The alcohols (figure 4) show greater variability with temperature than the aromatics, but the general pattern of drift tube reactions-clustering-fragmentation is evident in the ethanol and n-propanol.

Members of the chemical classes of ketones, alcohols, halocarbons, and esters were examined by IMS/MS at three temperatures to confirm the data obtained using the TIMS. At 50°C, ion cluster formation dominated mobility spectra and the formation of dimer and solvated ions was evident. At elevated temperatures (150° and 225°C), these ions were not observed or present at low levels. At 225°C, fragmentation was prevalent rendering mobility spectra less informative than those from lower temperatures.

Compilation of the TIMS and IMS/MS data leads to several observations cogent to the design of a hand-held GC/IMS. First, a portable GC/IMS will require the use of a heated IMS cell to obtain distinctive and informative mobility spectra. If the instrument is to be used as a monitor for a wide range of compounds, the optimum temperature range appears to be 150-200°C. Second, the cell temperature can be set to optimize the response of selected compound classes. For example, the halocarbons showed greater spectral detail at higher temperatures than did the rest of the target compounds. If the GC/IMS is to be used as an in-situ monitor for halocarbons, the IMS cell temperature could be set at 225°C. Finally, the variations in behaviors with temperature might be useful as an added discriminator in GC/IMS applications. For

example, acetone and isopropanol have similar chromatographic retention indices on many GC columns. At lower IMS cell temperatures, isopropanol and acetone both exhibit drift tube equilibrium reactions, and their spectra have many similar features that might confuse pattern recognition software. At 175°, the spectrum of isopropanol begins to show distinct stable peaks, while acetone still shows drift tube reactions up to ca. 225°. Thus, the selection of cell temperature could be used to help discriminate between these two compounds.

Stability and Reproducibility of IMS

Graseby Analytical (United Kingdom), manufactures a portable IMS that is used by western military establishments for detection of chemical warfare agents. This IMS (abbreviated as AVM for airborne vapor monitor) was coupled to a GC to evaluate three parameters. The GC used was a Hewlett-Packard (Palo Alto, CA) 5730 equipped with a Supelco (Supelco Park, PA) SPB-5 30 meter capillary column. Nitrogen was used as the carrier gas, and makeup gas was air. The AVM operated in a water chemistry mode. The effect of concentration on mobility behavior was examined first to determine if IMS mobility patterns were significantly influenced by analyte concentration. The stability and reproducibility of the IMS response over an extended period was evaluated as well. These findings were then used to determine if it would be practical to use an essentially unaltered AVM as the IMS cell for a portable prototype GC-IMS. These findings were also used to isolate and identify those features of the AVM that could be modified to improve its performance as a GC detector.

The effect of concentration on mobility was studied by injecting a series of dilutions of each of the target compounds into the GC-AVM. Review of the data obtained led to several unanticipated findings. First, the AVM spectra of many of the positive mode compounds were very similar. The data obtained at 50°C using the TIMS did not show these similarities. As the concentration of the target analyte decreased, the similarities between the spectra generally increased. Product ions were often shoulders off the reactant ion peak as opposed to the separate product peaks usually observed using the TIMS. Finally, a clear linear relationship between peak height and concentration was not obtained over the concentration range studied. As a result, no definitive statement

regarding the effect of concentration on mobility was possible.

The reproducibility of AVM was evaluated over a 1 month period. Peak heights, drift times, and mobilities were monitored for positive and negative background spectra. The spectra of known amounts of positive and negative mode standard compounds (ethylbenzene and CCl_4, respectively) were also examined. The results of the study are shown in Table 2. The variability of intensity of the reactant and product ions showed drift over the 30 days, but reduced mobilities varied slightly. Any attempt at quantitation using only mobility spectra patterns and relative abundances would be difficult using the AVM as configured. Table 2 also shows that the larger ions exhibit more reproducible behavior, as shown by the decrease in relative standard deviations with decreases in mobility. This fact was exploited in neural network pattern identification studies which followed.

Evaluation of Neural Networks for Identification of Compounds

Neural networks have in the last 10 years become very popular for pattern recognition in many disciplines. A network consists of a series of interconnected nodes (called neurons or perceptrons) in which mathematical weighting, summation, and submission to a function are performed. The output of each neuron is then sent on to another neuron where a similar operation takes place. The network itself can consist of a variable number of neurons in a layer, and variable numbers of layers. The network is trained by submitting to it target vectors consisting of input and the target output desired. In this work, the factors included in the training vector were retention index and mobility peak data. The target output was the name of the compound possessing these GC-IMS characteristics. The network takes each training vector and adjusts the weights applied in each neuron to get the correct value output. The next training vector is submitted using the previously obtained weighting factors, and the resultant error is used to adjust the weights again. This repetitive process continues until the weights are adjusted so each training vector submitted to the network yields the correct output. Training sets may consist of hundreds of facts, and the training process itself may take hours. Once the network is trained, however, response is rapid. For this reason, neural networks are well suited for use in a portable instrument.

For this study, neural networks were used with both the TIMS data (150°C) and the AVM data. The training vectors consisted of retention indices, reduced mobilities, and in some cases, the percent relative abundance of the mobility peaks. Aspects of network structure, training, and failures were examined with both data sets. The network was unable to train on the AVM data for the alcohols. Many of the alcohol spectra were very similar, and the network was unable to distinguish between them even with the retention index included. The network was able to train successfully using the TIMS alcohol data. The difficulty with the AVM data may arise from operating the cell at ambient temperature and from using a membrane in the inlet.

A network was trained using data from all the positive mode compounds obtained at 150°C. Approximately 10% of the initial test data was set aside as a test set. The network was trained using the remaining 90% of the original data set. The trained network was able to identify ca. 95% of the test set. Failures were associated with similar compounds, i.e., within compound classes. A typical problem was differentiating ethylbenzene from the xylenes. This problem was successfully addressed by using the retention index of the test compound to determine the correct identification. For example, if the network yielded both ethylbenzene and o-xylene as potential identifications, the retention index of the test compound was compared to the retention index of the standard target compounds. In all cases of multiple identifications, this approach eliminated the false positives. In no instances were false identifications seen across compound classes, i.e., never was a ketone mistakenly identified as an alcohol when the retention index criteria was used.

CONCLUSIONS

The findings demonstrate that GC-IMS is a viable field monitoring technique, and holds promise of evolving into a genuinely portable and powerful field screening device. Elevated temperature cells, operating without membranes, will be required for such devices. Commercial portable IMS units such as the AVM cannot, as currently configured, be used as detectors for GC-IMS. While these devices work well for specialized applications, use of the AVM as a generalized detector is not possible without modifications. Neural networks can be successfully used to identify compounds when

chromatographic data is included in the training process and mobility data obtained at elevated temperatures is used. When the pattern recognition process fails to identify a compound, retention index can be used to obtain the correct identification. Neural networks are system specific. The network can not be trained using data obtained on different GC-IMS system. Aspects of the chromatographic and mobility behavior (via temperature) can be modified to suit specific applications or can be set to cover a broad range of target compounds. The small size and low power requirements of GC-IMS combined with the ability to tune the instruments to different applications gives GC-IMS an advantage over many other portable techniques.

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Table I. Listing of analytes studied using GC-IMS.

Positive Mode

ALCOHOLS
- Methanol
- Ethanol
- n-Propanol
- i-Propanol
- n-Butanol
- i-Butanol
- s-Butanol
- t-Butanol

AROMATICS
- Benzene
- Toluene
- Ethylbenzene
- o-Xylene
- m-Xylene
- p-Xylene
- Styrene

ESTERS
- Methyl Methanoate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Ethyl Methanoate
- Ethyl Ethanoate

KETONES
- Acetone
- 2-Butanone
- 3-Metyl-2-Butanone
- 2-Pentanone
- 3-Pentanone

ALDEHYDES
- Propanal
- Butanal
- 3-Methylbutanal
- Pentanal
- Hexanal

Negative Mode

HALOCARBONS
- Methylene Chloride
- Chloroform
- Carbon Tetrachloride
- Trichloroethene
- 1,1,1-Trichloroethane
- Tetrachloroethene
- 1,2-Dichloroethane
- 1,1,2,2-Tetrachloroethane

CHLORINATED AROMATICS
- Chlorobenzene
- o-Dichlorobenzene
- 2-Chlorotoluene

Table 2
AVM Reproducibility Study

Description	Mean*	Rel. Std. Dev. (%)
Reactant Ions		
Peak Height		
Positive Mode	6911	11.2
Negative Mode	2109	22.2
Reduced Mobility		
Positive Mode	1.87	2.01
Negative Mode	1.60	2.18
Product Ions**		
Peak Height		
Positive Mode	935	8.65
Positive Mode	679	8.22
Negative Mode	1687	8.77
Reduced Mobility		
Positive Mode	1.64	1.19
Positive Mode	1.39	0.98
Negative Mode	2.22	0.99

*: Mobilities reported in $cm^2\ V^{-1}\ s^{-1}$ and peak heights reported in millivolts.

**: Ethylbenzene had 2 product ions.

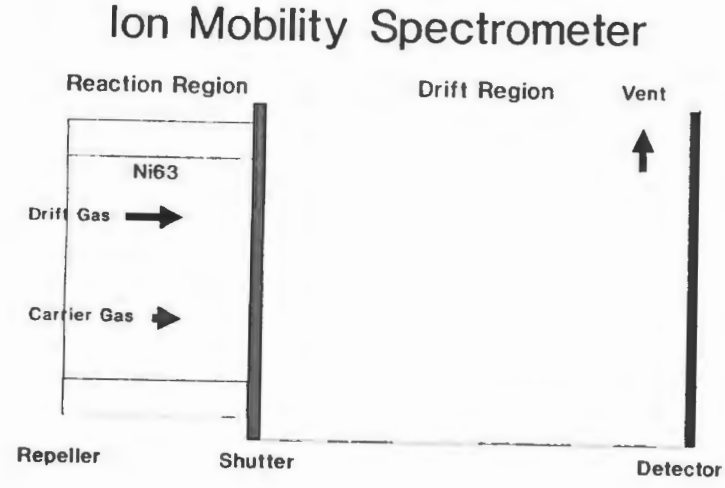

Figure 1. Schematic of ion mobility spectrometer

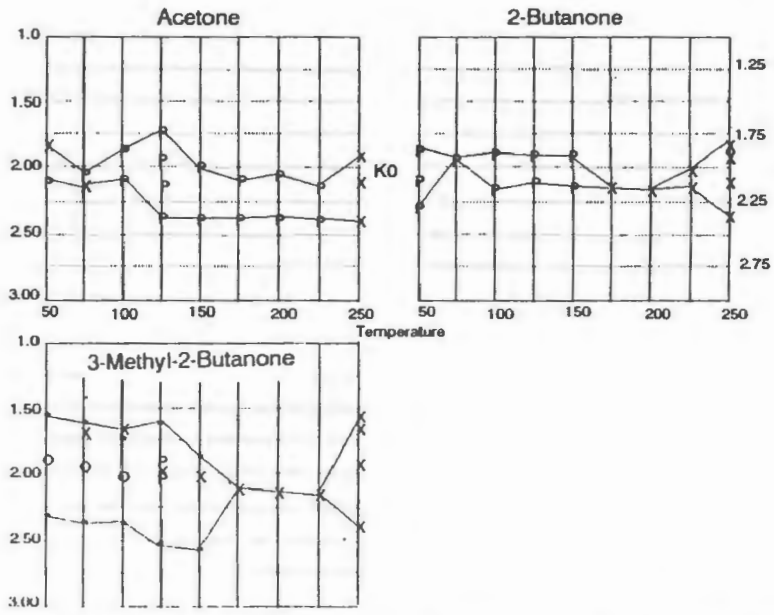

Figure 2. Behavior of selected ketones over the 9 temperatures studied. Legend for Figures 2 and 3: P: Peak that moved over the course of the elution. The P marks the extremes of the mobility. X: Distinct stable peak. *: Extremes of a drift tube reaction broadened peak. O: Approximate center of the peak associated with a drift tube reaction.

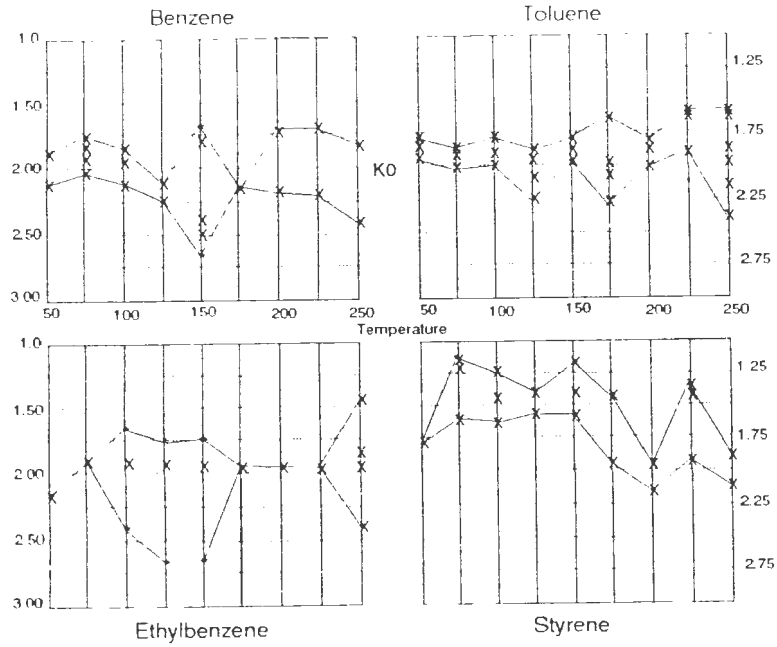

Figure 3. Behavior of selected aromatics over the 9 temperatures studied. See figure 2 for key.

DISCUSSION

COLLEEN PETULLO: Did you use the same IMS in the IMS-MS study or were several used?

SUZANNE BELL: The IMS-MS instrument was different than the heated instrument we used in New Mexico State. That's simply because we didn't have an IMS-MS available, so we simply used one that PCP was gracious to rent us for a week.

COLLEEN PETULLO: But you only used one in the study at any given time, right?

SUZANNE BELL: Right. The nine temperatures and 43 compounds were all run on one instrument. The IMS-MS was on another instrument, and then the GC/IMS was yet another instrument.

COLLEEN PETULLO: How long would it have taken you to train the neural networks if you would have programmed it for the 43 compounds?

SUZANNE BELL: I would assume it would take eight to ten hours, at the worst. The training time gets longer as you get more and more similar data. If we gave it, for example, 25 examples of benzene spectra over a wide concentration range, that would let the network generalize but you pay the price in training time. It could take hours or weeks to train the computer.

COLLEEN PETULLO: You had mentioned that you didn't do this because of time constraints.

SUZANNE BELL: Right.

COLLEEN PETULLO: How many did you ultimately program?

SUZANNE BELL: We ultimately trained 23 in the combined data set. This was about half.

Remote and In Situ Sensing of Hazardous Materials by Infared Laser Absorption, Ion Mobility Spectrometry and Fluorescence

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ABSTRACT

Three instruments will be described that were developed at the Technical University of Budapest for the sensing of hazardous materials. A remote sensing infrared differential absorption lidar based on the coherent detection of backscattered CO_2 laser light has been built. The lidar can be used for the detection of a wide range of molecular pollutants in the atmosphere from ranges of a few kilometers along a path to a topographic target. Results of field measurements to detect molecular pollutant clouds from km ranges will be presented. The experiments were carried out on NH_3 and DDVP but detection of more than 80 air-polluting components such as Freons, SO_2, etc. is also potentially possible. In addition, an ion mobility spectrometer will be discussed which has been developed for in situ measurements of impurities in air. The impurities are identified with the help of a dynamic dual-grid cell. Upon evaluation of the frequency-ion current spectrum, the detection of several impurities (e.g., NH_3, DDVP, HF etc.) was demonstrated. The instrument can operate either in a stand alone or a remote controlled mode and can be connected to a central computer. A fluorescence detector for the detection of surface contamination will also be discussed. Based on chemical indicator reactions, UV excitation and fluorescence detection via fiber optics, a mobile instrument for detection of pesticide contamination and control of decontamination has been built. Reliability detection of concentrations of 0.1 mg/cm^2 for DDVP was achieved with a measurement time of less than 5 sec. Applications of the instruments and methods will also be discussed.

INTRODUCTION

Sensing hazardous materials is a task that should be approached using techniques that are appropriate not only for the materials to be detected but also for the measurements required. A variety of sensing techniques are available to accomplish this end. In this presentation, three different methods and instruments that have been developed at the Technical University of Budapest will be described. As will be noted, these instruments are applicable for different specific purposes. The sensing techniques that will be discussed are as follows:

- A remote sensing lidar to measure pollutant clouds in the atmosphere from km ranges;
- An ion mobility spectrometer for in situ measurement of air samples; and
- An UV fluorescence detector to measure surface contamination without direct surface contact.

REMOTE SENSING LIDAR

Lidars are laser radars sensing backscattered laser light from long ranges making use of the special characteristics of laser light. Differential absorption lidars measure light intensities at two wavelengths corresponding to absorption maxima and minima of the absorbing atmospheric component along the beam path. Due to their broad tunability range in the infrared region around the 10 μm wavelength where several molecular pollutants have characteristic absorption spectra, systems based on CO_2 laser sources are of major importance [1]. In the group of more than 80 detectable pollutants, some of the more important ones are: NH_3, C_2H_4, O_3, SO_2, SF_6, C_2H_3Cl, as well as pesticides such as DDVP (2,2 dichlorovinyl dimethyl phosphate).

Two major problems associated with this technique were eliminating the disturbances due to the open path and keeping the system compact and transportable. These problems were solved by the development of the system, the optical part of which is shown schematically in Fig. 1. Electronic separation of the signals at the two wavelengths allow the measurements to be simultaneous and coincident, thus avoiding, for example, problems due to turbulence and differential backscattering. Using the internal amplification of the backscattered light by the lasers and heterodyne detection, make application of small CW lasers and a transmit-receive telescope of diameter 15 cm only possible. Topographic backscattering makes long path absorption measurement possible. The system used in the field tests is shown in Fig. 2 and the results of a field test using stationary topographic backscattering from 500m range with an artificial cloud of NH_3 is shown in Fig. 3. It is the time dependence of the differential absorption signal

$$E(t) = \ln \frac{I(\lambda_2,t)}{I(\lambda_1,t)}$$

that is displayed where $I(\lambda_{1,2},t)$ are the normalized detected light intensities at the two wavelengths at time t. The column content along the beam path cL (molecular concentration c times the path length L) is given by

$$c\,L = \frac{1}{\Delta\sigma} E$$

where $\Delta\sigma$ is the absorption cross section difference of the molecule for the two wavelengths.

The temporal variations of E in Fig. 3 are due to the concentration changes in the cloud blown across the beam path. The time resolution is 1 sec. Due to the atmospheric window around $\lambda = 10\,\mu m$, the reference range of the system is about 3 km (material dependent) and is not significantly influenced by the visibility conditions.

The measurement wavelengths and sensitivities for some specific molecules are as follows:

	λ_1 µm	λ_2 µm	$(cL)_{min}$ (ppb)(km)	$(cL)_{min}$ $(mg/m^3)(km)$
NH_3	10.33	10.32	8	8.6×10^{-3}
C_2H_4	10.53	10.59	8	9×10^{-3}
O_3	9.49	9.59	22	4.2×10^{-2}
SO_2	9.02	9.02	710	1.7×10^{-2}
SF_6	10.51	10.50	1.5	9×10^{-3}
C_2H_3Cl	10.61	10.50	34	8.4×10^{-2}

This system can be used in a stationary mode when with a scanning attachment it can monitor either large area (~30 km^2) pollution distribution (immission), or emission from certain selected sources. When coverage of a larger area is necessary, it can be used from a flying platform as well.

ION MOBILITY SPECTROMETRY

A simple and cost-effective technique for the in situ detection of air pollutants is through the use of ion mobility spectrometry. Here the air sample is ionized by a radioactive source in a chamber and the ions produced are moved by the use of an electric field. The arrival time and current of the ions characterize the products and their concentration. However, as the predominant charge carriers in the chamber are ion clusters consisting of fragments of water, Nitrogen as well as the molecule to be detected (e.g., NH_3, HF, CH_3COH_3, $C_2H_5OC_2H_5$, HCN, different pesticides), the selectivity of the system requires the application of sophisticated hardware and software solutions. [2].

The structure of the chamber is shown in Fig. 4. Ambient air is drawn in across a semi-permeable membrane allowing a portion of its component gases and vapors to be introduced to relatively dry air in the ionizing region. An alternating voltage with frequencies sweeping from 0-30 kHz is connected to a dual grid of transversal venetian blind type in front of the collecting electrode. Recombination on the grid is dependent on the mobility of the ions; therefore, evaluation of the ion current as a function of grid frequency improves the selectivity of the system. In Fig. 5. ion currents are shown as a function of grid frequency for clean air and air with NH_3. Automatic evaluation of these curves are carried out by a microprocessor taking derivatives of the ion current curve at five characteristic frequencies that correspond to f=OHz, $f(I_{min})$, $f\left(I = \frac{I(f=0)}{2}\right)$, $f\left(\frac{dI}{df} = 0\right)$ and $f = f_{max} = 30$ kHz. With the help of an algorithm, these values are compared with sets of stored data that had been determined empirically.

Many materials can be monitored in the low ppm region. The system shown in Fig. 6 can be used in a network through a RS232 line that is also supported by its low mass and power consumption (2kg, 1W).

SURFACE CONTAMINATION DETECTOR

Determining the contamination of surfaces of ground areas as well as equipment and personnel and the verification of the effectiveness of decontamination from hazardous materials are important considerations in assessing the extent of

residual chemical activity such as in the application of pesticides or in setting clean up goals for site remediation.

With the technique described here, the monitoring is based on the fluorescence analysis of chemical compounds produced in a reaction where a non-fluorescent compound, indole in an alkaline peroxidase solution is oxidized by the agent to be detected to give highly fluorescence indoxyl [3].

To detect trace impurities, fluorescence techniques show an inherent advantage compared to methods based on absorption. Namely while the extinction shows a logarithmic dependence on light intensity given by

$$E = \sigma c L = \ln \frac{I_0}{I_0 - I_a} ,$$

the fluorescent light intensity F exhibits an approximately linear relationship given by

$$F = Q_F I_a = Q_F I_0 (1 - e^{-\sigma c L}) \cong Q_F I_0 \sigma c L ,$$

where I_0 is the incident light intensity, I_a the absorbed light intensity, and Q_F is the quantum efficiency of the fluorescence. Therefore, with fluorescence the sensitivity can be improved by increasing the exciting light intensity I_0. Also surface contamination often appears in thin, sometimes discontinuous layers or droplets where the additional selectivity provided by the wavelength discrimination of the fluorescent light from the backscattered light can be exploited.

In the chemical reaction described above, the material to be detected plays the role of the catalyst; therefore, the quantity of the fluorescent material can be controlled to a certain extent by the amount of reagent added.

The advantages of this method compared with those requiring probe sampling are, that this method operates without physical contact, is not influenced by the surface type, and is highly selective. The application of this method consists of the following steps:

- spraying the contaminated area,
- illuminating it with UV light, and
- detection of the frequency shifted fluorescent light and evaluating the detector signal.

This system (shown in Fig. 7) consists of the following three units:

- a spray unit to store and pump the chemical reagents;
- an optoelectronic unit housing the Mercury vapor light source, the photomultiplier detector, the spectral filters matched to the compound to be detected and the electronics using lock in detection; and
- a sensor head unit (containing optical elements and controls) connected with 3 m long hoses, cables and fiber optic bundles to the other units.

Experiments carried out with DDVP and a reagent containing $NaBO_3$ and indol in water solution showed that the response time was less than 5 sec after spraying and the detection limit was at 100 $\mu g/cm^2$. Time duration of the fluorescence can be adjusted by proper selection of concentration of the reagents. This system can be used either in a stationary mode or on a moving vehicle to monitor large ground surfaces.

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3. Diehl W., Proc. 2nd Int. Symp. Protection Chemical Agents, Stockholm, Sweden, 173 (1986)

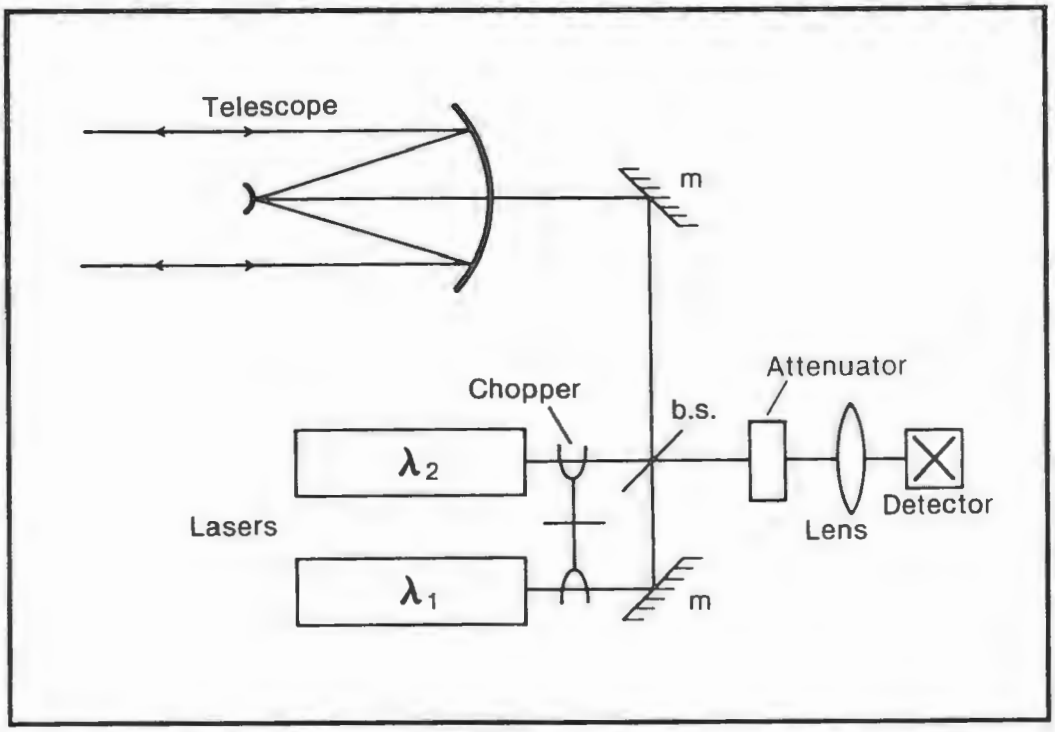

Figure 1. Arrangement of the differential absorption lidar.

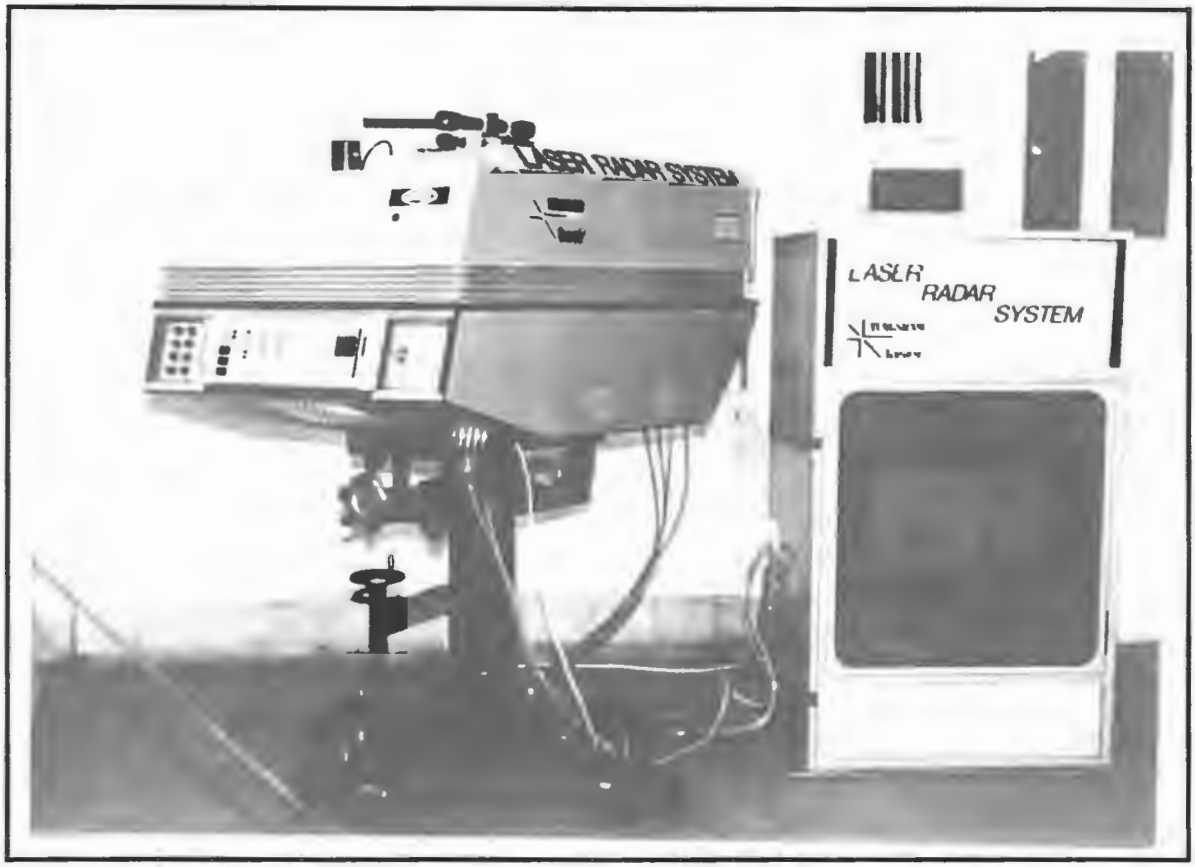

Figure 2. The lidar system.

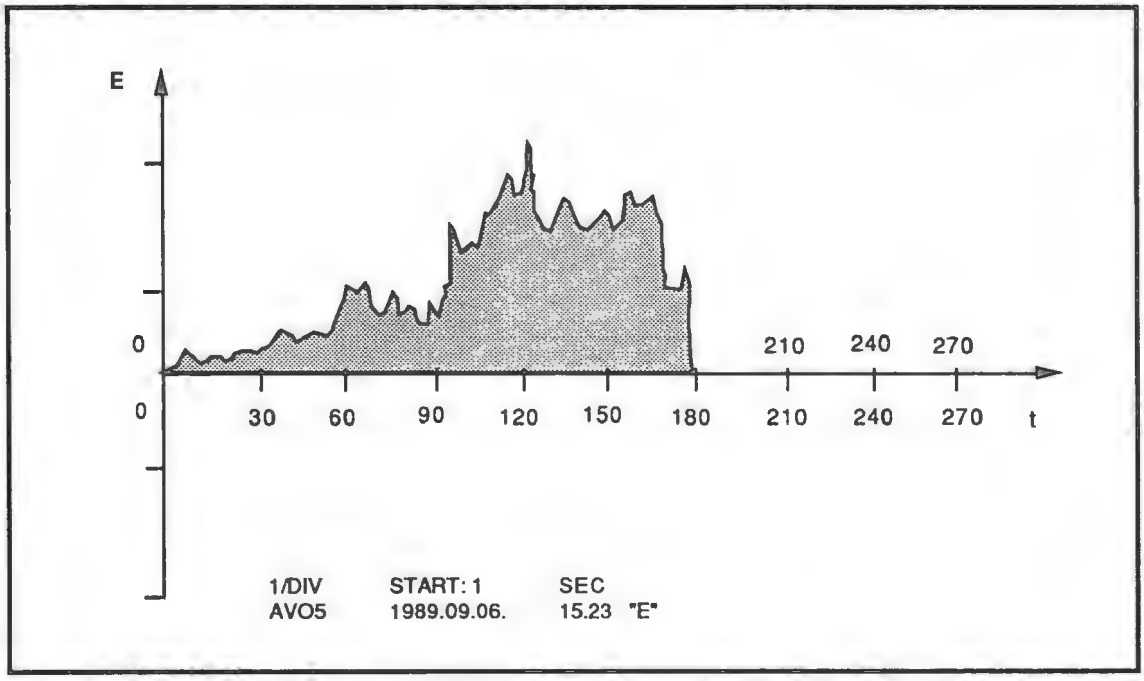

Figure 3. Time evolution of differential absorption signal for an artificial NH_3 cloud.

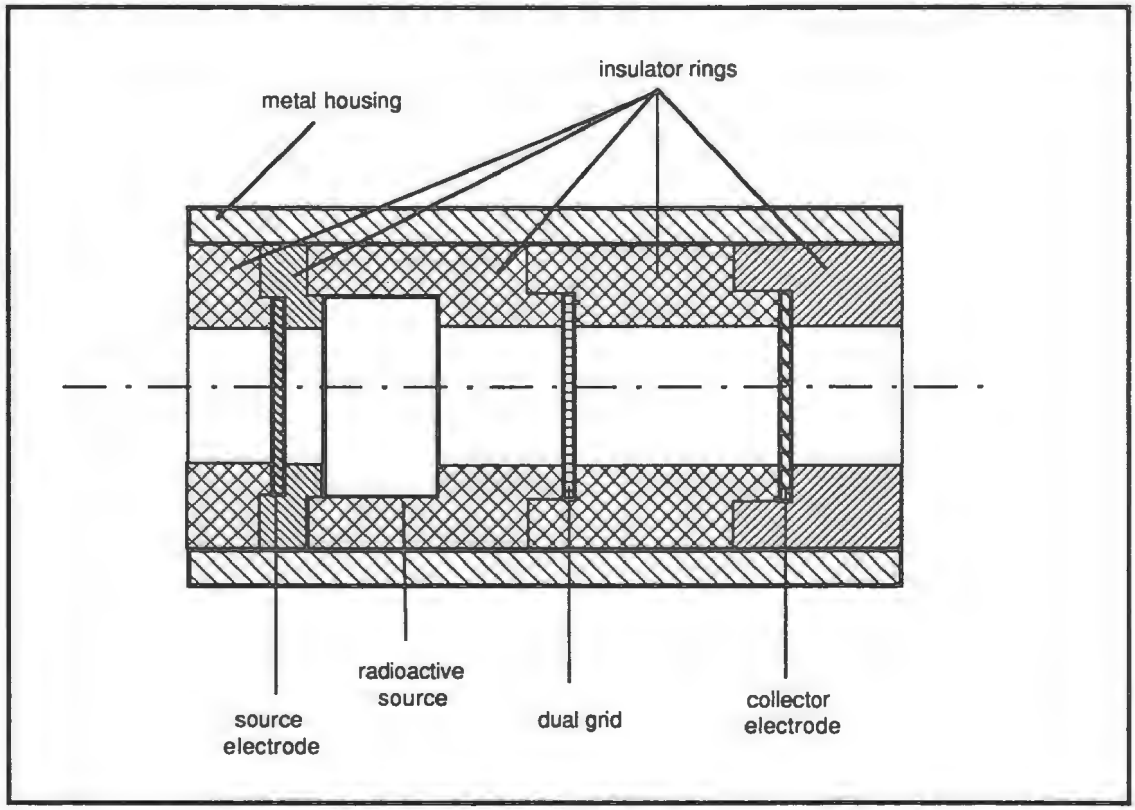

Figure 4. Structure of the ion mobility spectrometer chamber.

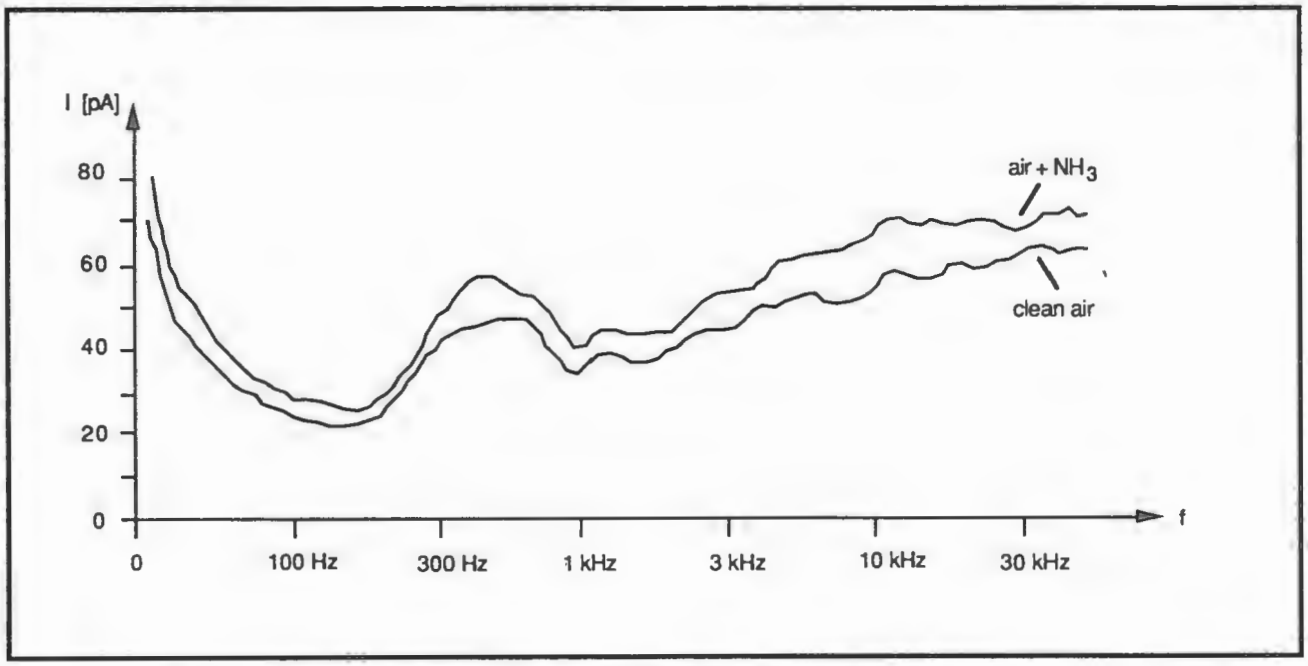

Figure 5. Dependence of ion current on grid frequency for clean air and air with 0.2 ppm NH_3.

Figure 6. The ion mobility spectrometer sensor.

Figure 7. The surface contamination fluorescence detector.

THE DEPARTMENT OF ENERGY'S ROBOTICS TECHNOLOGY DEVELOPMENT PROGRAM FOR ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT

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In August 1989, the new Office of Environmental Restoration and Waste Management (ER&WM) in the Department of Energy (DOE) published an ER&WM Five-Year Plan which established DOE's agenda and commitment to correct existing environmental problems, ensure compliance with applicable Federal, State, and local requirements, and effectively execute DOE's waste management programs. The plan includes a section covering the applied research and development needed to support the five-year plan. In November 1989, DOE issued a draft Applied Research, Development, Demonstration, Testing, and Evaluation (RDDT&E) Plan for ER&WM which expands on the applied research and development section of the five-year plan. The RDDT&E plan provides guidance to the new ER&WM Office of Technology Development (OTD) for its mission: "to manage and direct programs and activities to establish and maintain an aggressive national program for applied research and development to resolve major technical issues and rapidly advance beyond current technologies for environmental restoration and waste management operations." The development and application of robotics technology for the resolution of identified problem areas at DOE sites is a major element of the RDDT&E program plan.

The OTD has established a Robotics Technology Development Program (RTDP) to integrate robotics RDDT&E activities and to provide needs-oriented, timely, and economical robotics technology to support environmental and waste operations activities at DOE sites. DOE laboratories, private industry, and universities have existing robotics technology that provides a strong foundation for initiating an aggressive RDDT&E program to support ongoing and emerging ER&WM functions.

A major objective of the ER&WM Program's five-year RTDP is the application of robotic technology in the resolution of DOE's identified problem areas. The thrust of the application is to reduce exposure of personnel to hazardous substances and radiation while increasing productivity. An additional goal is to integrate all such activities to obtain the most economical approach to resolving site-related waste problems using robotic technology and to demonstrate robotic technologies that can be applied to major site-specific waste clean-up efforts.

The Robotics Five-Year Program Plan provides the focus and direction for the near-term (less than five years) and guidance for the long term (five to twenty

years) R&D efforts associated with resolution of site-specific waste problems. The goals include: (1) supporting the ER&WM Program and being responsive to the ER&WM Five-Year Plan, (2) focusing near-term robotic R&D efforts to be responsive to application requirements, (3) ensuring that robotic applications are responsive to site requirements and scheduler needs, (4) integrating all robotic activities to obtain the most economical approach to resolving site problems while reducing personnel exposure, and (5) providing guidance for the Office of Energy Research long-range (>5 year) robots research program.

Program Focus and Objectives

The Program currently addresses a number of important issues facing the ER&WM activities at the DOE sites. Among the areas included are:

- underground storage tanks (material characterization and remedial actions),
- buried waste retrieval,
- waste minimization,
- contaminant analysis, automation,
- decontamination and decommissioning,
- basic and applied research and development required to support the above areas.

The objectives of the Program are to develop, test, evaluate, and make available robotic technologies that:

- allow workers in waste operations and remediation to be removed from hazards,
- increase the speed and productivity with which ER&WM operations can be carried out when compared to alternative methods and technologies,
- increase the safety of ER&WM operations, and
- provide robotic and remote systems technologies that have lower life cycle costs than other methods and technologies.

In addition to developing robotics technology, the program promotes the availability of the technology and supports its deployment and use in ER&WM activities at DOE sites. The program further serves as a bridge between the ER&WM robotics RDDT&E and the basic robotics research carried out by DOE's Office of Energy Research, providing guidance for the basic research program and integrating its results in applied research and advanced development projects.

Program Organization

In order to execute the Program, the Program has been structured as shown in Fig. 1. Since the Program is an element of the DOE ER&WM Applied RDDT&E program, it is administered by the ER&WM OTD through the Program Manager (RPM).

To ensure that the Program responds to the needs of the DOE complex, RPM is assisted by an Operations Review Group (ORG). This group is familiar with the ER&WM issues facing the DOE complex. RPM also receives assistance from a Technical Review Group (TRG) of robotics and automation experts from the DOE laboratories and sites, universities, industry, and other federal agencies. A Program and Budget subcommittee of the TRG also assists the RPM.

The Robotics Applications Coordinators (RAC) develop robotics program plans focused on each of the major ER&WM issues.

The RAC is responsible for coordinating the flow of technical information relevant to the applications area among those groups having an interest in the area. RAC is also responsible for keeping the other groups in the relevant applications areas apprised of the results of RTDP

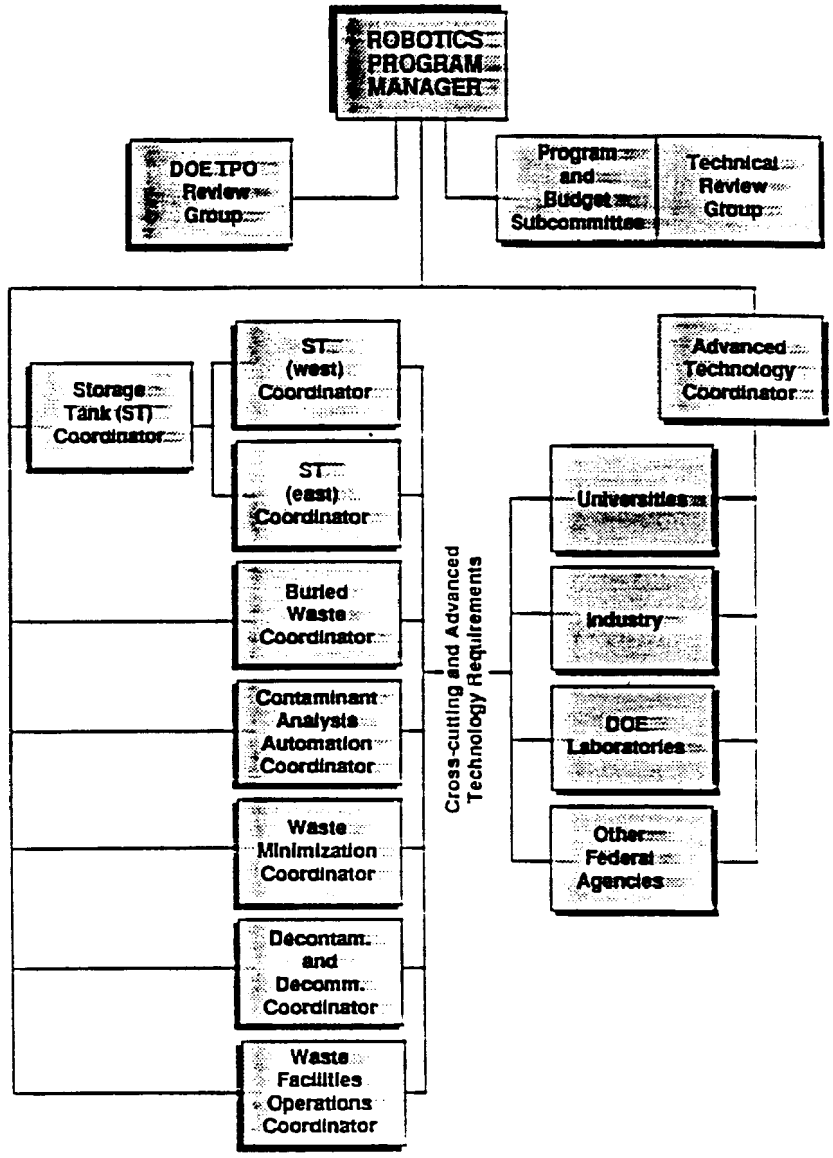

Figure 1 - RTDP Organization

funded activities. The coordinator, with the approval of the RPM also convenes occasional conferences on the applications area.

The coordinators function as the advocate for the technologies applicable to their particular problem area. To facilitate the application of the best technology with a high probability of success to the particular problem area, the coordinator actively solicits proposals from the entire robotics and automation community for routing to the RPM. A thorough familiarity with the ER&WM problems and issues is required of the coordinators. This familiarity will be maintained through site visits, personal contacts, and symposia where appropriate.

Applied research is funded through the applications center that has identified the technological need. This helps insure that the applied research is responsive to the needs of the group sponsoring the research. Coordinators who put together a team approach with industry, labs, universities, or other agencies are most favorably reviewed.

The R&D Coordinator (RDC) reports to the RPM and is responsible for coordinating the flow of technical information other than applied research. The RPM is familiar with all aspects of the RTDP and is able to identify areas of future need in robotics and ancillary systems which are not being addressed in the applied R&D areas. He is responsible for coordinating with universities, industry, DOE laboratories, and other federal agencies to bring proposals for need advanced technology to the TRG and RPM.

Program Planning

A comprehensive technical program plan has been developed during the first year of funding. This initial plan development is a significant effort since the plan is based on the needs of the environmental restoration and waste management operations as identified by the eight DOE field offices and the sites they administer. A major portion of the initial plan development is assessing and understanding those needs. The technical program plan covers a five-year period with primary emphasis on the one-year plan and secondary emphasis on the two- and three-year projections. The plan covers technical work, budget requirements, and schedules and is tied closely to the requirements and schedules of individual site environmental restoration and waste management projects.

FY 1990 Accomplishments: The RTDP accomplished a number of significant activities in FY 1990, which facilitated a fast start for robotics technology development and established a sound basis for program activities over the next five years.

Program Planning: Five priority DOE sites were visited in March 1990 to identify needs for robotics technology in environmental restoration and waste management operations. This 5-Year Program Plan for the RTDP was prepared on the basis of the needs identified at the DOE sites, and provides a needs-based road map for detailed annual plans for robotics technology development.

Initiating Interactions with the Robotics Technology Community: In July 1990, a forum was held announcing the robotics program. Over 60 organizations (industrial, university and federal laboratory) made presentations on their robotics capabilities.

Technology Demonstrations: To stimulate early interactions with the ER&WM activities at DOE sites, as well as with the robotics community, the RTDP sponsored four technology demonstrations related to ER&WM needs. These demonstrations integrate commercial technology with robotics technology developed by DOE in support of areas such as nuclear reactor maintenance and the civilian reactor waste program.

Rapid, swing-free movement of simulated waste containers was demonstrated using control algorithms developed at Sandia National Laboratories (SNL) with technology in computer control of large gantry bridges at Oak Ridge National Laboratory (ORNL). This technology decreases the time for materials movement and increases safety by eliminating the potential for collisions of swinging payloads.

A scaled waste tank remediation demonstration at SNL integrated sensors and advanced computer control into a commercial gantry robot. The extensive use of models for robot system control allowed graphical programming of the system complete with operator-supervised path planning to increase speed of repetitive waste removal tasks.

A teleoperated vehicle with advanced sensing technologies for mapping of buried waste sites was demonstrated at a small buried waste site at ORNL. Navigation technologies were coupled with the sensing information (from radiation, gas, and subsurface large object sensors) to automatically map subsurface materials.

A team consisting of LLNL, SNL, LANL, SAIC, and IBM demonstrated a robotic system for loading powder into a furnace in a Pu production line, and then transferring the product to the next operation in a mock up facility. This robotic system eliminates the need for operator hands-on transfer operations and reduces the generation of operator-associated waste materials such as wipes, protective clothing, gloves, and transfer bags.

SITE VISITS/NEEDS

In March 1990 RTDP planning teams visited five DOE sites. Additional site visits will be conducted in the future to expand the planning basis.

The purposes of these visits were (1) to understand the needs and requirements of the highest priority environmental restoration projects and waste management operations at the sites, (2) to obtain information for use in planning the program, and (3) to describe the RTDP to personnel at the site and discuss development of the program plan. Emphasis was placed on both technical and schedular (i.e., compliance dates) needs and requirements.

The results of these visits are documented in a Site Needs and Requirements Document. This document summarizes the findings at each site and highlights priority needs.

APPROACH TO NEEDS DIRECTED TECHNOLOGY DEVELOPMENT

The visits to five DOE sites led to selection of six areas of need for robotics technology to support ER&WM activities. These need areas are:

- Remediation of waste storage tanks,
- Retrieval of buried wastes,
- Automation of contaminant analyses,
- Waste minimization,
- Decontamination and decommissioning,
- Waste Facilities Operations

Plans for development and application of robotics technology are based on the need areas listed above. In addition, the plans reflect other aspects of needs at the sites such as regulatory compliance dates, planned remedial actions, and established schedules.

The fundamental approach to developing robotics technology to meet these needs couples available and emerging technology with advanced technology. Near-term needs can be met by integrating

available commercial technologies with emerging technologies available in R&D laboratories. At the same time, development of advanced technology will proceed to meet intermediate and long-term needs. In addition, attention will be given to development of cross-cutting technology which will be applicable to multiple need areas. Technology development will be keyed to integrated demonstrations at the DOE sites to further couple the robotics technology development to the site needs and to the deployment of remedial actions technology.

The DOE sites are evaluating alternative approaches to remedial actions. The robotics technology developed for each application must meet the needs, and match the approach selected by each site. The plans described for robotics technology development are based on reference concepts, selected as reasonable and likely concepts from the alternatives, which form the basis for identifying needed technology development, estimating schedules, and estimating budgets.

The robotics technology development plans are also keyed to demonstrations of technology at the DOE sites. Wherever possible, demonstration of the robotics technology is integrated with larger integrated remediation technology demonstrations.

CROSS-CUTTING AND ADVANCED TECHNOLOGY DEVELOPMENT

Near-term applications of robotics to ER&WM activities is necessarily focused on existing technologies that can be readily adapted to the specific cleanup tasks and environments. As the DOE cleanup activities progress and evolve, a larger body of robotic technology will be needed for application to ER&WM projects. A technology development program targeted at relevant cross-cutting and advanced technology development will make possible a more rapid insertion of beneficial technology into these activities. This technology development will be focused on high payback projects that offer safer, faster, or cheaper approaches to cleanup goals.

An advanced technology development program including a long term research and development component is a means to effectively incorporate the expertise of the universities, national laboratories and other basic research organizations into the nation's cleanup projects. Also, this offers educational training opportunities consistent with the DOE emphasis on developing the next generation technical work force.

Needs identified at DOE sites indicate that cross-cutting and/or advanced technology development in the areas listed below would be highly beneficial to application of robotics in ER&WM activities.

Mechanical Subsystems
- Manipulators
- End-Effectors
- Mobile Systems

Control Subsystems
- Computing, Graphics and Modeling
- Man-Machine Interfaces
- Communications
- Telerobotic Operations
- Motion Planning and Control

Sensor Subsystems
- Environmental Sensors
- Servo Mechanical Control Sensors
- Imaging & Vision Systems
- Multi-Sensor Integration

Cross-cutting and advanced technology developments need to focus on near-term, mid-term, and long-term implementations. By investing in a sustained long-term development program, emphasizing a balanced evolution in technology development with implementations continually encompassing technology advances, steady progress may be assured toward the technology required for the more complicated or demanding tasks of the decades to come. Development of advanced robotics technology that is commonly applicable to many environmental restoration, waste

management, and waste minimization activities can lead to higher efficiency, increased reliability, and reduced life cycle costs in these operations.

Participants in this program are the following whom we wish to thank for their contribution.

SAIC - Science Applications International Corporation
LANL - Los Alamos National Laboratory
SNL - Sandia National Laboratories
LLNL - Lawrence Livermore National Laboratory
ORNL - Oak Ridge National Laboratory
Y-12 - Oak Ridge Y-12 Plant
RF - Rocky Flats Plant/EG&G Rocky Flats
SR - Westinghouse Savannah River Company
WHC - Westinghouse Hanford Company
PNL - Pacific Northwest Laboratory
EG&G - EG&G Idaho
INEL - Idaho National Engineering Laboratory
WMC - Westinghouse Materials Company of Ohio
WINCO- Westinghouse Idaho Nuclear Company, Inc.
Fernald Feed Materials production Center

Field Robots for Waste Characterization and Remediation

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Abstract

Field operations for waste characterization and remediation offer real opportunities and compelling motivations for advanced robot work systems. The application of field robotic technology can enhance the quality of data collected at waste sites through standardization, verification, and repeatability of methodology. It can increase the coherence of data by enabling dense data collection, advanced correlational databasing, and the collection of previously unavailable data, such as position tagged data or interpretable 3D subsurface images. Field robots can operate were humans are precluded, in pipes, tanks, abandoned mines, and sea and river bottoms or where humans perform inefficiently in protective clothing and breathing apparatus. Thus, field robots can greatly increase the knowledge base gained during site investigations; this knowledge will expand remediation options performed by human and open the way for the use of field robots in remediation activities. Moreover, the development and use of field robotic technologies in the service of national efforts to characterize and remediate nuclear and hazardous waste will eventually have profound effects on large commercial industries and open new world markets for robotic technologies.

Introduction

Hazard has been the historical justification for the use of field robots; operations surrounding accidents at Chernobyl and Three Mile Island have world impact, preclude humans and call field robots to action. Less reactive than these crises are the innumerable nuclear, deep sea, military, and space operations that are inhospitable to humans and are significant both strategically and fiscally. The ultimate opportunities, however, for field automation are those immense and inefficient industries like construction, mining, timbering, hazardous waste management, subsea and outer space that dwarf the economics of manufacturing. Characterization and cleanup of the nation's weaponry complex alone is now estimated at 100 billion dollars: efforts of this magnitude require new technologies. As a growing technology, the potential of field robots to apply sensing and analytical capabilities and to perform precise, repetitive, and dangerous tasks is virtually untapped in the world.

Field robots work in environments as they are encountered, not idealized or altered to accommodate automation. While an assembly process can be structured into a limited number of predictable actions, a robot working in an unstructured environment encounters new situations that it has not been explicitly programmed to deal with.

Field robots are thus challenged to perform goal-driven tasks that defy pre-planning in unpredictable and changing environments. In order to explore, work, and safeguard themselves and the environment, field robots must sense complex phenomena in a dynamic world. As these robots move towards autonomy, they must plan and implement their work tasks.

Robots are quickly becoming mobile in natural terrains, perceptive, self-navigating, and competent in the field. Within the next few years, a number of robotic performance niches in waste characterization and remediation will be exploited where humans are precluded from the scene or where robots offer superior capabilities. Areas of opportunity include reconnaissance, surveying, subsurface imaging, soil gas sampling, perimeter monitoring, fast analytical screening, accident response, remote sampling and manipulation, remote coring, and excavation.

Automated Characterization

Perhaps the most frustrating aspect of waste characterization is the paucity of reliable data that scientists and engineers have to work with following an investigation. Field sampling is expensive, time consuming, and labor intensive. Although methodologies are standardized, human judgement and sometimes intuition are broadly applied when deciding where to sample or survey and how to interpret data once collected. This is particularly true for the selection of boreholes, the interpretation of geophysical data, and the selection of soil and soil gas sampling points. Analytical instruments and techniques have improved greatly over the past several years, but the results are only as good as the choice of sampling points, which often are too few and chosen poorly.

Field robots can deploy screening instruments far more rigorously, sampling hundreds or thousands of times per acre, achieving total site coverage. They can create a three-dimensional data base by analyzing air, soil gas, and the subsurface: they can screen organics on the fly and create 3D images of buried waste from radar data, sampling at centimeter resolution. Field robots can survey a site and layout a precise grid; take samples, position tag, package, and label them; position tag instrument data, store the data in a single spatially correlated data base, and present multiple types of data to users in a straightforward visual format.

Quality of Data

Capable field robots can greatly increase the quality of data from a waste site by obtaining verifiable data with a high degree of repeatability, and they can advance the process of data collection to a higher standard than is possible using present methodologies. Ultimately, field robots can also help ensure that the right samples are sent to analytical laboratories.

Standardized Data

Most waste sites have long lives; the time from preliminary assessment to the remedial action can stretch into years, and monitoring can take place for decades after. Throughout the life of a site, scores of scientists, engineers, technicians, and workman perform tasks, and as a site transitions from assessment to investigation to remediation, the cast of actors changes.

Although methodologies are standardized, no two investigations at a site are performed in exactly the same way; indeed, no two investigators can be relied upon to bring the same experience, judgement, and skill to a site or to collect data in exactly the same way, thus making it difficult to achieve standardization.

Moreover, because waste sites vary greatly in topography, soil types, geology, and the nature of contaminants, it is difficult to achieve standardization across a range of sites, partly because humans perceive the sites differently.

The use of field robots to collect and screen data can significantly improve standardization. Robots can be relied upon to treat data in the same way in each investigation. Robots eliminate human variables and collect far greater quantities of data. The data thus become more reliable, and data from different sites can be compared legitimately. Ultimately, a single, complete data base can follow a site for its entire life. Created during the preliminary assessment, a three-dimensional computer data base can be an interactive repository in which each new set of data is entered.

Verifiable and Repeatable Data

Field robots can verify data taken previously at a site and repeat the collection and screening process precisely. Because robots process and store data at the time of collection, the chain of custody can be maintained more reliably and securely. Repeatable outcomes translate into defensible conclusions and reduce uncertainly when

planning remedial actions and issuing a record of decision. Field robots can become an important tool in the process.

Relevant Data

Two ways to increase the relevance of data are to collect it in quantities great enough to yield high statistical reliability and collect several types of data at the same time. Field robots can build dense data bases. They are also capable of deploying a range of sensors that humans cannot; e.g., three-dimensional laser rangefinders, infrared sensors, sonar, radar, etc. In addition, they can deploy analytical instruments simultaneously and determine their position accurately in global coordinates.

The site investigation robot (SIR) under development at Carnegie Mellon's Field Robotics Center collects ground penetrating radar data (GPR) at two centimeter intervals, accumulating in excess of a 400,000 data points per acre. GPR data are inherently three-dimensional and can be processed into 3D images, if the data are dense enough. A human cannot attain the positioning accuracy or deploy the sensor with enough precision to collect dense data, as a robot can. The result is not just more data but new and better data. Further, the robot can be configured to collect additional types of data or samples simultaneously, e.g., organics in air or soil.

Interpretable, Usable Data

Investigators are often confronted with data that do not easily yield to interpretation or, at worst, require the investigator to make a guess as to what the data show. Field robots can process data, making it easier to visualize and understand.

CMU's Site Investigation Robot provides a visual image that is not only quantitatively better but qualitatively better than standard GPR data bases. The user is provided with an image defined accurately in x, y, and z, making the data more interpretable, even to a novice.

Data bases become more usable when one is able to see correlations among data in new ways. The availability of multiple types of data superimposed on a computer-generated site map will enable investigations to gain a whole site profile in a single visual image. This kind of user power will not only speed the investigation process but give entirely new insights to investigators.

Accessible Data

Finally, when data are accessible to many people over time, the likelihood of good use being made of the data increases significantly. Data collected by field robots can be stored on central file servers, available to all who need to determine what is known about a site or who have new data to add to the file.

When Humans Are Precluded

Some investigations and remedial activities preclude physical human access, such as the interiors of pipes, tanks, and ducts; abandoned mines; and river, harbor, and sea bottoms. Field robotic technologies offer the best access to collect data and to perform remedial activities.

Generations of competent pipe crawlers have been developed and are in service in petroleum and natural gas industries. In-tank inspection robots and remediation robots are needed at DOE complexes. One such robot is being developed by RedZone Robotics to inspect tanks containing nuclear waste. At CMU's Field Robotics Center, we are developing autonomous navigation and vision systems for underground mining equipment and autonomous navigation systems for walking machines and wheeled vehicles to traverse rough terrain. Others have significant experience with competent sub-sea robots and have demonstrated their capabilities and utility.

Another class of sites precludes humans because of health and safety concerns, e.g., high-level waste, mixed waste, transuranics, unbreathable atmospheres, unknown waste, and accident response. These sites present high-motivations for robots to perform not only reconnaissance and sampling activities but forceful manipulation and heavy work to a high degree of precision. These activities include excavation, loading, haulage, and packaging of diffuse materials; removal of sludges and mixing of materials; removal of debris; barrel handling; boring on gassy landfills, and the handling of explosive materials or operations in explosive environments.

Field Robotic technologies have now progressed to the point where the robotics community can begin to build competent, rugged, and reliable systems to meet the performance needs of waste characterization and remediation programs.

Integrated Characterization and Remediation Systems

Robotic technologies can fulfill the need to better integrate characterization and remediation systems. An excellent example of this is the case of trenched transuranic wastes. Conditions preclude most invasive means of characterizing the volume and position of the waste, and having a human onboard of an excavator is precluded during the remediation.

The work can, however, be performed by robots in a coordinated sequence. A site investigation robot (SIR), using ground penetrating radar, can produce measurements of buried waste in x an y to a reasonable accuracy (7 to 14 inches), which would allow a robotic excavator to trench on both side of the waste to install steel sheeting. The excavator would have the SIR's position data and subsurface map available to it to guide it through the digging process, along with active sensing of its own.

The SIR also surveys the z axis, determining the depth of the waste and the distance from the soil surface to the waste. Through a sequence of iterative sensing and excavation, the clean overburden could be removed, leaving 4 inches of soil covering the waste. The excavator could then remove the waste autonomously.

In this scenario, robots working together can perform the tasks more efficiently and with greater accuracy than human operators. Five years ago sensing and control in both robots to the degree of accuracy described above would have been wishful thinking; two years ago it was beyond the reach of the technology; today it is within reach, and although it is not yet ideal for selectively finding and excavating, deeply buried hot spots, it is likely the safest, most cost effective approach to retrieving radioactive, trenched wastes that can be expected in the next several years.

Future Opportunities

Commercial applications for capable field robots will number in the hundreds. Among them are significant field robotic applications that are achievable in the near term with evolutionary extensions to our current technology base. Moreover, there are significant opportunities, some of which are unique to the U.S., e.g., robotic timbering, surface mining, and large-scale agriculture.

Federal agencies should not miss opportunities to develop and apply robotic technologies in programs where they have a legitimate interest and obligation to protect human health, increase productivity, and decrease costs. Because robotic technologies are extensible to many applications, there should be a coordinated effort by Federal agencies to 1) focus performance-based research to move the technologies forward; 2) apply the technologies in Federal programs where they will produce high-leverage results, sufficient to pay for the investment; and 3) ensure that programs will be sufficiently stable over time to attract world-class researchers to the field.

There is an opportunity to reduce significantly the total cleanup costs of chemical and nuclear waste sites through the programmatic development of robots to perform site investigation, data collection, and remedial activities. The core technologies have reached a stage of development to begin the task of putting together integrated, teleoperated and semi-autonomous systems for this purpose. The opportunity is to alleviate a major national problem and, at the same time, to develop and apply new technologies that will impact the world.

DISCUSSION

BRIAN PETERS: You mentioned American leadership. What about the position of the Japanese in this area? They're well known for corporation robotics on automobile assembly lines, for example.

WILLIAM WHITTAKER: The Japanese are a significant force in this arena. Particularly, they have programs that have matured, driven in a strategic way, top down, over several years, and they look very good. They look extremely good in construction. They have lesser presence in subsurface and in space. Consider, if you will, that we enjoy a 20- or 30- year history in space, and they're just building their first rockets. But to bring it to terms here, I look for the United States to drive this agenda because we are the ones who pioneered some of the nuclear technologies, and we are the ones that have the volumes and the programs to go after this.

For instance, if you looked at the navigation technologies, there aren't a lot of places in Japan that have enough roads to drive something like that. And so if you look at the agenda in the program, I think that is enough to really focus operations here. I actually have a video tape of condensed Japanese technology that I just put together this week. After this session I'll be happy to show that.

GREGG DEMPSEY: On your remote vehicles that stand completely alone, (they run on telemetry or whatever) is the technology such that if there's an accident out on a site or something, and you lose communication, can the machine actually turn itself around and come back?

WILLIAM WHITTAKER: Yes, that technology is available. However, I think it's important to know that it's in very select pockets of seasoned research groups, and very select pockets of small organizations that can move fast to put it together. Specifically, that kind of technology source is from the DOD Strategic Computing Initiatives and DARPA's Road Following Programs, which were funded at the hundred million dollar level over a number of years, going back three or four years.

GREGG DEMPSEY: I remember when the robots went into Three-Mile Island there were problems with the camera lenses darkening up because of the radiation exposure. Has that problem been solved to any great extent?

WILLIAM WHITTAKER: In the first deployment in November of 1984, it's true that the cameras didn't function well. And that's because we were using a CCD technology. It was small, and it was very new! But within a month that was straightened up. And with the years that have gone by, particularly out of military and space initiatives, rad hardened CCD's are a known technology. It's very straightforward now.

GREGG DEMPSEY: So we have technology that can operate in the thousands of roentgens per hour now?

WILLIAM WHITTAKER: Yes.

SPACE TECHNOLOGY FOR APPLICATION TO TERRESTRIAL HAZARDOUS MATERIALS ANALYSIS AND ACQUISITION

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ABSTRACT

In-situ and remote measurements of elemental, molecular and mineralogical composition of materials has been part of the space science program since its beginnings. There is a great deal of commonality between space science missions and terrestrial hazardous materials screening in the types of measurements, methods and instrumentation used. There are also strong parallels between the hostile environments of space and those of a hazardous material site.

This paper discusses the measurements, methods and instrumentation used on past, present and future space missions for in-situ and remote analysis of materials. Specific instrumentation discussed includes gas chromatographs, mass spectrometers, imaging spectrometers, X-ray and gamma-ray spectrometers. Work sponsored by the National Aeronautics and Space Administration's Sample Acquisition, Analysis and Preservation technology program is discussed, including concepts and hardware for multi-spectral remote sensing, instrument data analysis and interpretation, material acquisition and processing. Some new concepts for micro sensors for making various chemical measurements are also discussed. Possible applications of space technology to terrestrial hazardous materials field acquisition and analysis are presented.

INTRODUCTION

In-situ and remote measurements of elemental, molecular and mineralogical composition of materials has been part of the space science program since its beginnings. Two of the best known surface science missions were the Viking mission to the surface of Mars and the Soviet Venera series to Venus. The Galileo spacecraft is carrying a probe to sample Jupiter's atmosphere and the National Aeronautics and Space Administration (NASA) has just started a project to make a variety of in-situ measurements of the comet Kopff. NASA is currently working on technology to enable robotic and human missions to the Moon and Mars. Such missions will include a wide variety of in-situ and remote science and engineering measurements. There is a great deal of commonality between space science missions and terrestrial hazardous materials screening in the types of measurements, methods and instrumentation used as well as in the hostile nature of the environment in which these measurements are made. NASA is very active in the design, development and utilization of the instruments. Table 1 contains a listing of some science data requirements and associated instrument(s) that are used and/or under development within NASA for its past, present and future missions.

NASA has established a technology program called Sample Acquisition, Analysis and Preservation (SAAP) to address the specific needs of in-situ science and engineering measurements. SAAP is intended to develop critical and significantly enhancing technologies for remote identification, acquisition, processing, analysis and preservation of materials for in-situ science, engineering characterization and earth return. Although the technology being developed in the SAAP program is not currently being applied to specific missions, the SAAP program will broaden the base of technology available for future missions. Specifically, SAAP is developing concepts and hardware for multi-spectral remote sensing, instrument data analysis and interpretation, material acquisition and containment [1,2,3,4]. Some new concepts for microsensors for making various chemical measurements are also under development. There are many possible applications of space technology to terrestrial hazardous materials field acquisition and analysis.

SPACE INSTRUMENTS, MEASUREMENTS AND APPLICATIONS

There is very high scientific value to direct surface measurements, independent of whether a sample is returned to a laboratory. In particular, the analysis of volatiles is probably best done in-situ due to the potential for loss or chemical change after prolonged storage. For space applications, in-situ measurements may be a necessity because of the limitations on sample return.

Table 1. SCIENCE DATA REQUIREMENTS vs INSTRUMENT TYPES	
Required Data	Example Instruments
Elemental Composition	Gamma-ray Spectrometer, a-p-x Spectrometer XRF, a-Backscatter
Mineralogical Composition	Visible-Infrared Spectrometer Mossbauer Spectrometer, DSC, XRD
Water Detection and Mapping	Neutron Spectrometer, Electromagnetic Sounder
Atmospheric Composition	GCMS, Laser Spectrometer
Subsurface Structure	Electromagnetic Sounder, Active Seismometer
Seismometry	Passive Seismometer
Volatiles	DSC-EGA, Visible-Infrared Spectrometer
Imaging	Camera, Imaging Sectrometer
Exobiology	Viking Biology Instrument
Magnetic Fields	Magnetometer

Although terrestrial applications do not face the same limitations, major advantages in speed and accuracy can be gained by employing field analysis prior to selecting samples for laboratory study.

Below are listed some of the characteristics of a few instruments that have been flown by NASA or are being proposed for NASA future missions. The constraints on mass and power, combined with the need to function in a hostile environment, place severe requirements on these instruments. The technology developed to meet these requirements could benefit the production of similar instruments for terrestrial applications.

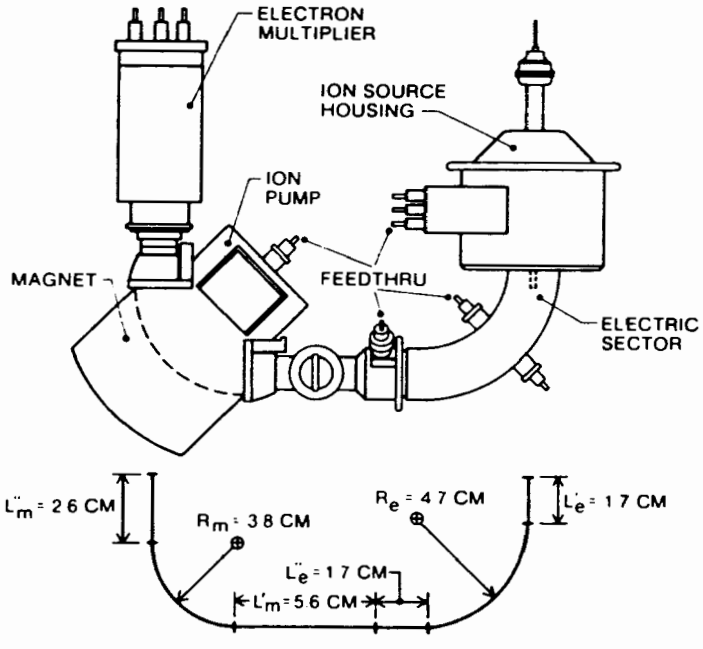

Figure 1. The mass spectrometer for the Viking Lander GCMS. The electric sector has a radius of 4.7 cm.

Chemical Analyzers

The prime example of a chemical analyzer is the Biology Experiment on the Viking Landers. The experiment included a GC-MS system for analysis of organic compounds in Martian soil [5]. The GC-MS part of the system had a mass of 16 kg, measured 28 cm x 38 cm x 27 cm and consumed 25 to 125 W when active. When the system was presented with a soil sample it could sift a soil sample into a pyrolysis tube, seal the tube to a GC inlet, perform a controlled heating on the sample, and perform a mass spectral analysis of the GC effluent with exceptionally high sensitivity. The mass spectrometer also had a direct inlet for analysis of the Martian atmosphere. Figure 1 shows a diagram of the mass spectrometer.

Currently under development for the Comet Rendezvous/Asteroid Flyby mission is the Cometary Ice and Dust Experiment (CIDEX) instrument that incorporates a 3-column GC system for evolved gas analysis over a sample temperature range of -90 to +1000 C. The instrument also includes an x-ray fluorescence experiment in a 15 kg package that uses an average of about 22 W. The system will analyze comet dust for organic materials and elemental composition.

New GC-MS systems have been proposed that combine the analytical speed of microbore GC columns with the exceptionally high sensitivity of a focal-plane mass spectrometer equipped with an integrating focal plane detector. Such a flight system would be comparable in size and mass to the Viking Lander GC-MS, but with analytical cycle times of a few minutes and the ability to analyze GC peaks separated by a few hundred milliseconds. Such a system could measure dynamic processes or determine planetary atmospheric composition while descending on a probe or parachute. The robust, portable nature of such an instrument would make it a good candidate for deployment in terrestrial field screening activities as well. A gas chromatogram from a laboratory prototype is provided in Figure 2.

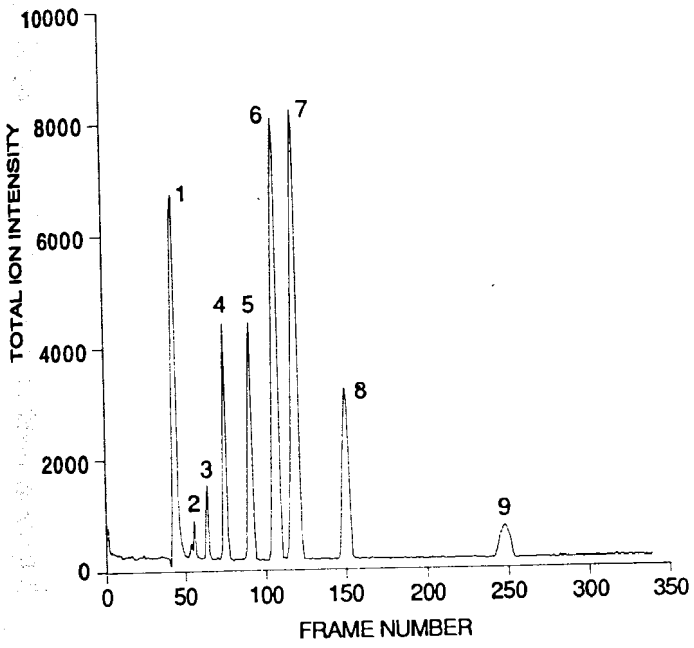

Figure 2. Chromatogram of a mixture of EPA priority pollutants. Each 50 mg frame contains a time-integrated mass spectrum from mass 25 to 500 amu. (Peak 1 is air and peak 9 is toluene.)

Elemental Analyzers

Gamma-ray spectrometers have been used in orbiting spacecraft to obtain elemental maps of atmosphere-free bodies such as the moon. The Mars Observer spacecraft will contain a gamma-ray spectrometer for elemental mapping of the Martian surface through its thin atmosphere. The recently built and proposed gamma-ray systems for elemental analysis have tended to follow commercial technology by use of cooled germanium detectors. These detectors use radiators aimed into cold space to achieve the required temperatures. The detected elements are those with naturally radioactive isotopes or which are excited by cosmic rays. Long counting times are needed. Related instruments may be useful in the remote determination of radioactive isotope composition at terrestrial sites.

New, high efficiency x-ray fluorescence analyzer systems have been proposed for lunar and Martian landers that use new toroidal focussing crystals to achieve many orders of magnitude increase in x-ray flux from microfocus x-ray tube sources to achieve rapid and high sensitivity analyses [6]. With the use of uncooled mercuric iodide x-ray detectors, such an x-ray fluorescence system might have mass of 4 kg, consume 10 W, and occupy a volume of about 35 cm x 25 cm x 25 cm. The same microfocus x-ray source could be used in a high-efficiency, toroidal-focussing powder x-ray diffractometer for identification of minerals. Both instruments can work in an atmosphere of low x-ray absorption density, such as that on Mars, or in vacuum.

VISIBLE AND NEAR INFRARED REMOTE SENSING

Imaging spectrometers play a major role in both Earth observation and planetary exploration. The Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) images with 20 m x 20 m spatial resolution in 224 spectral channels from 400 to 2450 nm wavelengths [7,8]. The data, obtained from NASA ER-2 aircraft at 20 km altitude, is spectrally and radiometrically calibrated to provide information for disciplines such as ecology, geology, oceanography, inland waters, snow hydrology and atmospheric science. An AVIRIS type instrument might be used for aircraft tracking of ocean oil spills, smoke plumes, or other indicators of chemical contamination.

In addition to visible and near infrared imaging spectrometers, NASA has developed a portable backpack point spectrometer (Portable Instantaneous Display and Analysis Spectrometer - PIDAS). At a mass of about 30 kg, PIDAS obtains and records with integrating detectors, reflectance spectra in 830 bands from 400 to 2450 nm. The instrument, developed at JPL, has been used to support geological and ecological disciplines, and can be calibrated for identification of a wide range of materials. The instrument field of view is 10 to 30 cm when hand held. NASA is currently working to develop an adaptive, reliable and compact imaging spectrometer system for autonomous site and sample selection and analysis of materials. This system will provide wide area as well as close-up identification of minerals which is enabling for surface science and engineering missions.

The key element of the SAAP remote sensing subsystem is a multi-spectral imager based on the solid-state acousto-optic tuneable filter (AOTF). This device operates on the principle of acousto-optic interaction in an anisotropic medium and acts as a controllable narrow band filter. The current breadboard version can collect spectral images at 4 nm spectral resolution in the visible range (0.5 and 0.8 microns). It has been implemented with a 1000x1000 fiber optic bundle between the foreoptics and the AOTF. The fiber optic cable enables the mounting and articulation of the foreoptics, remote from the main spectrometer body. Figure 3 shows the current breadboard hardware.

By altering the pass band sequentially, only the desired spectral bands are collected. Each pixel has a spectral signature associated with it and classification is accomplished on the basis of elemental content and spatial location. Figure 4 shows a set of spectrometer images of a rock containing the rare earth mineral neodymium taken in the range of 783-710 nanometers. The absorption characteristics of this mineral at around 750 nanometers is evident in the dark spot in the right-center of the second row of images. Figure 5 shows the complete spectral signature of neodymium as taken by the AOTF spectrometer.

Although the current instrument operates in the visible region, the AOTF technology will also allow construction of tunable filters for the infrared and ultraviolet regions of the spectrum, with a total range between 0.35 and 25 microns. This may provide a new class of tunable spectral analyzers for a variety of space and earth applications.

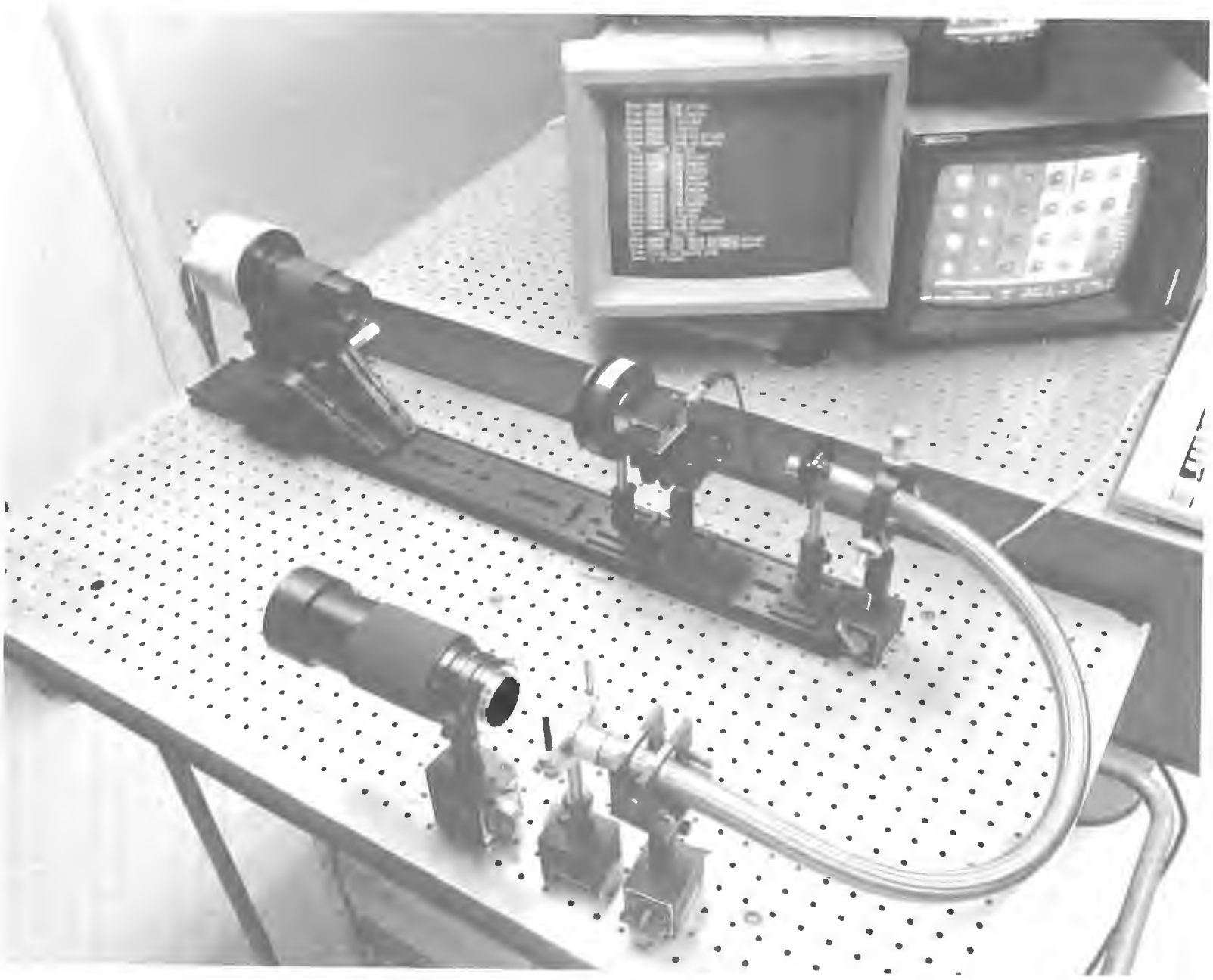

Figure 3. AOTF Spectrometer Breadboard

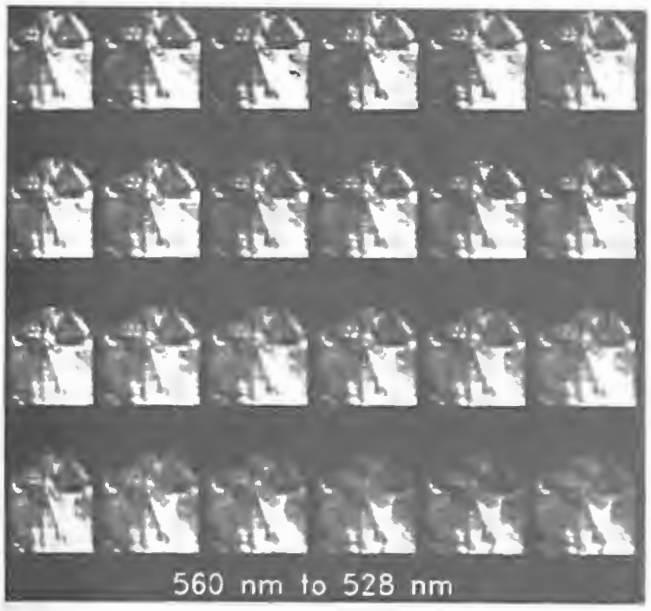

Figure 4. AOTF Spectrometer Output in 710-783 nm

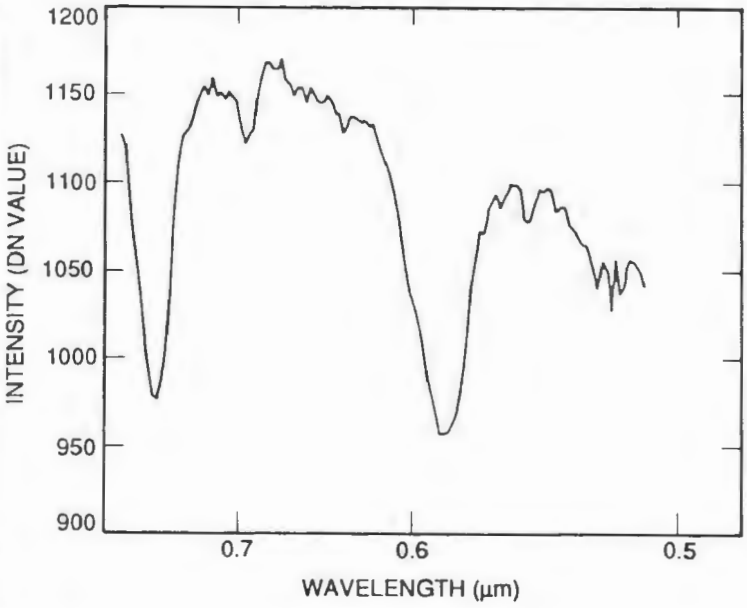

Figure 5. Neodynium Absorption Spectrum from AOTF Spectrometer

The completed imaging spectrometer will be capable of collecting high resolution images at hundreds of discrete wavelengths. Processing of such a large amount of information (>1 gigabit per scene) will strain computational systems without some means of data reduction. Hierarchical analysis schemes, in combination with neural nets, have been shown to produce several orders of magnitude reductions in total computation time and are discussed below.

INTELLIGENT DATA ANALYSIS

Spectral data from a variety of instruments is used in many areas of chemical analysis. The proceedings of the First International Symposium on Field Screening Methods for Hazardous Waste Site Investigation [9] report on the use of fieldable instruments for mass spectroscopy, x-ray fluorescence spectroscopy, infrared spectroscopy and Raman spectrosopy. For any of these instruments, the spectral data produced is complex, requires a highly trained chemist to assist in the interpretation process, and often requires extensive computer work for proper analysis. In many cases the data analysis and interpretation step presents a significant bottleneck which prevents the most efficient utilization of the instruments.

Work done within the SAAP program has concentrated on the the analysis of visible and near infrared spectra for mineral determination [10]. The developing system incorporates a number of data analysis methods and algorithms which will transfer readily to use with other types of spectral data. Application of these approaches to the instrumental analysis required for field screening of toxic waste will improve the speed and efficiency of the analysis step. Table 2 shows a comparison for speed and accuracy of four classification methods. The first matched filter is a brute force approach using full dimensionality of all patterns, and requiring the most computation. By reducing the dimensions used for matching, or performing the matching in several steps (e.g. a grouping step and a finer classification step), the computation is reduced. The hierarchy of neural network pattern classifiers combines these approaches. Images consist of 32-band spectra for all pixels, and are classified as one of 28 known minerals in each case.

Neural networks are trained to recognize spectra or classes of spectra by presenting many examples of each spectrum, complete with noise and normal variation in features. Following training, new variants of the spectra contained in the training set may be identified with a high degree of accuracy. During the training procedure, the network extracts the common features among the training examples representative of each type of spectrum, and learns to recognize these as important identifying factors, while the noise is discarded. Thus new spectra are classified based on the presence of the diagnostic features specific to a type of compound, without significant interference due to normal variation, noise, and background contamination. The major components in mixture spectra may also be identified, if the mixing process does not obscure the critical features.

The neural network spectrum classifiers currently used within the SAAP system work hierarchically, placing spectra into progressively more detailed classes. This approach allows either a rough estimate of mineral composition, or a very detailed analysis and identification. The final analysis step includes an assessment of the classification accuracy. This allows the system to identify those spectra which were poorly classified, and which may represent mixtures or other unexpected spectra. Since the

Table 2. COMPARISON OF 4 SPECTRAL CLASSIFICATION METHODS

METHOD	DATASET	TOTAL OPERATIONS	ACCURACY
Single Matched Filter	Mars	16,226,560	80%
	AISA	5,017,600	
Reduced Dimension Matched Filter	Mars	8,113,280	80%
	AISA	2,508,800	
Two Step Matched Filter	Mars	6,374,720	69%
	AISA	1,971,712	
Hierarchy	Mars	4,858,284	89%
	AISA	1,006,099	

Note: Mars dataset is a simulated multispectral image derived from a Viking Lander image. AISA dataset is a real multispectral image taken by the Airborne Imaging Spectrometer.

final application of this spectral analysis system requires almost complete automation of the analysis process, the results of the spectral analysis are integrated into an automated decision making procedure. The decision making is goal-driven: specific classes of minerals may be searched for and analyzed in great detail, while other less important compounds are discarded at an early step in the analysis procedure.

The goals of the existing (planetary) spectral analysis and decision making system include identifying interesting and uninteresting areas on the basis of spectral information, and identifying samples which should be acquired for more detailed analysis. Similar goal driven systems could be designed with the objectives of finding specific types of chemical compounds or determining which samples will prove most informative regarding chemical distribution in an area. The hierarchical goal driven architecture allows the system to analyze many samples rapidly, and to provide the user with information regarding which samples are most important for further examination.

Application to field screening for hazardous waste:

Two aspects of the work done for spectral data analysis in planetary exploration will be of interest for the field screening of hazardous waste. The neural network based spectral analysis approach will be useful for the analysis of IR, XRF, Raman, and mass spectra, if networks are trained with real spectra gathered under the anticipated field conditions. The hierarchical analysis architecture that incorporates goal driven decision making may be adapted to assist field workers in making rapid decisions regarding the areas requiring special attention during a field screening operation.

Although special neural network pattern recognition systems will be required for each type of instrument data, the basic algorithms developed for the analysis of visible/near IR mineral spectra should transfer readily to the analysis of other spectra. A hierarchical, neural network based spectral identification system will have several applications:

1. Unknown identification.

A network based hierarchy can replace a library search procedure with favorable results for the identification of unknown spectra. Progress is being made in the implementation of hardware network pattern matchers which will allow the equivalent of very large library search procedure to occur in microseconds.

2. Searching for specific compounds.

A hierarchy of networks is particularly well suited to the search for specific compounds. A spectrum is presented to the hierarchy, and is progressively classified until it becomes apparent that the spectrum does not represent the desired compound (or until the desired compound is found). A negative result is usually determined fairly quickly, since at each step of the hierarchy, a large group of spectra may be eliminated since they are not potential matches.

3. Searching for classes of compounds based on specific features.

This is a variant of the hierarchical search for a specific compound, with the difference that a positive result may occur when a given branch point of the hierarchy is reached, rather than only at the end of the search. The

hierarchy is designed so that the groups of spectra that represent important classes are together within a branch of the hierarchy. The selection of critical spectral features for identifying a class is ensured by using specific spectral bands for training the networks. Extensive knowledge of the chemistry is required at the training step for optimal results.

4. Extracting major components from mixtures.

Identification of spectra of mixtures presents problems for traditional library search and match techniques. Since mineral spectra generally derive from mixtures of pure minerals, this problem is being addressed in the work within the SAAP program. The neural network approach has the advantage of basing results on important features which are extracted from the anticipated data in advance, rather than on complete spectral matching. This allows identification of major components in many mixtures. Situations where mixing causes masking or shifting of critical spectral features require special treatment.

SYSTEM CONCEPTS

In-situ analysis systems can range from single instruments placed on the surface to multi-purpose, mobile units looking for specific materials or unique materials units. An autonomous space exploration system will require the functions of planning, analysis, execution control, reflex action, data processing and interpretation, in order to operate in real time in a hostile environment.

For an in-situ analysis subsystem, the spectrum of possible architectures can be characterized by two extremes. At one end is a set of disjoint, self-contained elements working more or less independently to perform the required functions. At the other extreme is a fully integrated system with many interdependent relations between the elements. The former case is probably more comparable to the terrestrial applications, where several independent instruments are operated by humans. This system design causes some problems for space systems since it is not efficient in terms of mass or power and compromises science due to uncoordinated measurements. Multi-instrument data fusion and corroboration is an important consideration in this system design.

An extreme example of the latter case is a multi-purpose, factory-like system, implementing a set of processes that may vary significantly depending on the desired outcome or product. Physical material, not just data, must move between the elements. Current requirements and desires for coordinated measurements as well as mass, power and volume limitations make an integrated design approach the logical basis for technology requirements, but this approach clearly pushes technology. Technology developed for such an integrated system could be applicable to the automation of sample gathering and analysis in extremely hostile earth environments, in cases where human interaction must be remote and limited for safety reasons.

Technology will be validated in the laboratory and then integrated into the series of evolving SAAP testbeds. The representative environment provided by the testbed will be used to verify technologies and demonstrate overall SAAP operational capability. By the end of September 1992 an initial laboratory testbed will be constructed to demonstrate sample identification and acquisition. By the end of 1995 a fully functional system testbed will be in operation which will transition into a complete self-contained transportable testbed for end-to-end "field" operations. A preliminary system conceptual design of a SAAP platform with a full complement of subsystem components except for a regolith deep core drill is shown in Figure 6. This configuration can be considered a preliminary model for the full-up system testbed; no final payload or mission configuration has been selected.

SAMPLE ACQUISITION

The capability to acquire physical samples robotically, without human intervention, would be significantly beneficifial in many hazardous waste screening applications. The principal requirement driving sample acquisition for planetary exploration is to obtain samples of weathered and unweathered materials from accessible rocks or outcrops. These samples must not be significantly altered either mechanically or thermally during acquisition. Conceptual designs and early experimental work have been completed to help understand the mechanical, controls and automation issues for sample acquisition in the hostile environment of a planetary surface. Effort has focused on mechanical designs to achieve functional capability and is now proceeding to include testing of control and automation methodologies. Laboratory validation at the component level will be followed by further development and verification at the system level in a series of SAAP testbeds.

Various techniques have been studied for sample acquisition including sawing, coring and chipping. Of these, core drilling represents an efficient way of obtaining surface and subsurface samples that are easy to handle by a preparation or storage subsystem. Terrestrial coring processes, however, require direct human supervision and utilize high power and introduce large volumes of fluid to aid the cutting process by cooling the bit and removing cuttings of rock and/or soil.

SAAP has developed the means for core drilling low porosity, high compressive strength rocks without the use of coolant. High velocity diamond matrix core barrels are used under the control of robotic manipulators. Under study are various control approaches and a variety of sensors modalities including, position, force, vision, spectral, temperature and vibration. Progress in this area should improve the prospects for remote robotic acquisition of solid samples from hazardous areas on earth as well.

In addition to tools, work is underway to identify and develop end effector and manipulator technologies necessary for the sample acquisition operations. Preliminary studies of end effector and manipulator dexterity versus reliability, mass, power and performance have been made for some mission scenarios. The current

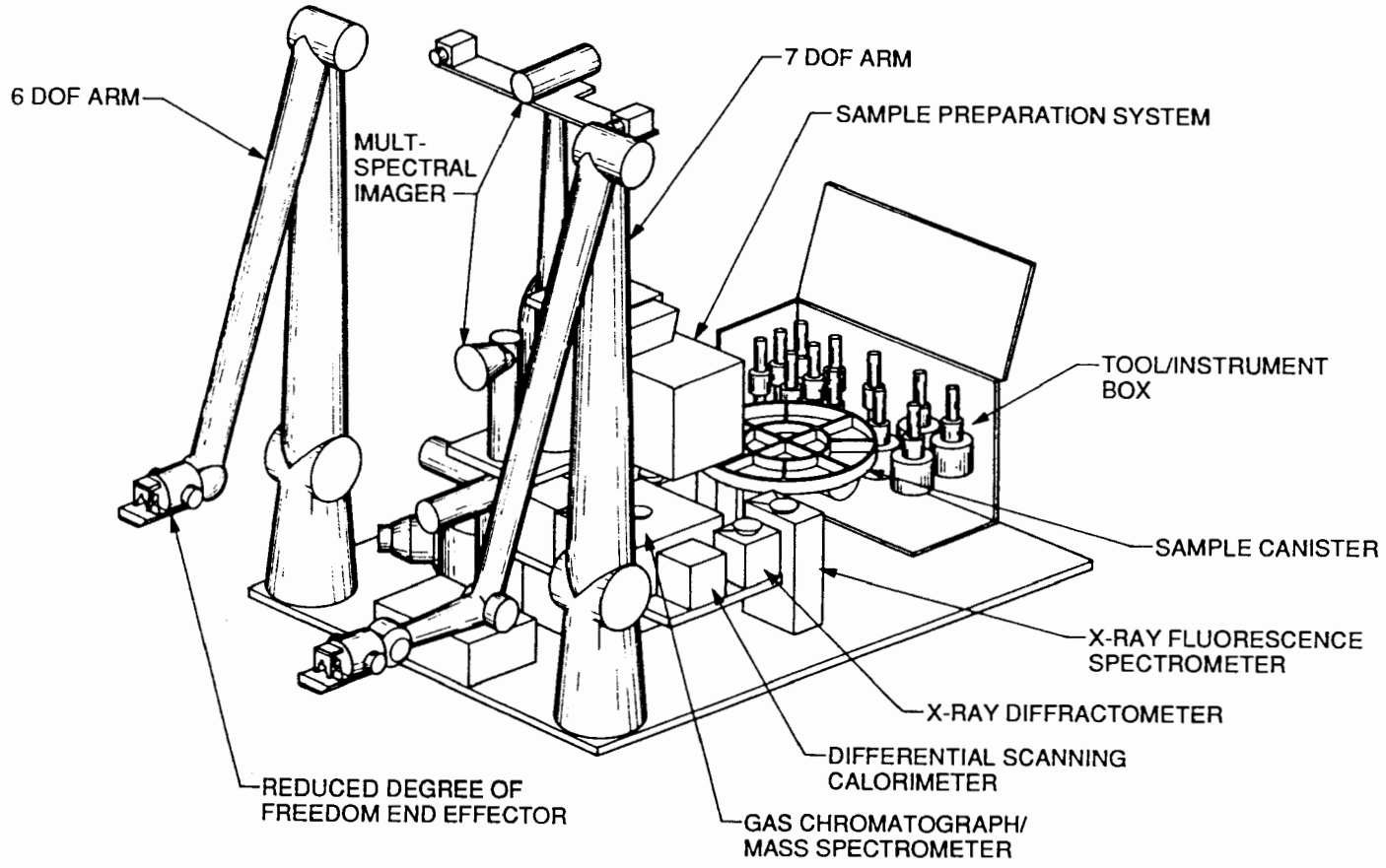

Figure 6. SAAP Preliminary System Conceptual Design

state-of-the-art in end effectors consists of either very limited capability industrial vise-type grippers, or extremely complex anthropomorphic designs being studied in research laboratories. In general, the fewer degrees of freedom the better for simplicity. However, to achieve high inherent reliability, mechanical redundancy at each degree of freedom will be required. Concepts that provide adaptability or flexibility and involve trade-off's of degrees of freedom with redundancy will be studied further.

ADVANCED CONCEPTS

NASA is interested in developing new sensing device technology for in-situ science investigations. Currently available instruments for in-situ science investigations are often incompatible with mission requirements due to their excessive mass, volume and power consumption. Science capabilities may be significantly extended by the development of sensing device systems which represent smaller payloads. The sensing device development is directed to enable compact, low-mass, low-power consumption instruments for a variety of mission requirements. The advanced technology of silicon micromachining for device fabrication will be employed to implement highly capable, sensitive, and robust instruments while retaining compact structure and low mass attributes.

The development of silicon micromachined gas sensors will be based on the compact gas chromatography (GC) instruments recently demonstrated in silicon micromachined structures. The key components of the compact GC systems include a silicon micromachined gas dispersion column, integral gas metering valves, and silicon thermistor gas detectors, fabricated entirely on a single silicon wafer. The successful operation of this prototype time-of-flight GC system indicates the range of opportunities for unique instruments of this type. In this task, specific gas detector applications will be identified and instrument requirements will be formulated. Gas sensors and instruments will fabricated and tested for operation in the Martian atmospheric environment. Finally, with results of device testing, complete instruments will be designed for specific mission applications.

CONCLUSION

This paper has discussed some of the measurements, methods and instrumentation used on past, present and future space missions for in-situ and remote analysis of materials. Work sponsored by NASA's Sample Acquisition, Analysis and Preservation technology program included concepts and hardware for multi-spectral remote sensing, instrument data analysis and interpretation, and material

acquisition, and new concepts for micro sensors for making various chemical measurements. Much of the technology under development in the SAAP program has application to terrestrial hazardous waste materials acquistion and analysis.

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DISCUSSION

BRIAN PIERCE: My question concerns the fiber optic bundle. You said infrared. Do you mean the near infrared or closer to the mid I.R.?

SUSAN EBERLEIN: Right now the fiber optic bundle that we've actually worked with has only been in the visible range. We're looking this year in the near infrared of 1.2 to 2.5 microns. In the long-term maybe more, but I gather that as you go further into the infrared you get more trouble with your fibers.

BRIAN PIERCE: Yes, that's right. You also mentioned very intriguing hardware neural networks. What do you mean by that?

SUSAN EBERLEIN: What I mean by hardware neural networks is micro silicon chips where the connection weights for the neural network matrices are actually in the resistances in the chips. JPL is fabricating some of these. They are still in the early stages, and not as precise as we need them. Some other companies are working on making them commercially as well. If in fact they turn out to be a viable technology that can be space qualified, they offer very, very rapid processing for specific problems.

DEVELOPMENT OF A REMOTE TANK INSPECTION (RTI) ROBOTIC SYSTEM

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ABSTRACT:

RedZone Robotics, Inc. is developing a Remote Tank Inspection (RTI) robotic system for Westinghouse Idaho Nuclear Company to perform remote visual inspection of corrosion inside high level liquid waste storage tanks. The RTI robotic system provides 5.8 m (19 ft) of linear extension inside the tank to position a five degree-of-freedom robotic arm with a reach of 1.8 m (6 ft) and a payload of 15.9 kg (35 lb). The primary end effector is a high resolution video inspection system. The RTI Intelligent Controller provides a standardized, multi-tasking environment which supports digital servo control, I/O, collision avoidance, sonar mapping, and a graphics display. The RTI robotic system features an innovative, standardized, and extensible design with broad applicability to remote inspection, decontamination, servicing, and decommissioning tasks inside nuclear and chemical waste storage tanks.

I. APPLICATION

Westinghouse Idaho Nuclear Company (WINCO) will use the RTI robotic system at the Idaho Chemical Processing Plant (ICPP) to perform remote visual inspection of corrosion inside high level liquid waste (HLLW) storage tanks. The ICPP tank farm consists of several HLLW storage tanks that are 15.2 meter (50 ft) in diameter with a capacity of 1,135,500 liters (300,000 gallons). The domed roofs of the tanks are buried 6.1 m (20 ft) below ground level. The bottom of the tanks are located approximately 12.5 m (41 ft) below ground level. The tanks will be drained of liquid prior to inspection; however a 30 cm (1 ft) layer of caustic sludge will remain on the bottom of the tanks. The only access to the tanks is through 25 cm (10 in) and 30 cm (12 in) diameter riser pipes which extend from ground level down into the tank roof dome. Accessible risers are typically located 0.8 m (2.5 ft), 3.6 m (12 ft), and 6 m (20 ft) away from the tank wall. Currently, the RTI system will only be deployed through the 30 cm (12 in) tank risers. Cooling coil arrangements line the tank walls and the tank floor.

The primary mission of the RTI robotic system is to perform remote visual inspection of the interior walls of the tanks for corrosion which may have been caused by the combined effects of radiation, high temperature, and caustic chemicals present. Due to the location and limited number of accessible risers inside a tank, the intent is to inspect only a pie-shaped portion of the tank to qualify the typical condition of corrosion inside the tank. Thus the application does not require a robotic arm with a long reach.

II. SYSTEM OVERVIEW

The RTI robotic system features a vertical deployment unit, a robotic arm, and a remote control console and computer. One of the major design constraints for the RTI system is that the in-tank components are inserted through a 25.4 cm (10 in) diameter riser. This criteria lead to the design of compact, electric actuators for the robotic arm, which provide high torque and absolute position feedback. The RTI robotic system is initially lowered by a facility crane into the top of the riser. The vertical deployment unit then provides another 5.8 meters (19 ft) of servo controlled extension inside the tank. The RTI robotic system transmits minimal loading to the riser pipe since it is self-supporting via a support structure that rests on the ground above the riser. Figure 1 provides an illustration of the RTI robotic system installed inside a tank.

A five degree-of-freedom robotic arm provides 1.8 meters (6 ft) of articulated reach to accurately position a high resolution video inspection camera to examine the tank walls. The arm has sufficient dexterity to position the camera normal to the curvature of the tank wall. The controller provides coordinated end point motion so that the operator can easily jog the arm inside the tank. A graphics display is provided at the control console to give the operator a sense of how the arm is positioned inside the tank. The robotic arm also positions a pressurized spray nozzle to wash down the tank walls prior to inspection. In addition, the end of the arm has an interchange flange to allow the robotic arm to carry a gripper instead of the inspection camera. Another camera system is mounted at the top of the robotic arm to provide the operator with an overview of the arm operating inside the waste tank. The RTI robotic system is capable of manual recovery to retrieve the system in event of motor failure.

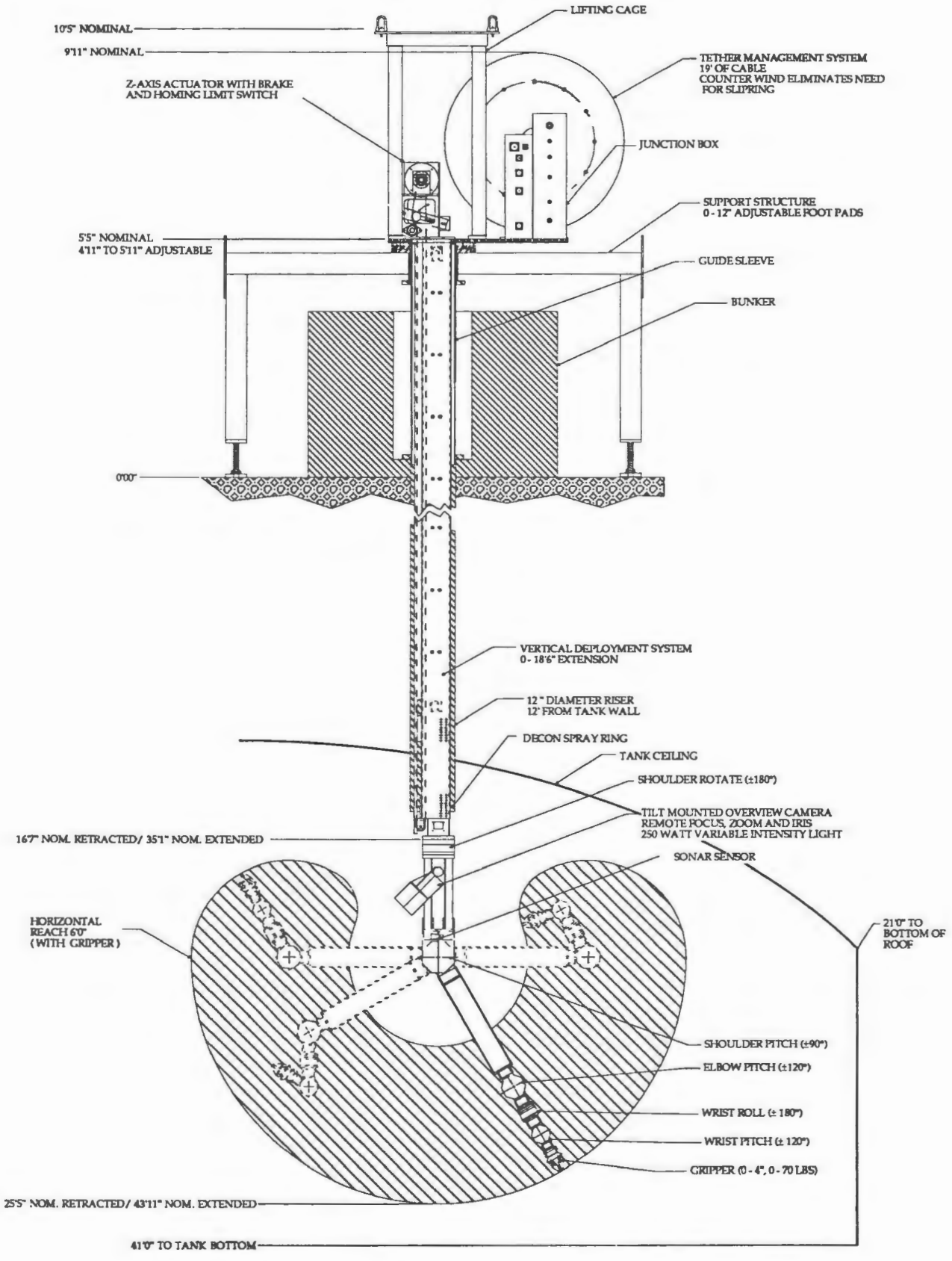

Figure 1. RTI Robotic System Deployed Inside HLLW Waste Tank

The RTI system is radiation and environmentally hardened to assure reliable performance in the tank environment. The design criteria requires that all in-tank components be capable of withstanding a 20 psi washdown of 10% nitric acid and 10% oxalic acid, radiation field of 100 Rad/hr for a total accumulated dose of 10,000 Rad, and operating temperatures of 4 to 49 °C (40 to 120 °F) at 100 percent humidity. The RTI system uses sealed components such as connectors, video equipment, sensors, and actuators to preclude the intrusion of decontamination fluids. Bearing and wear surfaces are stainless steel and non-stainless components are anodized or coated with epoxy paint to prevent damage from caustic decontamination fluids.

The RTI's control system uses RedZone's standardized Intelligent Controller for Enhanced Telerobotics to provide a high speed, multi-tasking environment on a VME bus. Currently, the robot is controlled in a manual, joint jog mode or a coordinated end point motion control mode. Control capability is available to develop a pre-programmed, automated or teach/playback mode of operation. The control system incorporates sensing and software safeguards to prevent an operator from inadvertently colliding with the tank wall. Collision prevention is implemented in software and backed up with four proximity sensors. A sonar range finding sensor is used to establish the orientation of the RTI robotic system inside the tank.

III. MECHANICAL DESIGN

The major components of the RTI mechanical system are the support structure, vertical deployment unit, robotic arm, accessories, and strongback. These assemblies are described in the sections that follow.

A. Support Structure

The support structure rigidly supports the vertical deployment unit at ground level. It consists of the alignment guide sleeve and support stand assembly. The support stand is a four legged structure that spans the riser pipe and bunker. Its leg pads provide 1 foot of vertical adjustment and allow the stand to be levelled. A facility crane is used to position the support structure over the riser and to insert the alignment guide sleeve into the riser pipe. The guide sleeve follows the inclination of the riser pipe to guide the vertical deployment unit during insertion. The objective is to avoid loading the riser pipe if it is not absolutely vertical.

B. Vertical Deployment Unit

The vertical deployment unit provides 5.8 m (19 ft) of servo-controlled vertical extension, at speeds of up to 7.6 cm/sec (3 in/sec), to position the robotic arm inside the waste tank. The vertical deployment unit consists of a telescoping tube assembly, cable management system, drive motor, and junction box. The telescoping tube assembly contains a fixed outer tube and an inner extending tube to minimize the overall retracted height of the system. With the inner tube extended, the wrist flange of the arm can reach the tank floor. An adjustable hard stop is provided to safely reduce the extent of vertical travel. The outer tube is a 20 cm (8 in) square stainless steel tube and the inner tube is a 15 cm (6 in) square tube. The vertical deployment tubes are designed for deployment through 30cm (12 in) risers. However, the robotic arm is designed to pass through a riser as small as 25 cm (10 in). The inner extending tube is supported and guided along the upper tube by stainless steel linear bearings and rails. The rails are mounted along the length of the inner tube and the bearing blocks are attached to the inside of the outer fixed tube.

An electric motor drives the lower tube, Z-axis, by a dumb-waiter arrangement of a drive chain and pulley. The motor package includes an integral gear reducer, brake and resolver. The motor's output shaft is directly coupled to a drive sprocket which drives a steel chain attached to the upper section of the inner tube. The chain moves within the gap between the upper and lower tubes. The drive sprocket was designed so it can be driven from either side. In the event of a motor failure, an identical backup motor package can be quickly mounted in order to drive the telescoping tube assembly. Due to the relatively large gear ratio and large travel of the chain, absolute position feedback on the vertical deployment was avoided. Instead, a resolver is attached directly to the motor shaft and a limit switch is used to home Z-axis position at start-up.

After insertion into the riser, the top flange of the vertical deployment unit is bolted to the guide sleeve. On top of the vertical deployment are located the cable management drum and a junction box. Cabling is payed out from a spring loaded cable drum which has a large diameter so that only two wraps are required to pay out the 5.8 m (19 ft) of cable length. This design obviates the need for electrical slip rings. The vertical deployment junction box is connected to the control console with 30.5 m (100 ft) of cable. The junction box contains some pneumatic and valve equipment and terminal strips but no circuitry. Its main purpose is to serve as a termination point for cables routed down the vertical deployment unit to the robot arm.

At the base of the vertical deployment unit is a mounting flange for the robotic arm. Cables are routed internal to the inner tube and exit the tube at its bottom. At the bottom of the outer fixed tube, a spray ring is mounted to spray decontamination fluid on the inner tube as it retracts upward. This minimizes the spread of contamination inside the telescoping tube assembly.

C. Robotic Arm

The RTI robotic arm mounts to the bottom of the lower extending tube. The arm is a five-degree-of-freedom revolute arm consisting of shoulder rotate, shoulder pitch, elbow pitch, wrist roll and wrist pitch axes. The primary function of the robotic arm is to position the WINCO inspection camera system mounted to the wrist flange. The arm has sufficient degrees of freedom to position the inspection camera normal to the curvature of the tank wall. Coordinated end point motion control allows the operator to move the inspection camera in/out and along the curvature of the tank wall. An overview camera is packaged between the shoulder rotate and pitch joints to rotate with the arm, allowing a continuous view of the end of arm. A spray nozzle is attached to the robot wrist so that the robot can wash down the tank wall prior to corrosion inspection.

The robotic arm weighs approximately 100 Kg (220 lb) and has an overall length of 2.5 m (8 ft). The arm has a 1.6 m (64 in) length to the wrist mounting flange, providing the

robot with a 1.8 m (6 ft) reach when positioning the inspection camera. The last three joints of the arm, elbow pitch, wrist roll and wrist pitch, are clustered in close proximity to provide dexterous manipulation. All axes are electrically driven, feature absolute position feedback, and are actively servoed to hold position. Upon loss of power, the controller automatically shorts the motor leads to provide dynamic braking. Gravity will backdrive the arm into a nearly vertical position so the RTI system can be removed from the riser in a manual recovery mode. Table 1 provides performance characteristics of the arm.

Table 1. Performance Specifications

Description	Travel	Max Velocity
Shoulder Rotate	± 180°	1.0 rpm
Shoulder Pitch	± 90°	1.0 rpm
Elbow Pitch	± 120°	2.4 rpm
Wrist Pitch	± 120°	5.5 rpm
Wrist Rotate	± 180°	5.5 rpm
Reach of Arm	6 feet	
Coordinated End Point Motion		2.5 ips

Key: ips = inches/sec, rpm = rev/minute, ° = degrees

The five joints of the robot arm are driven by three different sized actuator packages as specified in Table 2. The three actuators are similar in concept and design but provide differing torque and speed characteristics. The capabilities of these actuators were optimized to meet the goal of providing a 15.9 Kg (35 lb) payload for the robot. The actuators are designed into a compact, pancake-style package. In the case of the shoulder pitch it was necessary to keep the actuator small enough to fit sideways, in profile, through the 25 cm (10 in) riser. Frameless DC high torque brush motors were used as they offer the smallest size, highest torque and lowest speeds available. Each motor is coupled to a pancake type Harmonic Drive gear reducer, providing a single step reduction of up to 200:1. These drive components are integrated with slim line ball bearings and a resolver to produce compact servo-actuators capable of large torques. The integral resolver is directly coupled to the joint output allowing precise, absolute, servo control of the arm.

Table 2. Mechanical Characteristics of Actuator Packages

Robot Joints	Actuator Size	Dimensions	Max Torque (in-lbs)	Max Speed (RPM)
Shoulder Rotate&Pitch	Heavy	9.0" dia x 4.5" 35 lbs	8400	1.1
Elbow Pitch	Medium	6.5" dia x 3.5" 18 lbs	2500	2.4
Wrist Roll & Pitch	Light	5.2" dia x 3.0" 8 lbs	800	5.5

The actuators and links are constructed of aluminum, which is anodized on all exterior surfaces. The actuators are environmentally sealed to protect them from the decontamination solution. Since the actuators are not equipped with brakes, they experience a 100% duty cycle when the arm is loaded, causing the motors to heat up significantly. Analysis of the system indicates that the actuators' capabilities are thermally limited. That is, the maximum payload of the arm is dictated by the motors maximum winding temperature of 155 °C (311 °F) and not by the maximum mechanical torque of the actuators. To increase the actuator and arm payload capabilities an air line is run into the actuators to provide cooling for the motors. Cabling to each of the joints and tooling is routed along the I-beam shaped linkages of the arm. Submersible, molded connectors are provided on each motor.

D. Accessories

Accessories for the RTI robotic arm comprise the quick change interface, decon spray nozzle, gripper, overview camera system, sonar sensor, and proximity sensors. A description of each accessory is provided below:

- A manual quick change interface is provided at the wrist mounting flange to change end effectors (inspection video system and gripper). The interface consists of an electrical connector, pneumatic connectors, and a common mounting plate.
- A decontamination spray nozzle is mounted directly above the wrist flange to wash down the tank walls. It has an adjustable flowrate of up to 15 liters (4 gallons) per minute.
- A pneumatic parallel jaw gripper is provided with a 10 cm (4 in) stroke and adjustable gripping force of up to 482 kPa (70 psi).
- The overview camera system consists of an environmentally sealed color camera with a zoom and focus lens. The camera is mounted inside a cut-out section of the robot shoulder linkage. A rotary actuator provides the ability to pitch the camera along the robot arm while zooming in for close views. Remote control of the camera, rotary actuator, and light intensity is provided at the control console.
- A miniature sonar detector is used to determine the relative orientation of the robot inside the tank. The sonar detector is mounted on the shoulder of the robot arm to calibrate shoulder rotation to distance of the tank wall. Since the risers are not located on the center line of the tank, radial extensions from the riser to the tank wall vary in length. An applications software package automatically controls the sonar sensing and rotation of the shoulder axis. The software processes the data to identify the location of the wall closest to the riser. Once distance to the tank wall is known as a function of shoulder rotation, distance of the robot's end of arm to the tank wall can be calculated based on forward kinematics. Distance to the wall is displayed on the graphics monitor and also used for software collision avoidance. The accuracy of this information is dependent the combined accuracy of the robot, sonar detector, data processing, arm dimensions, and the assumed location of the riser.

- For impending collision detection, four photoelectric proximity sensors are mounted on the leading edge of the robot arm linkages to detect close proximity to the tank wall.

E. Strongback

The strongback fixture rigidly supports the RTI robotic system during shipment. It is designed to attach to the bed of a semi-trailer truck. The strongback consists of a tubular framework to cradle and support the full 10.7 m (35 ft) horizontal length of the RTI system. For additional protection, the robotic arm is housed inside a reinforced cage before it is placed onto the strongback. A facility crane is used to pivot the RTI robotic system vertical from the strongback during deployment at a riser.

IV. CONTROL CONSOLE

The RTI control console is the remote station from which an operator can control and monitor the robotic arm to perform visual inspection of the tank. The control console will be located on a desk top inside a trailer located up to 30.5 m (100 ft) from the RTI mechanical system. The console consists of two side-by-side 48 cm (19 in) racks which maximize the useful working and viewing area to the operator. The racks are encased in structural foam and housed together in one self-contained shipping container. A removable front cover protects the monitors and control panels during shipment. All cables enter the control console through external chassis mounted connectors.

The control console is composed of industrial grade components, rated for operation in indoor, industrial environments. The inspection and overview camera each have their own display monitor and camera control panel. VCR's are provided to record the video output signal of the cameras.

As shown in Figure 2, the control console displays the following equipment to the operator:

- Operator Control Panel
- 8-inch Color Monitor to display Overview Camera
- 9-inch Black & White Monitor to display B&W Inspection Camera
- Two Super VHS Recorders
- Overview Camera Control Panel (camera, zoom, pan, & lights)
- Inspection Camera Control Panel (camera, zoom, pan & tilt, & lights)
- Control Panel (B&W Camera focus & iris)
- 20-inch Color (Video & Graphics) Monitor to display inspection cameras or computer graphics

The control console also contains the following components within its cabinet:

- Intelligent Controller Rack
- Servo Amplifier Rack
- Power Box
- Fan Panels

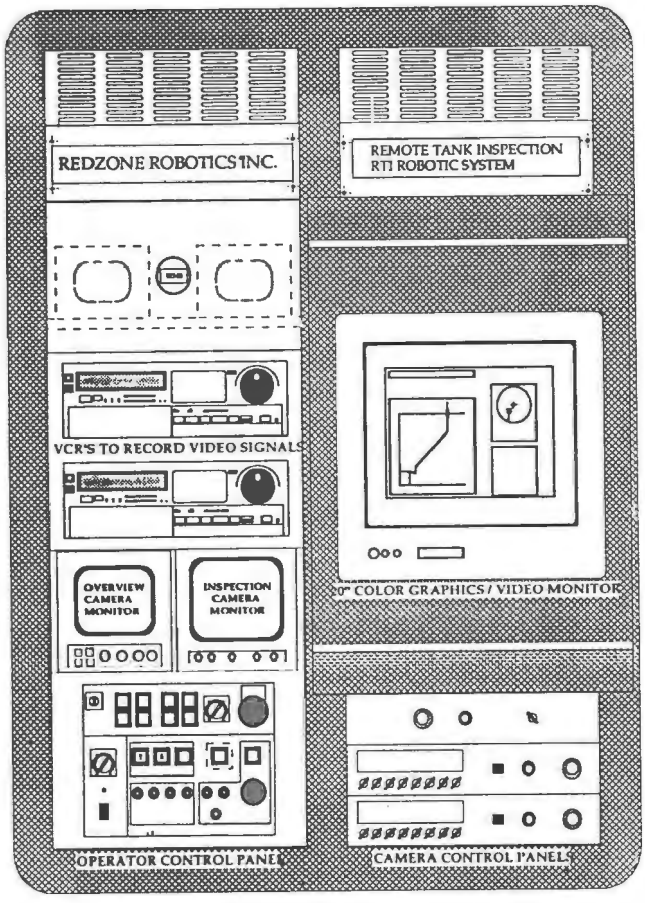

Figure 2. Operator Control Panel (Front View)

A. Operator Control Panel

The operator control panel provides the operator with a complete interface to drive the RTI system. All devices and accessories are operated from the control panel with the exception of the cameras which have independent control panels. The operator control panel is wired directly to the digital I/O boards of the controller. The controller acknowledges operator commands by illuminating activated switches. The controller performs safety checks of operator commands before executing them.

The operator control panel provides switches for speed selection and jogging of each individual axis. To prevent accidental activation, each "Axis Jog" toggle switch must be held down continuously by the operator to jog the axis. The axis will move at the selected speed (slow, medium or fast). Once released, the toggle switch returns to its neutral "off" position. In the event of a controller failure, the robot can be driven in an open-loop mode by hooking up a battery power supply directly to the motor amplifiers. An emergency stop pushbutton is provided on the operator panel.

The operator must depress a pushbutton to select coordinated end point motion. A 4-position joystick is provided to jog the end point of the arm towards or away from the tank wall and clockwise or counterclockwise along the tank wall. Consistent orientation of the end point is maintained. In coordinated motion control, the Z-axis, wrist roll and wrist pitch axis jog keys are also active. Depending on the orientation of the robot arm, wrist roll and pitch control the relative pan & tilt of the inspection camera mounted at the end point.

Controls are also provided to open and close the gripper and to control the decon spray ring and spray nozzle. The operator control panel provides an up/down arrow and enter key so the operator can make selections of menu commands displayed on the graphics monitor.

B. Intelligent Controller

The design of the RTI controller is based on RedZone's Intelligent Controller for Enhanced Telerobotics, a proprietary, standardized platform for computation and communications for the control of a wide variety of multi-axis robotic systems. The Intelligent Controller is housed inside a 12-slot VME bus chassis inside the control console. The Intelligent Controller performs the following functions, in a multi-tasking environment, for the RTI robotic system:

- Translation and execution of all operator commands originating from the operator control panel.
- Digital servo control of all movement including individual axis joint control and coordinated end point motion of the robot arm.
- Execution of automatic routines; system self check, power-up, sonar map control, and shut-down sequences.
- Safety monitoring of proximity sensors, joint overtravel, joint and velocity tracking errors and overtorque conditions.
- Continuous monitoring of potential collision states.
- Logging significant events in a data file.
- Displaying on the graphics monitor: plan view and side view of robot arm inside tank, distance and orientation of end point to wall, absolute position of each axis, error message & diagnostics, and menu prompting of routines.

The computational devices of the RTI Intelligent Controller consist of the following boards:

- 68020 CPU Boards (2) with floating point processors.
- RGB Video Board to interface the controller to the graphics display monitor.
- Resolver to Digital Boards (2) to transform resolver output to the digital signal used to compute current position and velocity of each axis.
- Digital to Analog Board to convert the digital control signal generated by the CPU to an analog control signal to drive the motor amplifiers.
- Timer Interface Board to measure time-of-flight of sonar echoes generated by the sonar ranging module.
- SCSI Interface Board to interface to the removable cartridge disk drive.
- 44 MByte Removable Cartridge Disk Drive to provide portability with hard disk performance. All software resides on the disk drive.
- Digital Input Boards (2) to provide 64 opto-isolated channels that are interrupt driven to the controller. Digital I/O serves as primary interface between CPU and operator control panel.
- Digital Output Board to provide 32 dry reed relay outputs. Allows CPU to control devices and indicator lights on each switch.

Control of robot motion is achieved by a control law implemented in software on the main CPU. Motion control boards are not required as servo control is flexibly implemented in software. The CPU reads resolver inputs, computes forward and inverse kinematics, and generates a digital control signal. This digital control signal is then converted into an analog input to the motor amplifiers. The CPU performs all of the control calculations for robot motion, interprets user commands from the operator control panel, and maintains the graphics display. Two CPU boards allow the computational load to be distributed by running the motion planner on one board, and the remainder of the software modules on the other. This results in stiffer motion control and faster updating of the graphics display.

V. SOFTWARE

Under separate contract to the Department of Energy (DOE), RedZone is developing an Intelligent Controller for Enhanced Telerobotics to provide a standardized, multi-tasking, VX Works ™ environment for software development. The RTI system uses the hardware and software architecture defined by the DOE Intelligent Controller architecture. All software is written in the C-language and resides on the disk drive. Figure 3 is a block diagram of the major software modules of the system. The software is organized into five main modules: the task executive, the motion planner, the motion controller, the data processor, and the graphics module. Communication between (and in some cases within) these modules is performed using RedZone's proprietary Robotic Communications Protocol (RCP) which is the heart of the Intelligent Controller. RCP provides both intra-cpu and inter-cpu communications as well as global variables, functions calls and semaphores between modules. Below, each module is described in detail.

A. System Control

The system control module is the "front-end" of the RTI controller. It contains four sub-modules: digital input/output drivers, task executive, health monitor, and data logger. The digital input and output drivers provide a standardized software interface to the digital I/O boards. The task executive's main function is to monitor the state of the operator panel and of the robot. It directs action based on these inputs. The data logger records events, errors, and change of state into a file. The log is maintained on the hard disk to help understand and troubleshoot failure or accident scenarios.

B. Motion Planner

The motion planner module provides a collection of high level path generating modules, collision detection modules, and kinematics utilities that operate with a nominal cycle time of 10 milliseconds. The path generating modules include joint space profile generation, cartesian space profile generation, and control for sonar mapping. Cartesian space points are transformed via inverse kinematics into joint space goals to generate a smooth trajectory for each joint in motion. The sonar map utility automatically controls the arm while the sonar mapping sequence is in progress. The collision avoidance module monitors the proximity of the arm to the tank wall. The kinematic module contains the mathematical model of the arm, including link lengths and axes of rotations. Forward kinematics are used to compute the end point position of the arm based on axis joint positions for collision avoidance checks. Inverse kinematics are used to compute the axis joint positions necessary to achieve a desired end point position for coordinated motion control.

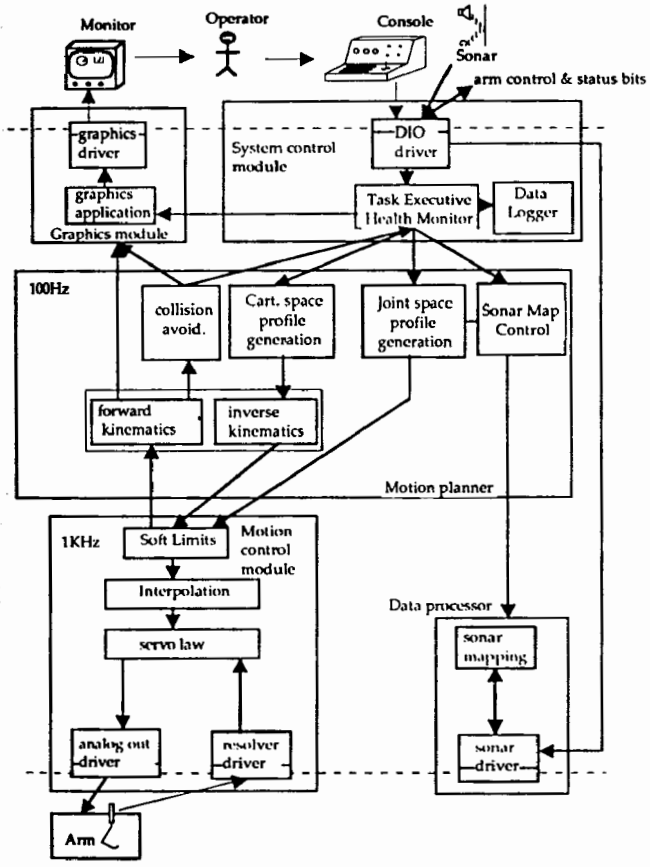

Figure 3. Software Organization

1. Jog Control. Robot motion is initiated whenever the operator holds down an axis jog toggle switch or the coordinated motion joystick. The controller responds to the switch transition state. An acceleration ramp is immediately generated to ramp up to the preselected speed range. The motion control module then generates new, incrementally small, position goals for the joint every 10 milliseconds.

2. Coordinated End Point Motion. The operator's primary objective is to position the robot's inspection video camera relative to the tank surface. It is often difficult and tedious to position the end-of-arm while jogging individual axes. To facilitate easier positioning of the camera, coordinated end point motion is provided in two axes while maintaining a consistent orientation of the tool faceplate: horizontal extension of the arm to the tank wall and following the curvature of the wall at a constant distance. Coordinated motion for the RTI robotic system is constrained in the cylindrical world frame of the tank. Control is simplified by requiring the arm to be in a preferred orientation. Should the operator choose to deselect coordinated motion and jog in joint mode, a resume function is available to allow the operator to return to his former position and resume coordinated motion.

3. Collision Avoidance. The collision avoidance software consists of a real-time background program that continuously checks the position of the arm to avoid a collision with the tank. The computer checks for penetration by the arm into a safety zone that extends from the tanks walls and floor. If the robot enters the safety zone, the computer executes an interrupt of the current motion and warns the operator of the condition. Once the robot arm is in the software collision state, the software only allows the operator to jog arm motion away from the tank surface. Proximity sensors are also provided to detect an impending collision and initiate an emergency stop. A manual override button is provided so the operator can override collision avoidance so that the RTI can touch the tank wall or floor.

C. Motion Control

The motion control module reads the joint absolute position from the resolver-to-digital driver every millisecond. The servo law, an enhanced PID control, uses commanded and actual position read from the resolvers to calculate a command output to send the power amplifiers. Robot motion is controlled in a position controlled mode, not a rate controlled mode, as commonly used on robotic manipulators. Position control provides stiffer motion control with more damping. It also allows an easy upgrade to programmed operation at a later date. Execution of the motion control task is triggered by a clock interrupt to ensure precise timing. The motion control module also enforces soft stop limits and performs linear interpolation on the commanded positions.

D. Sonar Data Processor

The sonar data processor module reads and processes the sonar data to map distance to the tank wall as a function of shoulder rotation. Radial extensions from the RTI to the tank wall vary in length, since the RTI system is inserted through a riser that is offset from the tank center. The sonar sensor produces a digital pulse each time it is

fired. The length of the pulse is proportional to the time from transmission of the sonar signal to the return of the first echo. The sonar driver measures this time-of-flight which is converted into distance and recorded in an array with the corresponding shoulder rotation angle. The sonar mapping module performs pre-processing of the signal to remove erroneous data and compensate for the wide beam width of the sonar. Signal processing of the sonar signal is performed to derive a circular model of the tank from the raw data.

E. Graphics Module

The graphics display on the large color monitor provides the operator with a physical sense of the robot arm's position inside the waste tank. Objects are portrayed as two-dimensional diagrammatic models. A plan view shows the orientation of the arm inside the tank and a side elevation view shows the robot arm configuration to the tank wall. The monitor displays robot joint angles, as well as the distance and orientation of the end of the arm to the tank. These views and information will greatly enhance the operator's efficiency in operating the robot within the tank. The graphics software module continuously reads the current position of all axes and uses the kinematic model to compute and display the configuration of the arm. The graphics display module also provides menu commands, status information, and messages to the operator.

VI. CONCLUSION

RedZone Robotics will deliver the RTI robotic system to WINCO in April 1990. The RTI robotic system will then become one of the first robotic systems deployed to remotely inspect hazardous waste tanks. The initial mission of the RTI will be remote visual inspection of corrosion inside the ICPP waste tanks. WINCO is currently planning additional development of the RTI robotic system including advanced tooling to sample the sludge and inspect the bottom of the tank, supervisory control to provide enhanced force control of the tooling, and a programmed mode of operation.

The RTI robotic system provides a 15.9 Kg (35 lb) payload, 1.8 m (6 ft) reach, five degree of freedom robotic arm that can be inserted through a 25 cm (10 in) diameter opening. The vertical deployment unit provides 5.8 m (19 ft) of servo controlled extension. The robotic arm can manipulate a variety of tools: inspection viewing systems, gripper, spray nozzle, or other specialized end of arm tooling. The arm can be flexibly mounted on a variety of platforms or even a mobile base. Its compact, high torque, electric, servo-controlled actuators can be re-configured with different linkages to customize a robotic arm of any configuration and degrees of freedom. The RTI robotic system is radiation and environmentally hardened to assure reliable operation in hazardous environments. The Intelligent Controller provides a multi-tasking environment to support digital servo control, I/O, collision avoidance, sonar mapping, and a graphics display. The controller, based on the standardized DOE architecture, is extensible to servo control almost any multiple axis application. In conclusion, the RTI robotic system and its components offer an innovative, standardized, and extensible design with broad applicability to remote inspection, decontamination, servicing, and decommissioning tasks.

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AUTOMATED SUBSURFACE MAPPING

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Abstract

Non-invasive imaging of the underground is an essential component of hazardous waste site investigations, yet, despite advances in sensor technology, high quality maps of the subsurface are difficult to obtain. Subsurface mapping depends on the spatial correlation of individual sensor measurements taken at multiple locations. Current manual data collection techniques, however, are suboptimal for precisely positioning subsurface imaging sensors and, in general, are quite inefficient. Use of the sensors also requires considerable experience on the operator's part to acquire and interpret sensor data. In short, locating and identifying buried objects and geological features is a process that relies heavily on human adeptness and expertise. Thus by applying automation and computer vision technologies to the problem, subsurface mapping can be improved.

In our Site Investigation Robot (SIR) project, prototypical robots are used to position ground penetrating radar (GPR) equipment with the accuracy needed to generate three dimensional subsurface maps. Estimating its site location by a combination of dead reckoning and inertial measurements, a rough terrain mobile robot deploys a gantry mechanism to scan the ground with the GPR antenna. Radar data are digitized and stored in three dimensional arrays for spatial correlation and image enhancement on a color graphics workstation. We have also applied basic image processing and visualization techniques to assist in the interpretation of these subsurface maps. Control of the robots and access to the software are through user-friendly interfaces, which facilitate the subsurface mapping process.

Introduction

For years, robotics and automation have increased productivity in manufacturing industries through standardization and repeatability. Core robotic technologies have now progressed to the point that robots are moving into the field and offering similar benefits performing tasks in unstructured settings. One class of these field robots is emerging to meet one of the most important challenges now facing the world: the clean up of hazardous waste sites.

One of the cost drivers in remediation of a site is the lack of information about the site itself. A detailed and costly investigation is required to develop a knowledge base of site geology, hydrology, chemistry, the extent of contamination, etc., that can be used to select appropriate remediation technologies and effectively plan the cleanup effort. Much of this expense can be attributed to inefficiencies in manual data acquisition techniques, lack of standard data collection procedures, and the cost of insuring and protecting the personnel who conduct the investigation. As an alternative, automation offers the prospect to collect large quantities of data in a form that supports more complete assessments and at a significantly lower cost.

Most investigations include efforts to locate buried objects that are potential sources of contamination (such as drums), identify and measure the extent of contaminant plumes, and determine the morphology of geological formations that affect pollutant migration. Commonly used methods to generate such information include resistivity measurements, acoustic techniques and ground penetrating radar. While each has unique advantages, no single method alone provides complete information, and all have limited utility owing to the inaccuracies and inefficiencies of manual sensor deployment. Ideally, the data resulting from the application of these non-invasive techniques can be used to construct an accurate graphical representation of the geometry of buried structures - a map of the subsurface.

In this paper we present the Site Investigation Robot, a system for automated subsurface mapping with ground penetrating radar (GPR), as one aspect of a program to automate hazardous waste site characterization. The Site Investigation Robot is a mobile robot that collects and spatially registers GPR data and recovers them to its base station where they are correlated, enhanced and displayed so that inferences about the shape and location of buried structures can be made. This program's broader goal is to develop robotic systems to make the data acquisition process faster and more complete and to apply advanced data processing techniques that will make these data more accessible and easier to interpret.

System Overview

The Site Investigation Robot consists of a robot and controller, data acquisition system, and a body of subsurface mapping software to manage, process and visualize data collected during investigation missions. The present configurations of these subsystems are described below; future enhancements planned for each are described in the section that follows.

Robot

The Site Investigation Robot prototype is pictured in Figure 1. We have employed an existing mobile robot, the Terregator (short for terrestrial navigator), a driverless, outdoor vehicle built for autonomous driving and exploration research, for the data acquisition aspect of this project. Terregator is a rugged, six-wheel, skid-steer locomotor scaled and powered to negotiate moderately rough terrain and steep slopes.

On both the right and left sides of the base locomotor, three wheels are linked together with chains and driven by a low-speed, DC motor through a harmonic gear unit. This drivetrain, in conjunction with off road floatation tires, gives Terregator excellent tractive characteristics to overcome obstacles and grades. For position feedback, each motor is coupled to an incremental rotary encoder. Theoretically, this arrangement gives the Terregator open loop positional accuracy in the sub-millimeter range; in practice, tire deflections, vehicle/ground surface interaction and other non-linearities limit Terregator's dead-reckoning ability to distances on the order of centimeters.

To position subsurface imaging sensors, a single-axis gantry mechanism is attached to Terregator's frame forward of the generator such that the direction of motion is perpendicular to the mobile robot's path. The mechanism consists of a buggy that is pulled along parallel fiberglass 'I'-beams by a chain belt driven by a DC motor. The GPR antennas are suspended from the buggy with threaded rods for height adjustment. A rotary encoder directly coupled to the motor allows the antenna to be positioned accurately to one centimeter over the entire two-meter length of the gantry. Limit switches at each end of the gantry ensure safe operation and provide a convenient way to identify the antenna's limits of travel.

A 3kW, 120 VAC gasoline generator and ventilated, shock-isolated electronics enclosure are mounted atop Terregator's base to provide power for the locomotion, computation, sensing and communications. Raw generator output is tied in to the base locomotor's 90 VDC power supply; the generator output is also conditioned by an uninteruptible power supply (UPS) for more sensitive devices, including telemetry equipment, onboard computers and disk drives, safety logic, sensors and interface electronics. Substantial auxiliary power is available for mission specific payloads, such as GPR equipment.

At the heart of the Terregator is a VMEbus card cage that houses a 68020 CPU card with 4 Mbyte onboard memory, SCSI and ethernet ports. The system CPU functions as a multi-tasking controller, coordinating and sequencing locomotion and gantry motions, GPR data acquisition, communications with the base station and system monitoring functions. Other boards in the card cage include a serial interface card, two 2-axis motion control cards, and a sensor interface card with eight channels of analog-to-digital (A/D) conversion, four channels of digital-to-analog (D/A) conversion and 16 bits of digital I/O. All connections to these boards are made through an intermediate patch panel that facilitates the addition of new sensors and other peripherals to the basic system. For development purposes, a single board workstation and disk are located on the equipment deck above the electronics enclosure and interfaced to Terregator's CPU via an ethernet cable. The organization of these components is shown graphically in Figure 2.

Controller

The Site Investigation Robot is intended for use by persons who are much better versed in the practices of field screening, data collection and analysis than they are in operating a robot. It is thus essential to hide the complexities of controlling the robot from its users and make interactions with the SIR as simple and straightforward as possible. This motivated us to develop a control architecture that allows SIR users to command and monitor the robot at a high level while masking the details of implementing expressed user intentions.

The SIR command interface presents the user with a set of 2-D surface maps of the site, that show the size, spatial location and orientation of boundaries, known man-made structures (e.g., buildings and roads) and natural features (e.g., trees and surface water bodies) in a consistent, user defined site coordinate system. These maps are created with a simple CAD package, developed specifically for this purpose, at the outset of a site investigation, and can be updated and edited as the investigation proceeds. To initiate a data acquisition run, the user first displays a map of the site on the base station computer by recalling a file that contains a CAD description of a particular region of interest. Site boundaries are indicated by straight line segments while all known objects and other obstacles to the mobile robot are shown as polygons. Using the computer mouse, the user then draws a bounding box (a rectangle that encloses part of the map) around the area of the site from which data is to be collected.

A set of routines to plan a path that covers all of the obstacle-free ground surface within the bounding box are then invoked. First, the dimensions of the bounding box and all obstacles it contains are adjusted using dimensional parameters of the SIR. In this algorithm, the robot's effective turning radius is calculated by finding a circle within which all parts of the skid steered locomotor will remain when it turns in place. All sides of the bounding box and all included polygonal obstacles are 'grown' by an amount equal to the radius of that circle. Should the transformed bounding box be found to intersect a site boundary, which is a pathological case for the current path planner, the initial bounding box is rejected and the user instructed to redraw it. Once an acceptable bounding box is found, the robot can be modelled as a single point travelling through a more constricted space, thus simplifying subsequent path planning.

Planning paths for the Site Investigation Robot is a departure from traditional mobile robot path planning in the objective is to cover as much of the ground surface as possible, rather than finding the shortest route between two points. The SIR path planning problem is constrained by the mobility characteristics of the Terregator mobile robot. Terregator can faithfully execute straight line motions of specified length by dead reckoning, in which the wheel encoders are used to measure distance travelled; it can also make accurate turns in place, using a gyroscope to measure the angle of rotation. However, the indeterminacy of Terregator's skid steering makes following an arc of specified curvature difficult even on hard, flat surfaces. For this reason, we have limited all driving to straight line motions and point turns. This is acceptable given the data acquisition protocol described below.

SIR's path planner examines the resulting free space in the transformed bounding box and finds a way to cover it such

that the number of turns are minimized. If obstacles are present the user selected area is divided into smaller obstacle-free areas, and a path is planned for each. Since there are often multiple ways to perform the subdivision, solutions are not always unique. Furthermore, there is no way to guarantee that the resulting path is optimal. However, once a path is found, it is overlaid on the site map for validation. This affords the user the opportunity to draw smaller bounding boxes and specify point-to-point moves that connect the subregions of the map.

The final path description is translated into a sequence of driving commands (straight lines and rotations) that are placed in a queue and transmitted to the robot via a wireless modem. Using a software joystick, the robot is then teleoperated to its starting point and set on its route. While driving, the robot transmits its location back to the base station which is displayed as an icon on the site map. Other status information is similarly relayed so that the user can supervise the data acquisition mission.

Subsurface Mapping Software

The Site Investigation Robot deploys and supports a commercial ground penetrating radar set (Geophysical Survey System, Inc. SIR-3) to acquire subsurface data. A data acquisition run is comprised of combinations of Terregator drive motions and gantry movements in which the basic procedure is to move the antenna from one limit to the other and then drive forward some incremental distance. At regular intervals through the antenna's travel, a series of radar pulses are transmitted into the ground and the energy reflected to the receiving antenna amplified, filtered and digitized. These signals are stored adjacently in a buffer until the antenna has completed a full scan. The result is a two dimensional data array, in which the columns are individual GPR waveforms, stored on disk as an image along with the mobile robot's site coordinates. More details on the principles of GPR are presented in the Appendix.

Every row of pixels in the GPR image contains data acquired at a constant time delay relative to the transmitted pulse. That time delay is converted into a distance from the antenna by the speed of electromagnetic wave propagation in the imaged subsurface media based on measured and/or inferred electrical parameters. Since the position of the mobile robot and the position of the antenna relative to the mobile robot are measured for every recorded GPR waveform, it is possible to assign three spatial coordinates to each pixel in the image. It is this position tagging that makes it possible to spatially correlate and visualize GPR data in three dimensions.

Each recorded waveform spans a depth range that is governed by the wavelength of the transmitted energy and the electrical properties of the subsurface medium. Generally speaking, there is a trade-off in depth of penetration and the physical dimensions that can be resolved. The 500 MHz antenna used in this work can image structures buried to depths of 3 meters with 5-10 cm resolution in the best of conditions (e.g. dry, sandy soils); lower frequencies penetrate deeper at the sacrifice of resolution. GPR performance is poorer in materials with high conductivity and high dielectric constant - conditions associated with high moisture content - due to attenuation of the radar energy. In saturated soils and clays, imaging potential may be limited to depths of only one meter,

This data acquisition procedure is repeated until the robot has covered its entire planned route. Once the robot returns to its base station, all acquired images are transferred from its onboard disk to mass storage devices connected to the base station computer for archiving and processing. Acquired GPR data are arranged in volumes, each containing a set of parallel subsurface sections stored as images. Individual sections are stored as files that also contain other parameters, including location of the scan, date and time of acquisition, and radar gain and time base settings. These files are organized in a Unix file system such that each subdirectory corresponds to a unique site volume. Each subdirectory also contains an additional site index file that is used to retrieve and store individual images. Figure 3 shows an example of a site map from which nine volumes of the subsurface would be scanned.

Since the intuition of experienced field screening personnel is still required to apply the appropriate processing steps and

choose parameter values to make sense of the images, we have developed a set of programs to process GPR data acquired by the Site Investigation Robot that are called by the user through a common menu-driven interface. This software package, known as *gpr-shell,* includes routines for reading and writing data files, applying time domain filters to individual records, displaying of 2D subsurface sections as color or gray-scale images, scaling and windowing images, spatial correlation all GPR records in a subsurface volume, and a variety of image enhancement functions. To facilitate processing, *Gpr-shell* also provides command line completion, prompting, and on-line help. It also provides the user with an 'on-line lab notebook', in which the steps and parameters used to process each image are automatically recorded for future reference.

In order to transform raw GPR data scans into high resolution images, several processing steps have been implemented, as illustrated in Figure 4. (We have yet to identify a single methodology or set of parameters that can be successfully employed to generate interpretable subsurface maps from all GPR data, however, the following steps are generally taken.) First the signal is deconvolved with the return signal from a pulse transmitted into air. Deconvolution is a matched filter operation that removes the effects of the secondary pulses from the return signal and effectively transforms a return from the transmitted pulse into the return that would have been caused by an ideal impulse function. The resulting signal is then low pass filtered to remove noise components introduced by the deconvolution.

The waveform recorded at each grid point is actually a composite of all radar reflections within the antenna's conical beam pattern due to the poor focusing of the GPR antenna. However, since the spacing between surface grid points is accurately measured, we are able to correlate all of the measurements and synthetically focus the antenna. A process known as 'migration' is applied to convert the deconvolved and filtered data into a representation of the subsurface. Migration is very similar to the synthetic aperture focusing techniques used for high resolution pipe location. in that its underlying principle is data from adjacent scans tend to reinforce one another.

A three dimensional array of GPR data is constructed by sampling data from vertical sections in the scanned volume. The value in each cell, or voxel (for volume element), is then added to all array locations equidistant from the transmitter and within the antenna beam. This effectively 'spreads' each part of the return signal over surface that is a locus of points with the same time of flight from the antenna. By applying this algorithm cell in the array, the recorded signals originally associated with individual voxels constructively interfere with one another. This reinforcement indicates the presence of an impedance discontinuity at the corresponding subsurface location and emerges in the migrated image. Migration can thus be used to effectively focus the transmitted radar beam. (We note, however, that its success requires a good estimate of the soil's dielectric constant, which determines the speed at which GPR waves travel through the subsurface, and the antenna beam pattern and soil conductivity, both of which influence attenuation.)

Once a volume of data has undergone 3-D migration, vertical and horizontal sections are extracted from it as individual images. These images are then enhanced by a number of image processing operations, including 2D low- and high-pass filters of varied bandwidths, edge detectors and region growing operators, depending on the image features of interest.

Figure 5 through 7 show the results of these processing steps. All three are images of a small metallic drum containing water buried in sand. Figure 5 is a vertical section of raw data and Figure 6 is the same image after deconvolution and migration. In this case, the barrel cross section is best seen by the thresholding of the image after it is finally processed by the 2-D high pass filter (Figure 7).

Future Enhancements

A number of enhancements to our current system are planned to increase its ability to operate on waste sites, ease its use, and improve the quality of the subsurface maps it generates.

For sites with very rough terrain and/or numerous obstacles, improving the mobility of the base locomotor will result in a greater percentage of ground surface that SIR can cover. This can be accomplished with suspension, greater ground clearance, replacing the wheels with tracks, etc. An even more significant performance increase can be realized by improving SIR's position cognizance, regardless of its mobility characteristics. The most promising technologies to provide a more accurate measurement of the robot's location on the site are inertial navigation units (INS) and global positioning (GPS) receivers, both of which can be deployed onboard and readily interfaced to the robot controller. By providing a position estimate that is independent of the robot's dead reckoning, the robot can be navigated with a closed loop path tracking control scheme, a paradigm in which the robot's actual (measured) position is used to correct for deviations from the planned path that may result from wheel slippage or other controller disturbances. Path tracking control using combined INS and GPS has successfully guided our NavLab mobile robot at speeds exceeding 20 km/hr; more recently, the same controller has been ported to an off-road dump truck.

More accurate GPR antenna positioning can also be achieved by replacing the gantry mechanism with a multi-degree-of-freedom robot arm. Our concept for such a sensor deployment arm (SDA) is a long reach mechanism able to position and orient sensor payloads weighing up to 10 kg. over a 2 meter x 2 meter area, adjusting to any undulations of the terrain. The principal advantage of an SDA is greater integrity of the sensor position measurements - complete a 3D data array can be collected with a common frame of reference, eliminating the possibility of positioning errors between adjacent scans due to motions of the mobile base, which are typically an order of magnitude less accurate than manipulator movements.

There appears to be a synergy between the Site Investigation Robot and geographical information systems (GIS), another emerging technology for waste site investigations. Geographical information systems are software tools for cataloging; manipulating and displaying any form of data that can be related to a cartographic map. GIS applications include land use management, record keeping of legal boundaries, roads and utility networks, agriculture, and many others. A GIS can be also linked to a relational data base to provide a powerful tool for site investigation. Many available GIS packages include routines to enter previously digitized terrain maps and survey data which would aid in the development of site maps for the SIR user interface. The other attractive feature of GIS is simplified storage and retrieval of data: entry of acquired position tagged data into the GIS data base can be automated and its recall reduced to the simple positioning of a cursor in the display window.

Two advances in subsurface mapping software are currently being pursued. One is the development of more general three dimensional migration algorithms that will account for the non-homogeneous nature of the subsurface nature of the subsurface medium. This will entail assigning permittivity and conductivity values to each voxel in the scanned subsurface volume in order to better model GPR wave propagation. Techniques to measure and/or infer these parameters will have to be developed to make the best use of this algorithm. In addition faster processing engines and techniques will be required to achieve results in useful time frames. The second advancement will be the application of three dimensional enhancement and rendering techniques to subsurface maps. Such techniques exist in the domains of medical imaging and geological exploration, but have yet to be adopted for GPR.

Finally, our goal is to integrate these hardware and software elements into the more complete system for waste site characterization, as shown in Figure 8.

Summary

Subsurface mapping is a discipline that has advantageously adopted technologies from the domains of robotics and computer science. In this research, we have successfully implemented registration of sensor position and automated acquisition of sensor data using a robot, and thereby created opportunities to apply processing techniques to create 2-D and 3-D subsurface maps of higher quality than previously attainable. This and other spatially correlated information that the Site Investigation Robot generates can be used to

more effectively characterize waste sites and ultimately lower the expense of site cleanups.

More generally, robotics and automation can benefit waste site characterization in a number of ways.

- The enormous data requirements will be satisfied faster and at lower cost when data are acquired by robots.
- The quality of those data will be enhanced through standardized, repeatable measurement techniques.
- By automatically indexing measurements by position in a geographical information system, opportunities for numerical modeling, graphical visualization and straightforward data correlation are created.

The Site Investigation Robot is an example of an emerging class of robots dedicated to the solution of hazardous waste problems. We view the SIR be the first in a family of robots for environmental applications. Systems that follow will have additional perceptive capabilities and self-reliance to perform detailed site assessments.

Acknowledgments

This research is sponsored through a cooperative agreement with the U.S. Environmental Protection Agency and a grant from the Ben Franklin Technology Center of Western Pennsylvania. We also acknowledge RedZone Robotics, Inc., for its participation in the Site Investigation Robot project.

Appendix: Principles of GPR Sensing

Ground penetrating radar works by transmitting an electromagnetic pulse into the earth which spreads as a conical wavefront as it travels further from the antenna. When the radar wave reaches a discontinuity in electrical impedance of the subsurface, an echo is returned, the strength and the phase of which indicate the magnitude and sign of the change. Mathematical descriptions of these interactions in all but the simplest of cases defy closed form solutions; even finite element methods are too cumbersome for practical modeling of the GPR phenomenon. Fortunately, modeling the physics using geometrical optics can produce meaningful results. With this simplification, the transmitting antenna is treated as a light source from which rays emanate and are reflected to the receiving antenna. The distance to the point of reflection (assuming a direct reflection) can thus be estimated with time-of-flight measurements, i.e., the latency of the echo relative to the transmitted pulse.

A difficulty with the optical assumption is the poorly focused radar beam. Commercially available GPR antennas are designed to limit beam spread of the transmitted wave to an elliptical cone, however, for a single return, the exact location of an echo within this volume cannot be determined. To resolve this ambiguity, the antenna is scanned in a line over the ground surface to create an ensemble of return signals. Latency of echoes are lowest when the antenna is directly over an object and increase as the antenna moves away. By combining recorded echoes from points along the scan line, distinctive curves are generated which are then interpreted by GPR experts to identify subsurface features.

In practice, there are several factors that complicate the radar return. Time of flight measurements on return echoes depend on knowledge of the propagation velocity of the transmitted pulse, which is not a constant but instead depends on electrical permittivity (or equivalently, dielectric constant) of the subsurface material. This introduces uncertainty in the measurements, which is currently resolved either by calibration in the field or simply by estimation of subsurface permittivity. Both the transmitted and reflected radar waves are attenuated due to losses in the media that are governed primarily by its conductivity, another parameter requiring estimation. Geometric dilution of the wave energy as the beam spreads with distance travelled is a further complication since the exact shape of the antenna beam pattern within the subsurface medium cannot be determined. Finally, the difficulties of controlling the shape of the transmitted pulse at GPR operating frequencies (one hundred megahertz to over one gigahertz) introduce additional return signals that confuse the main return echo and must be removed.

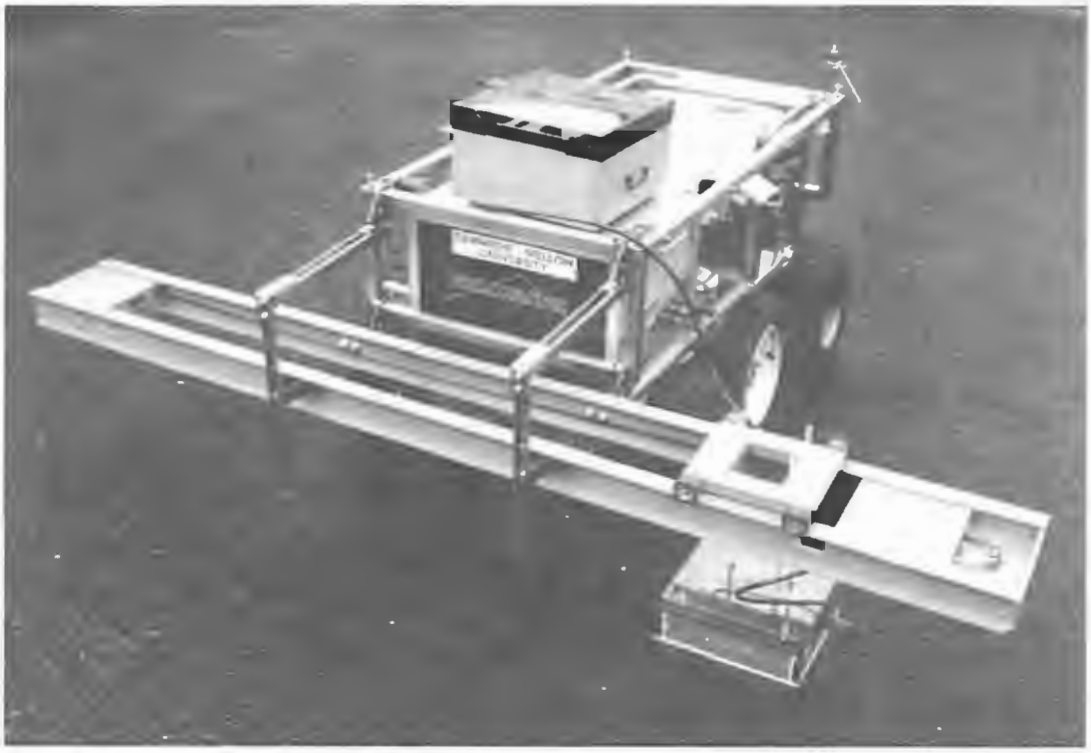

Figure 1. Site Investigation Robot prototype

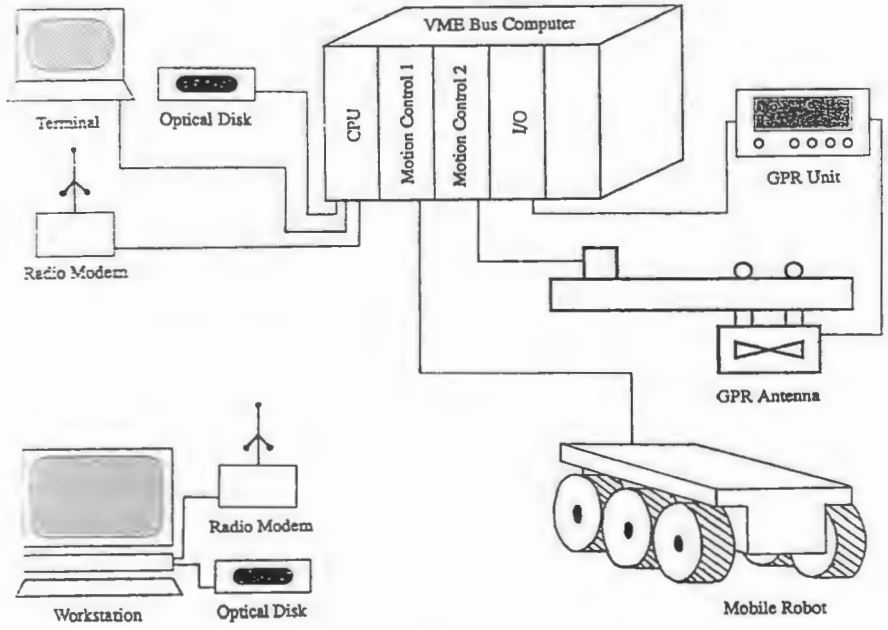

Figure 2. SIR schematic

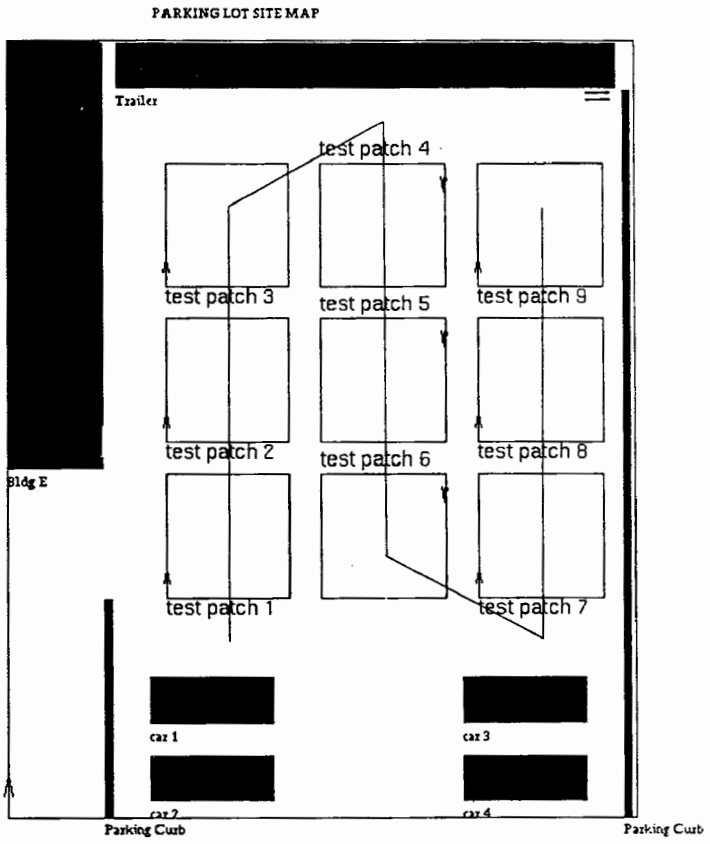

Figure 3. Site map with nine scanned subsurface volumes

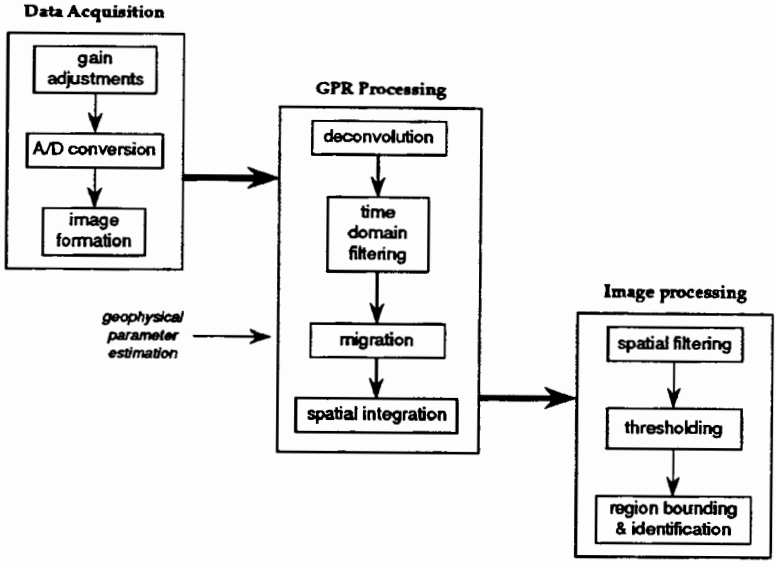

Figure 4. Ground penetrating radar processing steps

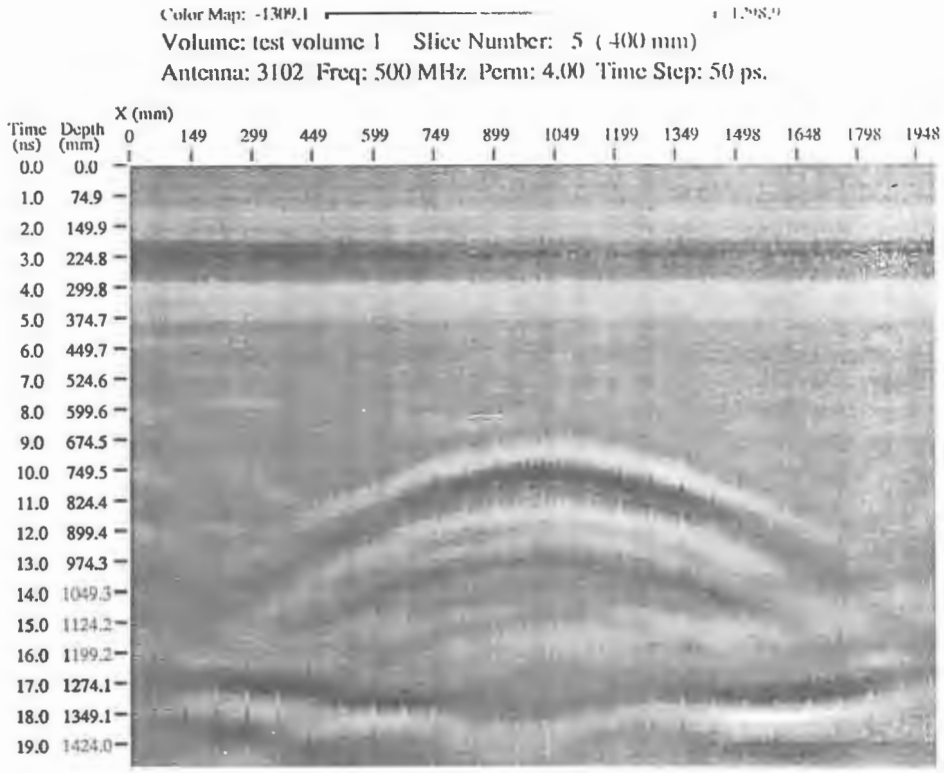

Figure 5. Vertical section of buried drum (raw GPR data)

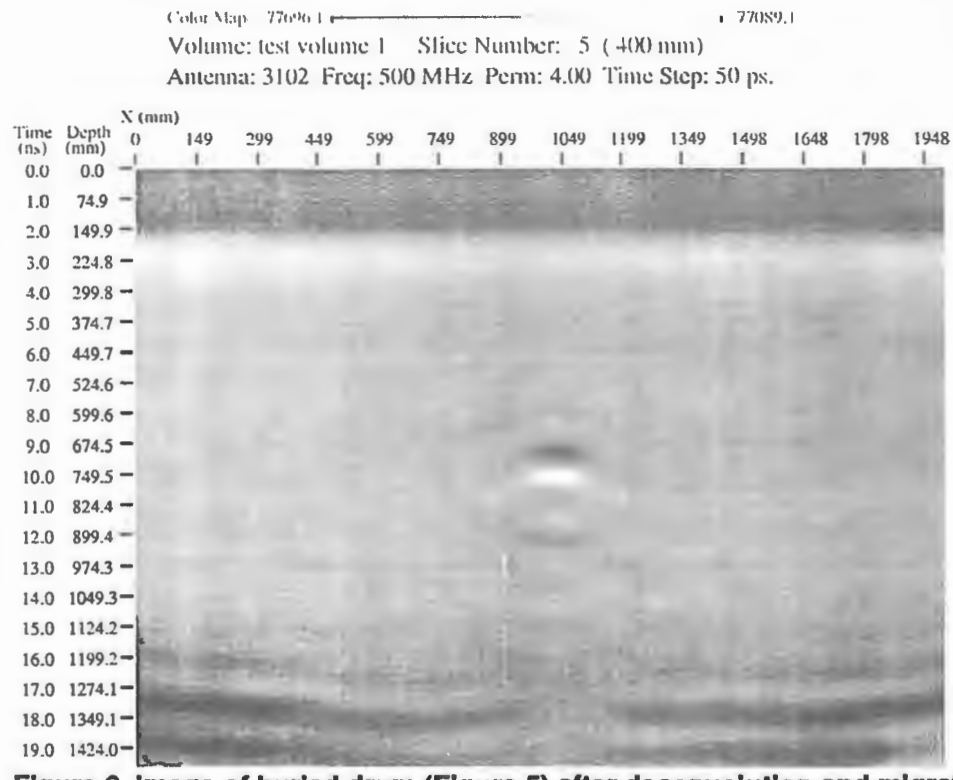

Figure 6. Image of buried drum (Figure 5) after deconvolution and migration

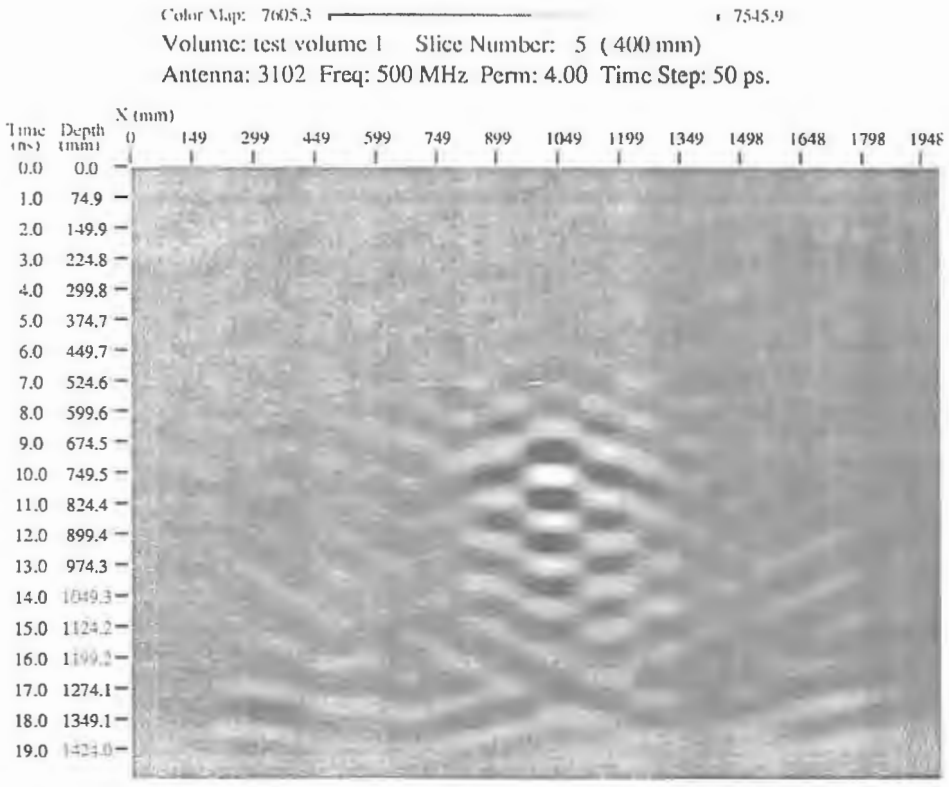

Figure 7. Drum image from Figure 6 following 2-D high pass filter and thresholding

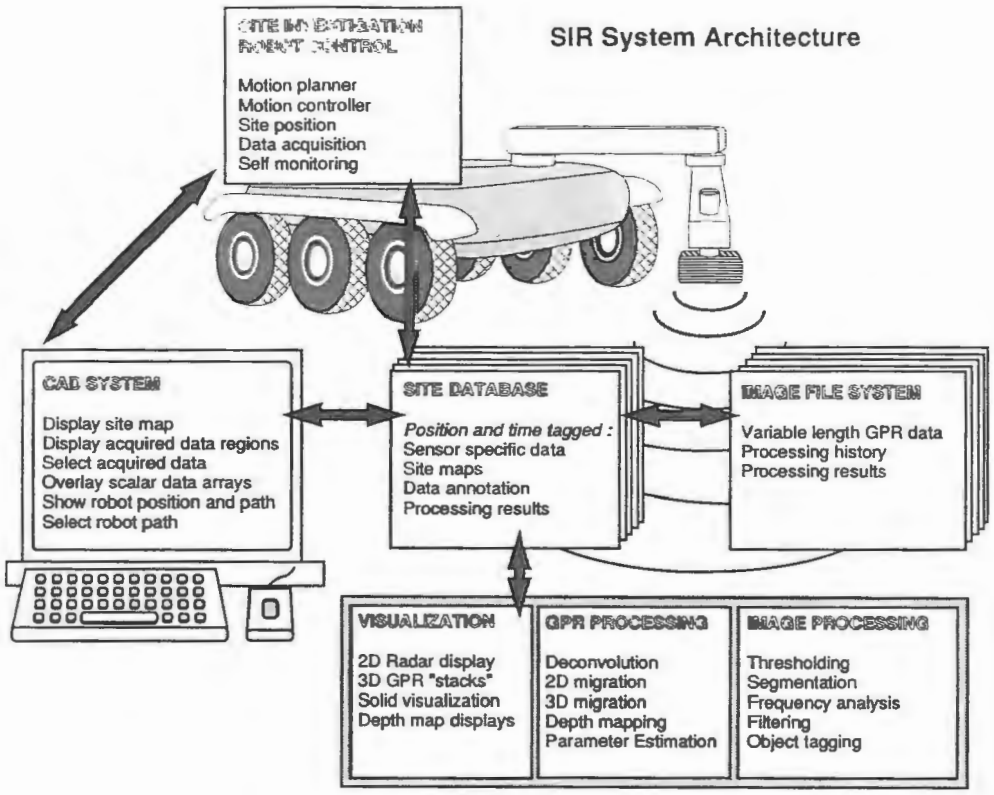

Figure 8. Site Investigation Robot system architecture

DISCUSSION

BRIAN PIERCE: My first question has to do with using ground penetrating radar, as just one example, or using a magnetometer as another type of sensing device. And the second question has to do with the use of a pair of robots or a team where you could take advantage of forward scattering using the ground penetrating radar. Right now it seems to me you're just using back scattering in a monostatic configuration.

JAMES OSBORN: That's certainly correct. If you recall the viewgraph that Ann put up, they are actually going to pursue the magnetometry type of sensing. In fact, there is really a whole class of sensors that can be put on it. Each one has unique requirements. In particular, some of the magnetic techniques can't be near these very metallic robots. So you've got to come up with long deployment booms. The idea of doing bistatic radar soundings is an interesting one. I can think of a couple ways that do that. One is to have a multiple arm system on a single mobile base. And the other is to actually go with two mobile bases. I would, at this time, say the preferred way would be the former (two arms) because of the ability to register a manipulator and/or affect your position with much higher accuracy than you could a mobile robot.

CHRISTOPHER FROMME: There are some excellent available technologies for registering line of sight over short ranges, like the distance between the two of us right now. So the idea of a pair of robots working in unison and precision may have some merit.

DOUGLAS LEMON: Is this technology resident in the university or is it in the RedZone Robotics Company, and who has funded this?

CHRISTOPHER FROMME: The project is funded by EPA. And the technology is currently in the university, although we have had some collaboration from RedZone, in particular to turn out that robot controller that drives the system. So we are getting some collaboration from RedZone, but the project is resident at CMU.

DOUGLAS LEMON: Do you expect this technology to eventually be commercially available? Is that where you're headed?

CHRISTOPHER FROMME: Yes. If not, then it doesn't make any sense to do it.

A QUALITY ASSURANCE SAMPLING PLAN FOR EMERGENCY RESPONSE (QASPER)

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Abstract

Integration of critical elements into a comprehensive Quality Assurance Sampling Plan (QASP) is crucial to implementation of an effective plan. How can a project manager ensure consideration of all these elements? Utilizing a software package called QASPER, a project manager is prompted to consider elements necessary to generate a comprehensive Quality Assurance Sampling Plan for Emergency Response.

QASPER is a PC-based software package which compiles generic text and user provided, site-specific information into a draft QA/QC Sampling Plan for the Removal Program. QASPER addresses the nine sections of a QA/QC Sampling Plan, as specified in OSWER Directive 9360.4-01, Removal Program QA/QC Interim Guidance, Sampling QA/QC Plan, and Data Validation Procedures (revised April, 1990). Sections include: Initial data, background information, data use objectives, QA objectives, approach and sampling methodologies, project organization and responsibilities, QA requirements, deliverables, and data validation.

QASPER was created to facilitate the timely assembly of a comprehensive sampling plan for emergency response actions. By thorough consideration and attention to the necessary requirements of QA/QC sample planning through an automated process, it is anticipated that reliable, accurate and quality data can be generated to meet the intended use.

The On-Scene Coordinators (OSC) or the Technical Assistance Team (TAT) contractors are the primary users of QASPER. These individuals will have access to the site specific information and the sampling objectives which characterize a particular hazardous waste site investigation. They are also responsible for assembling the information into an acceptable plan for implementation.

The system, however, is applicable to many regulatory programs that require the completion of QASPs.

Features of QASPER are numerous. QASPER is self contained, no other software is required for support. ASCII outputs are generated so that files may be uploaded to other word processing packages for further manipulation. Database files on all previous sampling plans are retained. Consistency and comprehensiveness of sampling plan creation efforts are maintained throughout office, region or zone, therefore, sampling plans are created more efficiently. Redundant data entry is minimized by integrating repetitive information throughout the plan after one entry. The user is provided access to standardized generic text with the capability to overwrite and edit. QASPER allows for flexible data entry throughout the plan. QASPER runs on an IBM PC or 100% compatible, with a hard drive, 640K RAM and a printer (for hardcopy output).

Introduction

The U.S. Environmental Protection Agency (EPA) has divided the Superfund cleanup program into short-term and long-term remedial activities. Short-term investigative and mitigative efforts, typically addressing imminent threat, are referred to as "Emergency Response Actions" under EPA's Removal Program. To ensure adequate and comprehensive response, sufficient time must be allocated for thorough planning; however, planning is often regarded as a luxury in an emergency response scenario.

The EPA has taken a number of steps to establish planning criteria for emergency response actions which are sufficiently detailed to ensure that data generated will be of known quality to serve its intended purpose and are commensurate with the emergency response timeframes. The first of these steps was the establishment of data quality objectives (DQOs) for the Removal Program. Second, EPA also established a minimum framework for an acceptable Quality Assurance Sampling Plan. Both of these guidelines are set forth in OSWER Directive 9360.4-01 released April 1990 (Publication No. EPA/540G-90/004).

This paper will describe the Removal Program DQO's, define the framework of the QASP, and describe a third, innovative step EPA has taken in creating a software package which facilitates the timely assembly of both into a comprehensive plan ready for implementation in an emergency response. The majority of this paper will describe the features of the software program.

Removal Program Data Quality Objectives

The quality of data is determined by its accuracy and precision against prescribed requirements or specifications, and by its usefulness in assisting the user to make a decision or answer a question with confidence. OSWER Directive 9360.4-01 guides the user in defining data quality within a framework that also incorporates the intended use of the data. The guidance is structured around three quality assurance objectives, each associated with a list of minimum requirements. The three QA Objectives, hereafter referred to as QA1, QA2 and QA3 are described as follows:

QA1 is a screening objective to afford a quick, preliminary assessment of site contamination. This objective for data

quality is for data collection activities that involve rapid, non-rigorous methods of analysis and quality assurance. These methods are used to make quick, preliminary assessments of types and levels of pollutants. The primary purpose for this objective is to allow for the collection of the greatest amount of data with the least expenditure of time and money. The user should be aware that data collected for this objective have neither definitive identification of pollutants nor definitive quantitation of their concentration level.

QA2 is a verification objective used to verify analytical (field or lab) results. A minimum of 10% verification of results is required. This objective for data quality is for data collection activities that require qualitative and/or quantitative verification of a "select portion of sample findings" (10% or more) that were acquired using non-rigorous methods of analysis and quality assurance. This quality objective is intended to give the decision-maker a level of confidence for a select portion of preliminary data. This objective allows the user to focus on specific pollutants and specific levels of concentration quickly, by using field screening methods and verifying at least 10% by more rigorous analytical methods and quality assurance. The results of the 10% of substantiated data gives an associated sense of confidence for the remaining 90%. However, QA2 is not limited to only verifying screened data. The QA2 objective is also applicable to data that are generated by any method which satisfies all the QA2 requirements, and thereby incorporates any one or a combination of the three verification requirements.

QA3 is a definitive objective used to assess the accuracy of the concentration level as well as the identity of the analyte(s) of interest. This objective for data quality is available for data collection activities that require a high degree of qualitative and quantitative accuracy of all findings using rigorous methods of analysis and quality assurance for "critical samples" (i.e., those samples for which the data are considered essential in making a decision). Only those methods that are analyte specific can be used for this quality objective. Error determinations are made for all analytes of the critical sample(s) of interest.

Quality Assurance Sampling Plan Framework

There are nine sections to a Removal Program QA Sampling Plan. Section 0.0 addresses basic information requirements such as site name, relevant work order numbers, primary personnel names and titles, etc. Section 1.0 solicits information about the location of the facility, type of facility, type and volume of materials to be addressed, sensitive adjacent environments, and action levels. Section 2.0 addresses data quality objectives (DQOs), i.e., regarding decisions the data will support. Section 3.0 addresses the linkage of DQOs with matrix and parameters. The project manager must decide which parameter will be assessed, by matrix, for which intended data use, at which QA objective (QA1, QA2, or QA3). Section 4.0 addressed the Sampling Approach and Methodologies, including documentation requirements. This section will include a discussion of sampling design, type of equipment, fabrication and whether equipment decontamination will be employed, standard operating procedures, numbers of field samples and control samples needed to achieve the stated QA Objectives. It also includes a timetable for sampling activities.

Section 5.0 addresses information about what personnel are assigned which responsibilities, and which laboratories will be analyzing which samples. Section 6.0 discusses the requirements necessary to achieve the quality assurance objectives identified in Section 3.0. Section 7.0 addresses the types of deliverables to be produced and what they will contain. Section 8.0 addresses the degree of data validation necessary to achieve the identified QA Objective.

Quality Assurance Sampling Plan for Emergency Response (QASPER)

QASPER is a PC-based software package which compiles generic text and user provided, site-specific information into a draft QA/QC Sampling Plan for the Removal Program. QASPER addresses the nine sections of a QA/QC Sampling Plan, as specified in OSWER Directive 9360.4-01, Removal Program QA/QC Interim Guidance, Sampling QA/QC Plan, and Data Validation Procedures.

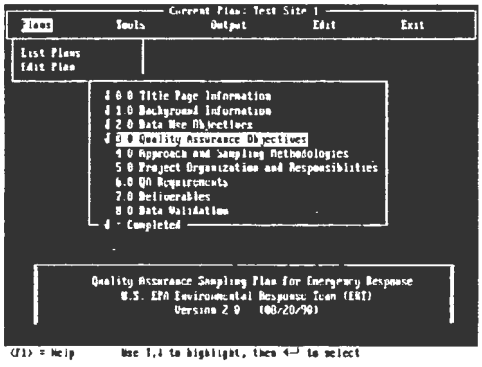
The site manager (On-Scene Coordinator) or contractors are the primary anticipated users of QASPER.

These individuals will have access to the site specific information and the sampling objectives which characterize the site investigation. It is their responsibility to assemble that information into an acceptable sampling plan for implementation.

QASPER has a database of standard generic text which is utilized in an electronic "cut and paste" process with user provided site specific information to create a draft QA Sampling Plan. This approach enables the user to focus on critical information while the software manages both the presentation and correlation of that information with other essential data.

Perhaps the best way to illustrate this process is to "walk through" QASPER. The user should progress in a sequential manner, starting with section 0.0 because the plan database will build on previously provided information. This feature avoids the need for redundant input of data which must appear in several sections of the completed plan. It is possible to skip sections, or avoid certain input requirements (e.g., when information requested is not yet known to the user). This allows the user to create those portions of the database at times that are convenient to the user. However, it may not be possible to complete certain sections (most notably the DQO sections: 3.0, 6.0, and 8.0) without providing certain information in preceding sections (e.g. Section 2.0).

Figure 1. Main Edit Plan Menu



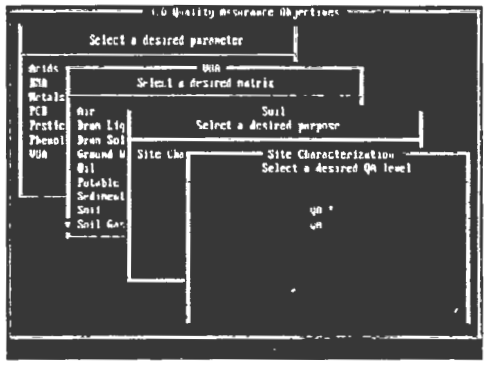
Section 0.0 identifies certain information required to complete the title page of a Sampling Plan; some of information will also be utilized elsewhere throughout the completed plan. If the user chooses not to enter the information requested,

the completed plan (through the Output menu) will be assimilated as if that information was not requested. Should the user wish to add alternate information currently not requested by QASPER, this would be accommodated through the Edit menu after the plan has been compiled from the database (through the Output menu).

Section 1.0 solicits background information about the site. The user is first prompted to geographically locate the site, characterize its size and operating status, i.e., operational or abandoned. The user is requested to provide information about the type of facility. (This information request is currently limited to one response per category). For sites with multiple facility types, the user may enter this data through the Edit Text menu after the file has been compiled. Next, the user is requested to provide information about the materials handled, the surrounding environs and populations. Responses to these requests are facilitated by pop-up menus of standard responses. In the last three parts of this section, the user provides the information requested by typing onto free-form test screens. Although there is room for multiple page responses under each information request, one to several paragraphs should be sufficient.

Section 2.0 requests information regarding the objective and purpose of the sampling event. How does the user expect to utilize the resultant data? Several standard responses are provided and may be accessed by the arrow keys and or selected by the "Return" key. The user may input an alternate "objective" or "purpose" by selecting the "Other" category and specifying the other use. The return key is utilized to mark or unmark each item. A critical consideration for any data collection event is whether the data will be evaluated against an existing database or action level. Specification of the contaminants of concern and their respective actionable levels will help determine appropriate analytical methods and quality assurance needs later in the plan. Multiple selections are permissible from the screen. Selections under the "Purpose" group will be carried forward to other sections of the plan. This section, therefore, requires input in order to enable the user to complete portions of Sections 3.0, 4.0, 6.0, and 8.0.

Figure 2. Section 3.0 QA Objectives Menu



In Section 3.0, the user will select among various parameters to identify the class of compounds to be investigated. This parameter selection will initiate the DQO logic for a parameter, in a matrix (next menu), for a given purpose (subsequent menu), at a selected Quality Assurance Objective (subsequent menu). At the end of the logic path, the user will be brought back to the parameter menu to make another selection, if appropriate. QASPER remembers the last logic path, therefore if the user wishes to select the same parameter, same matrix, same purpose, and a different QA Objec-

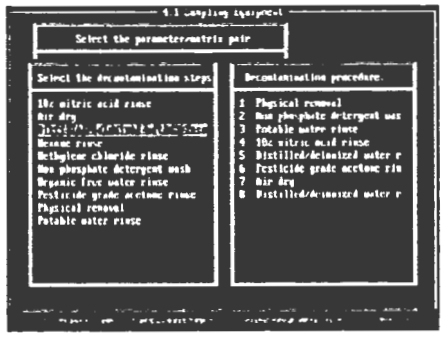
tive, he/she need only move the highlight on the last option.

Section 4.0 of the system solicits information about the proposed sampling rationale and how sampling will be conducted. There are five subsections which address the following:

1. Sample Equipment

The user is requested to identify sampling equipment that will be utilized, what material it is made of (fabrication), and whether it is to be dedicated and/or decontaminated. The user must identify the sampling tools which will be used to collect samples from the various matrices. This process is initiated by first selecting a matrix from among those previously identified in Section 3.0. Next, the user will identify the type(s) of equipment to be used in the various matrices selected. The emphasis here is on the equipment which will be utilized to obtain the sample from the environment and transfer it to the sample container. Most of the equipment in the menu has a corresponding Standard Operating Procedure (SOP) available in Subsection 4.3.

Figure 3. Sampling Equipment Decontamination Sequence Menu



The user is also requested to identify the equipment fabrication, or material of construction. This is important so that the quality of the sample is not compromised, inadvertently, by the materials it comes in contact with during sample collection. This is usually critical for low concentration investigations, or situations of incompatibility between sample contaminants and sampling device fabrication. If the equipment is not dedicated, QASPER will import generic text describing decontamination procedures and solicit additional information about the user's preference for the decontamination sequence and chemicals (e.g. solvents) of choice. The user will highlight, or select, the decontamination steps from a menu in the order he/she wishes the sequence to be conducted in the field. A manifestation of that sequence will be compiled in the plan output.

2. Sampling Design

In this section, the user will indicate the sampling design or grid proposed to achieve the sampling event objective. It is expected that the user will detail where and how many samples will be collected. A basis for the sampling scheme would be described herein, and a sampling map would be referenced. QASPER will print a blank page with the name of the site and the title, "Sampling Location Map", for incorporation of this map.

3. Standard Operating Procedures

There are three sections to the SOP subsection, addressing standard text for Sample Documentation, Sampling, and Sample Handling and Shipment. QASPER allows the user to choose existing generic text from the database, or

write new text to describe how sample documentation will be achieved. If the user selects "Write own Text", a free form edit screen of several pages will appear to receive the user's narrative.

Figure 4. Available SOPs Menu

QASPER enables the user to choose from an inventory of standardized SOP texts to prepare a description of how the sampling event will be conducted. There are several approaches for incorporating Sampling SOPs:

-The user may import only the titles of SOPs into the compiled plan. This reduces the bulk of the final plan document and may be appropriate where all users of the plan would have access to a repository of the actual SOP texts.

-The user may import title and text into the compiled plan. This allows the final plan to be a "stand alone" document.

-The user may import any portion of the generic titles and text available through QASPER and/or modify and add SOPs to the QASPER database.

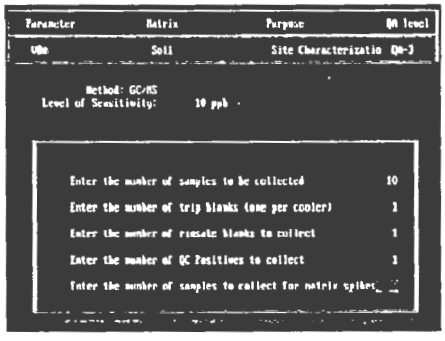
4. Schedule of Activities

The user is requested to provide a timetable for the sampling activities. This usually begins with the procurement process for laboratory services and may end with delivery of the final report. A tabular presentation will be created when the plan is compiled.

5. Tables

QASPER presents a summary table of each parameter, matrix, purpose, and QA objective as compiled in Section 3.0. The user will select by means of the highlight bar and "return" key to initiate a method selection for each parameter, identification of level of sensitivity, number of samples to be collected and QC samples needed to address the relevant QA objective. This information will be assimilated by QASPER into Field Summary and QA/QC Summary Tables.

Figure 5. Field QA/QC Summary Tables Menu



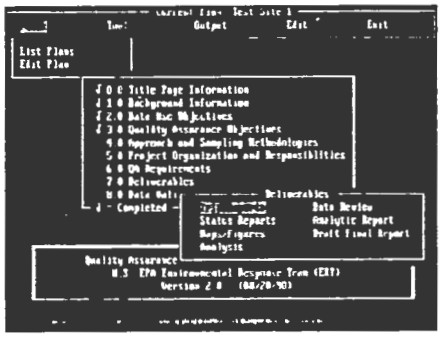
In Section 5.0, the user is requested to identify what personnel will be performing what tasks or responsibilities for the sampling event. Likewise, the user is re-

quested to provide the name of the lab and a city or state descriptor for an address. Labs will be characterized as either CLP, commercial, EPA or field under the space for lab type. Parameters may be identified by class of compound.

Section 6.0 of the plan database receives standardized text regarding QA requirements, based on the QA Objectives selected in Section 3.0. The user has the opportunity to view and edit the text in Section 6.0, since this is where the information will appear in the final compiled plan. There are also options for deleting generic text or writing unique text (requirements). The menu will indicate which QA Objective requirements are being imported (e.g. QA1, QA2, and/or QA3).

In Section 7.0, QASPER contains an inventory of standardized descriptions of the types of deliverables which may be prepared under a sampling event. The user need only select the appropriate deliverables, and the resultant plan will contain the appropriate text.

Figure 6. Deliverables Menu



Section 8.0 contains the requirements for validating the data generated under the plan. The text in this section will be automatically imported at the time the QA Objective(s) is selected.

After completing review and/or modification of Sections 0.0-8.0, the user may proceed to the output menu to compile the plan for eventual printing or sending to diskette.

Features of QASPER

If contained, requires no other software for support

-Generates ASCII outputs - file and hardcopy. Files may be uploaded to other word processing packages for further manipulation

-Creates (draft) hard copy QA/QC Sampling Plan document ready for approval signatures and implementation

-Retains database files on all previous sampling plans for future manipulation (e.g. recreating documents, searching for similar sampling plans by location, facility type, contamination, etc.)

-Capable of transmitting (compiled) sampling plan or database via diskette or modem

-Improves consistency and comprehensiveness of sampling plan creation efforts throughout office, region, or zone

-Improves efficiency for creating and reviewing QA/QC Sampling Plan documents

-Repetitive use of information throughout the plan without the need for redundant data entry

-Provides the user access to standardized generic text with overwrite capability for editing

-Flexible data entry throughout

Requirements

QASPER runs on an IBM PC or 100% compatible, with a hard drive, 640KRAM and a printer (for hardcopy output).

Conclusion

QASPER is a PC-based software package which compiles generic text and user provided, site-specific information into a draft QA/QC Sampling Plan for the EPA Removal Program. It is envisioned that this tool will primarily facilitate the timely assembly of comprehensive QA Sampling Plans in emergency response scenarios and, indirectly, educate users on the correlation of data quality objectives and sampling activities.

Mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

References

U.S. Environmental Protection Agency, Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures, Interim Final EPA/540G-90/004, April 1990.

A RATIONALE FOR THE ASSESSMENT OF ERRORS IN SOIL SAMPLING

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ABSTRACT

Considerable guidance has been provided on the importance of quality assurance (QA), quality control (QC), and quality assessment procedures for determining and minimizing errors in environmental studies. QA/QC terms, such as quality assurance project plans and program plans are becoming a part of the vocabulary for remedial project managers (RPMs). Establishment of data quality objectives (DQOs) early in the process of a site investigation has been stressed in EPA QA/QC guidance documents. Quality assessment practices, such as the use of duplicates, splits, spikes, and reference samples, are becoming widely accepted as important means for assessing errors in measurement processes. Despite the existence of various forms of guidance for hazardous waste site investigations, there have been no clear, concise, well-defined strategies for precisely how these recommended QA/QC materials can be utilized.

The purpose of this paper is to familiarize field scientists with an approach to these questions:

> How many and what type of samples are required to assess the quality of data in a field sampling effort?
>
> How can the information from these quality assessment samples be used to identify and control sources of error and uncertainties in the measurement process?

The primary audience for this paper is assumed to be RPMs who have concerns about the quality of the data being collected at Superfund sites but have little time to investigate the complexities of the processes used to assess the quality of data from the total measurement process. The approach outlined in this document for assessing errors in the field sampling of inorganics in soils may be transferrable, with modification, to other contaminants in other media.

This presentation is a summary of "A Rationale for the Assessment of Errors in the Sampling of Soils" by J. Jeffrey van Ee, Louis J. Blume, and Thomas H. Starks, 1990.

An in-depth treatment of the statistical approach is outlined in the Rationale (1), and it is recommended reading.

INTRODUCTION

This document expands upon the guidance for quality control samples for field sampling as contained in Appendix C of EPA's Data Quality Objectives for Remedial Response Activities - Development Process (2). That report outlines, in greater detail, strategies for how errors may be assessed and minimized in the sampling of soils with emphasis on inorganic contaminants.

Basic guidance for soil sampling QA, which includes a discussion of basic principles, may be found in EPA's Soil Sampling Quality Assurance Users Guide developed at the Environmental Monitoring Systems

Laboratory, Las Vegas (3). The Users Guide is intended to be revised on a periodic basis. It is anticipated that some of the guidance provided in this document will eventually be incorporated into the Users Guide.

The sampling and analysis of soils for inorganic contaminants is a complex procedure from experimental design to the final evaluation of all generated data. Sources of error abound but they can be successfully mitigated by careful planning or isolated by intelligent error assessment. Error (or variability) can be either bias or random. Biased error is indicative of a systematic problem that can exist in any sector of soils analysis, from sampling to data analysis. The first step in analysis of variability (or error) is to establish a plan that will identify errors, trace them to the step in which they occurred, and account for variabilities to allow direct action to correct them. In anticipation of errors, it is essential to ask two questions:

1. How many and what type samples are required to assess the quality of data in a field sampling effort?

2. How can the information from these samples be used to identify and control sources of error and uncertainty in the measurement?

Error assessment should be understood by the field scientist and the analyst. To aid scientists in the estimation and evaluation of variability, the Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) has developed a computer program called ASSESS. ASSESS can trace errors to their sources and help scientists plan future studies that avoid the pitfalls of the past.

BACKGROUND

Superfund and RCRA site investigations are complicated by: the variety of media being investigated, an assortment of methods, the diversity of investigators, the variety of contaminants, and the numerous risks to and effects on human health and the environment. Many phases exist in Superfund site investigations. An initial phase, generally described as a preliminary investigation, consists of collecting and reviewing existing data and data from limited measurements using practically any available method. The next phase, generally described as site characterization, uses selected methods and prescribed procedures to characterize the magnitude and extent of the contamination. Later phases include an examination of remedial actions, which involve an assessment of treatment technologies, and continued monitoring to assess the degree of cleanup at a site. A final phase may require long-term monitoring to substantiate that no new or additional threats occur to affect human health and the environment. Throughout Superfund site investigations QA/QC procedures change as data quality objectives vary and different phases proceed.

RANDOM ERRORS

Random errors can result in variations from the true value that are either positive or negative but do not follow a pattern of variability. During the measurement process, random errors may be caused by variations in:

1) sampling
2) handling
3) transportation
4) preparation
5) subsampling
6) analytical procedures
7) data handling

The greatest source of error is usually the sampling step. In the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund, or CERCLA) and the Resource Conservation and Recovery Act (RCRA), site investigations, analytical, and data handling variability are checked by the CLP protocol. When more than one laboratory is involved, handling, transportation, subsampling, and preparation can be checked at Level IV. All analyses are performed in an offsite Contract Laboratory Program (CLP) analytical laboratory following CLP protocols.

But how can the analyst know that the sample in the jar is representative of the surrounding samples at the site? How can the field analyst know that the more (or less) contaminated soil didn't stick to the auger or split-spoon?

It is strongly recommended that the traditional approaches used in mitigating the error in the last six steps be applied to sampling itself, i.e., use of duplicates, splits, spikes, evaluation samples, and calibration standards. A certain amount of random error is inherent in samples themselves. In fact, the total variance equals the measurement variances plus the population variances, as defined by the equations:

$$\sigma_t^2 = \sigma_m^2 + \sigma_p^2$$

where σ_t = total variability
σ_m = measurement variablity
σ_p = population variability

and

$$\sigma_m^2 = \sigma_s^2 + \sigma_h^2 + \sigma_{ss}^2 + \sigma_a^2 + \sigma_b^2$$

where σ_s = sampling variablity (standard deviation)
σ_h = handling, transportation and preparation variability
σ_{ss} = preparation variability (subsampling variability)
σ_a = laboratory analytical variability
σ_b = between batch variability

NOTE: It is assumed that the data are normally distributed or that a normalizing data transformation has been performed.

We can address the variance in measurement; the population variance, however, is a true picture of the complexity of the soil.

BIAS ERROR

Some sources of error are systematic, that is, in a given situation conditions exist that consistently give positive or consistently give negative results. This skewing of data can be introduced early in a sampling regime, e.g., by a sampling device that alters the composition of the soil matrix. It can occur in the middle of the sampling regime, e.g., by the preferential handling of a sampler who isn't trained in the intricacies of sample handling and preparation. Or it can be introduced in the later, analytical stages, where it is easier to trace because of interlaboratory comparisons and frequent calibration checks. The pervasive quality of an early bias error is its resistance to detection and the fact that other variabilities are added throughout the process until, finally, the reported data may be significantly non-representative of the true value. Bias errors can be traced to:

- faulty sampling design
- skewed sampling procedure
- systematic operator error
- contamination
- degradation
- interaction with containers
- displacement of phase (or chemical equilibria)
- jnaccurate instrument calibration

PREVENTION

To avoid both random and bias errors (or at least to be able to pinpoint their occurrence and estimate their extent), it is wise to plan a study well, anticipating possible sources of error. The inclusion of quality assurance samples used for quality assessment and quality control can help isolate variability and identify its effect.

An effective technique is to concentrate duplicate sampling early in the study and send the samples off for rapid CLP analysis. Dependent on the results, it may not be necessary to include as many quality assessment samples after these samples demonstrate reliability in the sampling process. Early detection of sources of error can help the field scientist customize the remainder of the study to meet the specific needs of the project.

QUALITY ASSESSMENT SAMPLES

A Remedial Project Manager (RPM) must ask: how many samples are needed to adequately characterize the soil at this site? The

key word is "adequately." By determining the data quality objectives (DQOs) in advance, the RPM can assure adequate sampling at a site. Too little sampling, as well as too much, is a waste of time and money. The extent of QA/QC effort is dependent on the risk to human health, the nearness of action levels to detection limits, and the size, variability, and distribution of contamination. Ultimately, the number of quality assessment samples is determined by the DQO for the site. Table 1 explains various types of quality assessment samples and their uses.

SOME STATISTICAL CONCERNS

Confidence in quality assessment sample data can be expressed as an interval or as an upper limit. All confidence levels/limits are based on the number of degrees of freedom and the limits get lower (or the intervals get smaller) as the number of degrees of freedom increases. For example, if 15 samples are taken at a site, and each split is extracted twice at a CLP laboratory, and 2 injections of each extraction are made into an Inductively Coupled Plasma/Mass Spectrometer (ICP/MS), the total number of degrees of freedom associated with this experimental design would be calculated as:

15 samples	X 2 preparations splits	= 30
	X 2 CLP extractions	= 60
	X 2 injection replicates	= 120

120 degrees of freedom for the whole process. But, if only the population variability in the field samples (which includes the sampling error) is being estimated, the number of degrees of freedom is 15-1, or 14. There are 15 independent samples but one degree of freedom is lost with the estimation of the mean. Therefore, there are 14 degrees of freedom for the sampling variance estimate. As another example, to estimate the variability in the extraction step, one has 30 independent pairs of numbers, each pair associated with one extraction. Thus, there are 30 degrees of freedom associated with the extraction error.

Obviously, the confidence associated with any particular sampling is directly related to the number of samples taken. In Table 2 (also Table 3 of the Rationale Document) or in a statistics manual, guidance is given for the number of quality assessment samples that must be used with the routine site characterization samples. These tables assume that data are normally distributed. The tables will show the user the confidence interval associated with the degrees of freedom. Then, decisions may be based upon the requirements of the DQOs. A synopsis of this targeted approach can be seen in Figure 1. The total measurement error is comprised of error in the sampling (σ_s), subsampling (σ_{ss}), handling (σ_h), batch (σ_b), and analysis (σ_a) steps. Each is addressed in the regime depicted in Figure 1.

SAMPLE COLLECTION CONSIDERATIONS

If Level IV CLP analysis is performed on the soil, we can assume that very little error occurs in the analytical stage. This focuses our attention on sources of error in the sampling, handling, and preparation steps. The two major considerations in collection of environmental samples are:

1. Will the collected data give the answers necessary for a correct assessment of the contamination or a solution to the problem?

2. Can sufficient sampling be done well and within reasonable cost and time limits?

ASSESS

The EMSL-LV has developed an easy-to-use program to calculate the necessary statistics, as described in the Rationale (1), from the generated data for an accurate determination of precision and bias. ASSESS is a public domain, FORTRAN program that is available from EMSL-LV and written for personal computers. It may be applied
to cases where no field evaluation samples are available as well as cases where they are. ASSESS is user-friendly and its use will greatly aid both field scientists and RPMs in decision-making based on soil studies.

TABLE 1

QUALITY ASSESSMENT SAMPLES AND THEIR USES

- ALLOW STATEMENTS TO BE MADE CONCERNING THE QUALITY OF THE MEASUREMENT SYSTEM
- ALLOW FOR CONTROL OF DATA QUALITY TO MEET ORIGINAL DQOs
- SHOULD BE DOUBLE-BLIND:

Types of Samples	Description
Field Evaluation (FES)	Samples of known concentration are introduced in the field as early as possible to check for measurement bias and to estimate precision
Low Level Field Evaluation (LLFES)	Low concentration FES samples check for contamination in sampling, transport, analysis, detection limit
External Laboratory Evaluation (ELES)	Similar to FES but without exposure in the field, ELES can measure laboratory bias and, if used in duplicate, precision
Low Level External Laboratory (LLELES)	Similar to LLFES but without field exposure, LLELES can determine the method detection limit, and presence of laboratory contamination
Field Matrix Spikes (FMS)	Routine samples spiked with the analytes of interest in the field check recovery and reproducibility over batches
Field Duplicates (FD)	Second samples taken near routine samples check for variability at all steps except batch
Preparation Splits (PS)	Subsample splits are made after homogenization and are used to estimate error occurring in the subsampling and analytical steps of the process

- SHOULD BE SINGLE-BLIND:

Field Rinsate Blanks (FRB)	Samples obtained by rinsing the decontaminated sampling equipment with deionized water to check for contamination
Preparation Rinsate Blank (PRB)	Samples obtained by rinsing the Blanks sample preparation apparatus with deionized water to check for contamination
Trip Blanks (TB)	Used for Volatile Organic Compounds (VOC), containers filled with American Society for Testing and Materials Type II water are kept with routine samples through the sampling, shipment, and analysis phases

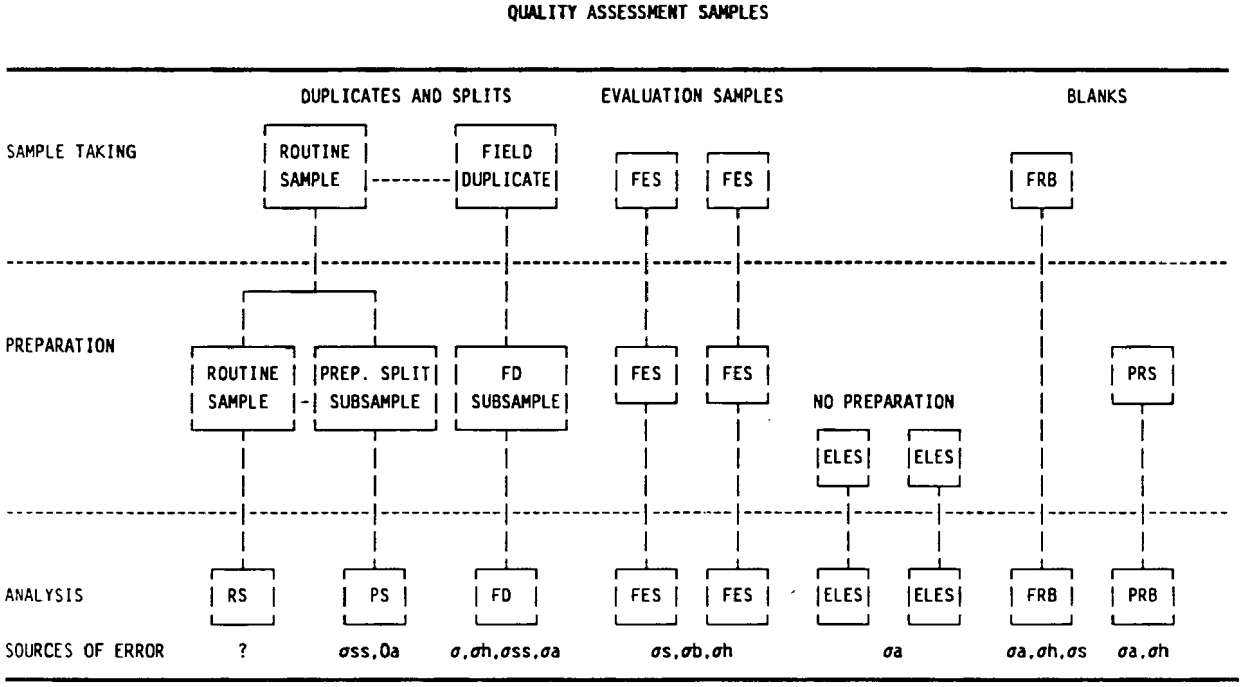
- MAY BE NON-BLIND: AS IN THE INORGANIC CLP PROTOCOL

TABLE 2

Some 95 Percent Confidence Intervals for Variances

Degrees of Freedom	Confidence Interval
2	$0.27s^2 \leq \sigma^2 \leq 39.21s^2$
3	$0.32s^2 \leq \sigma^2 \leq 13.89s^2$
4	$0.36s^2 \leq \sigma^2 \leq 8.26s^2$
5	$0.39s^2 \leq \sigma^2 \leq 6.02s^2$
6	$0.42s^2 \leq \sigma^2 \leq 4.84s^2$
7	$0.44s^2 \leq \sigma^2 \leq 4.14s^2$
8	$0.46s^2 \leq \sigma^2 \leq 3.67s^2$
9	$0.47s^2 \leq \sigma^2 \leq 3.33s^2$
10	$0.49s^2 \leq \sigma^2 \leq 3.08s^2$
11	$0.50s^2 \leq \sigma^2 \leq 2.88s^2$
12	$0.52s^2 \leq \sigma^2 \leq 2.73s^2$
13	$0.53s^2 \leq \sigma^2 \leq 2.59s^2$
14	$0.54s^2 \leq \sigma^2 \leq 2.49s^2$
15	$0.54s^2 \leq \sigma^2 \leq 2.40s^2$
16	$0.56s^2 \leq \sigma^2 \leq 2.32s^2$
17	$0.56s^2 \leq \sigma^2 \leq 2.25s^2$
18	$0.57s^2 \leq \sigma^2 \leq 2.19s^2$
19	$0.58s^2 \leq \sigma^2 \leq 2.13s^2$
20	$0.58s^2 \leq \sigma^2 \leq 2.08s^2$
21	$0.59s^2 \leq \sigma^2 \leq 2.04s^2$
22	$0.60s^2 \leq \sigma^2 \leq 2.00s^2$
23	$0.60s^2 \leq \sigma^2 \leq 1.97s^2$
24	$0.61s^2 \leq \sigma^2 \leq 1.94s^2$
25	$0.62s^2 \leq \sigma^2 \leq 1.91s^2$
30	$0.64s^2 \leq \sigma^2 \leq 1.78s^2$
40	$0.67s^2 \leq \sigma^2 \leq 1.64s^2$
50	$0.70s^2 \leq \sigma^2 \leq 1.61s^2$
100	$0.77s^2 \leq \sigma^2 \leq 1.35s^2$

Figure 1.



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NOTICE

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DISCUSSION

REX RYAN: You did an admiral job of explaining the strategy of breaking down what we call a "nugget effect" by using ANOVA techniques. I was a little bit shocked that you didn't discuss the amount of variance distance contributes within a sampling program. I was also surprised that you didn't discuss variograms or any of those kind of issues that would affect a sampling team's success in determining what is in fact going on at a site.

JEFFREY VAN EE: The two methods go together. The method I've described is useful in pinpointing sources of variability in the measurement process if you want to make changes. But the points that you're making address the larger question of where your samples are located and whether they're going to be representative of the site, assuming that the measurement variability is relatively low. That certainly needs to be looked at how representative are your sampling locations to the contamination throughout the site.

REX RYAN: In your experience which do you think is larger—which in fact could—in your professional judgment be a larger contribution to total variability: the problem of extending samples in distance or trying to replicate samples at the same location?

JEFFREY VAN EE: I don't think I have enough data to answer that question. I can pose a few questions for all of you to consider. Let's say that we're sampling volatile organics or a contaminant that varies with depth. This approach would be useful in determining whether the sampling of that contaminant is being done well. If you take a field duplicate sample and you go down, say, four inches and your contamination is in the first two inches of the surface, then this method will allow you to see that kind of variability from how the samples actually collected. This method would also allow you to look at the loss of volatile organics. By the time the samples get to the lab, it's more difficult with volatile organics and we need to do some more research to see if this approach is applicable. But those are some of the questions that can be answered by using this approach.

Both methods have been used together—at a site in Region VII, and they both yielded very useful information. The GEO Statistical Approach again, looks at the question of how many samples you need to collect to characterize a site and then our method looks at whether those samples are being collected properly, handled properly, those kinds of questions.

NABIL YACOUB: I have a question about a statement you made about a second sample collected at about an inch and a half and two inches from the original which relates directly to this concern. Would this be a measure of the effect of sample handling, the performance of the laboratory, containers, etc.? I beg to differ because we are introducing here a variable that might bias the results. Would you consider this sample as a split sample? If not, would you consider a split sample more representative of the effect of these operations rather than this end?

JEFFREY VAN EE: You need to use a combination of samples together. We are assuming, (although we can disprove it,) that the spatial variability in those two inches is insignificant. We can disprove it by the introduction of other samples throughout the process. Once we collect a field duplicate, we could split that sample and then analyze it separately to get a handle on errors down the line: handling in the subsampling of the core or analytical errors. If we do come back with this analysis and see that we do indeed have tremendous differences in moving two inches away and we compare that to the GEO Statistical Approach then we've got some real problems in characterizing that site.

A lot really depends how the contaminant was distributed at the site. If the contaminant was uniformly distributed at a site, then I would expect the spatial variability to be low. If we have leaking drums, we might just happen to hit on that area, and if we move two inches over we would get a dramatically different result. But the more samples we collect, the more field duplicates we collect, presumably we will get a more representative idea of where the variability is. If we were to rely on just one field duplicate or a few, then we would really be prone to some of the misjudgments that you're alluding to.

ROY KAY: As I understand it, the objective of sampling and population comparison within samples, is to provide a cost effective means of reducing the total sampling costs while maintaining a high level of accuracy. Am I correct there so far?

JEFFREY VAN EE: Yes.

ROY KAY: Has there been any cost evaluation information developed on the relative cost of going through the process of designing and multiple batching your samples versus simply expanding randomly the samples that you take—particularly if you're starting from an nonhistorical, time-zero point of view?

JEFFREY VAN EE: I think a lot depends on the objectives that you establish for that site. You need to look at the economics of collecting more samples, what type of samples, versus the kind of action that you're going to be taking. If you know that you're going to be cleaning up the site in large part then taking a lot of samples may not be appropriate.

But if the cost of that clean-up is significant, if the cost of disposing of the contaminant is significant, then you will want to pay more attention to how accurately you can characterize the site. And then, of course, you want to know whether the data that you're getting represents the site or whether it is more representative of variabilities in the measurement process.

I'm not sure I really answered your question well. It's a difficult question to answer, because it varies depending upon the site.

ROY KAY: I'm looking at a situation where in a time-zero, first evaluation of a site, there are certain theoretical things that you had assumed, like if you have an explosion of some kind, it would naturally be expected to disperse contaminants. Whereas a leaking drum would expect to leach in a continuous fashion and probably in all geometric dimensions. That is, of course, is a seat-of-the-pants guess in each individual case. But lacking historical experience on that particular site, do the sampling techniques dial in on the proper variables and reduction of their influence faster than simply expanding the sampling population?

JEFFREY VAN EE: In a situation like that I would weigh more QA samples, as well as more samples, period, early on in the process. You can hopefully back off as you learn more about the site. Now that's assuming you don't have historical information on how well that particular contractor performs out in the field, or how well that particular sampling method performs.

Let me demonstrate very quickly another value that comes out of this process. Say you're out sampling the site and you're concerned about the change of the contaminant over time, you may have different labs involved, and you may have different sampling crews involved. If you do not have a rigorous QA program instituted, then when the data comes back out of the lab, it's very difficult for you to say whether that data reflect the pollutant changing over time or whether it's your measurement process changing over a period of time. So, at some point, you've got to pay your dues and you've got to start developing that data. We have a tremendous amount of data right now on how well the contract labs perform, but we don't have enough data on how well those samples are transported to the lab and how well they're prepared. Say there's a rainfall event during your sampling study, how do you know that the data you collect after that significant event is comparable to the data before that event?

JANINE ARVIZU: Could you describe some of the programmatic applications of the program and whether or not there were any good real world experiences learned?

JEFFREY VAN EE: The philosophy I'm espousing today is relatively simple and it's relatively new. My hope is that more people will pick up on it whether they're in RCRA or Superfund Programs. I think we really do need to demonstrate where the variability is throughout the measurement process. Right now I'm simply advocating that we try it. How well it's used remains to be seen. We have applied it to a Superfund site in the middle part of the country and we looked at the spatial variabilities. As a result of our efforts using GEO Statistics, we saved about 6 million dollars in the sampling effort at this particular site. We were able to demonstrate that the sampling method that they were using, while it was crude, was sufficient to meet data quality objectives. We were able to tell them that they could back off on a number of samples that they're taking in certain areas, because the measurement variability was relatively low. They weren't getting a lot of variability in the compositing of the samples. We have had a few success stories, but not nearly enough. We can just hope with time there will be more stories like that.

A REVIEW OF EXISTING SOIL QUALITY ASSURANCE MATERIALS

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ABSTRACT

Assessment of the quality of environmental data often depends on the availability of quality assurance (QA) materials to measure errors at various stages of the measurement process. A rigorous approach has been developed to evaluate the quality of data from the sampling of metals in soils. "A Rationale for the Assessment of Errors in the Sampling of Soils" was written for application to hazardous waste site investigations. The rationale described is based primarily upon duplicate and split samples and QA materials known as performance evaluation materials. The rationale depends, in varying degrees, on performance evaluation materials being readily available for use in a hazardous waste site investigation. Unfortunately, early experiences in testing the rationale indicate that inadequate numbers, types, and volumes of performance evaluation materials and other types of soil QA materials exist to fully implement the rationale.

In order to begin to answer questions as to the necessity of, and alternatives to, soil QA materials, it is necessary to know the current availability and the state of research and development of soil QA materials. The intent of this paper is to provide such information - what materials are available and what is being done to provide more materials.

INTRODUCTION

SCOPE

Millions of dollars are spent in designing and implementing monitoring and remediation programs for hazardous waste sites. It is the Agency's responsibility to ensure that the data resulting from these programs are of adequate quality to be defensible in a court of law as well as to be considered scientifically sound.

Quality assurance (QA) materials are an important part of many environmental sampling and analysis programs today. Results from the analyses of hazardous waste site samples are often accepted or rejected solely on the basis of data obtained from QA samples analyzed for Agency programs ranging from water quality monitoring to hazardous waste remediation. It is alarming that only a limited supply of these QA materials is available for soil sampling and analysis (Table 1). What does a project manager do when no QA materials exist? It is the intent of this report to discuss the need for soil QA materials in many environmental programs[1,2] and to demonstrate the limited availability of these materials. An alternative to the use of manufactured QA materials is briefly described as are approaches for increasing the supply and variety of the most commonly needed soil QA materials. This report does not purport to have the answer to the scarcity of soil QA materials, but simply to point out the problem and explore some solutions with the hope that more attention will be given to the issue.

RESEARCH

Research in the area of QA materials has been limited. In fact, the bulk of the information gathered for this report came from catalogs, personal communications, and internal reports. The following examples were obtained through a literature search. Recently, Taylor[3] published a comprehensive book, Quality Assurance of Chemical Measurements. The book discusses the basic concepts of quality assurance and provides details on evaluation samples, traceability, and

reference materials. Seward[4] of the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), published a book which contains 25 papers describing national and international programs for the development of reference materials. The selection criteria, use of statistics, and steps for certification of standard reference materials are discussed. Reports of 15 panel sessions reviewing the use of and needs for reference materials are included.

Cali[5] of NIST, in another NBS monograph, examines the general use of standard reference materials and their role in the measurement system. Further, procedures for certification of standard reference materials are discussed, and examples of several selected industries are given in which standard reference materials have made a significant contribution. Steger[6] compiled the information on all of the available certified reference materials through the Canadian Certified Reference Material Project. Taylor[7] published a handbook for standard reference material users. The preparation and analysis of reference materials has been discussed and documented by several programs.[8,9,10,11,12,13] In other studies, the design[14] and stability[15] of reference materials have been evaluated.

Another search of "Chemical Abstracts" from the year 1979 to the present resulted in just five more references. Studies in which the QA materials were used range from proficiency samples discerning between immunoinhibition and electrophoretic measurement to soil and geological reference materials.

SOIL QA MATERIALS

DEFINITIONS

The uses of QA materials have been predefined for the purposes of this paper in the EPA report referenced in the abstract: "A Rationale for the Assessment of Errors in the Sampling of Soil."[1] Briefly summarized, there are two basic uses of QA materials: quality assessment or evaluation (QAS) and quality control (QC). QAS samples are intended to aid in evaluating data quality and can be used in QC. QC samples are used specifically on a real-time basis to detect and correct problems before a large body of erroneous or out-of-control data is generated. The main difference between the two uses becomes evident when the data generated from them is interpreted. QAS data are usually analyzed at the end of studies, whereas QC data is analyzed as it is generated; hence, the quality is "controlled."

QAS and QC samples exist in several types such as reference materials and performance evaluation materials. Reference materials are defined as having "one or more properties which are sufficiently well established to be used for the calibration of an apparatus, for the assessment of a measurement method, or for assigning values to materials."[16] Reference materials are typically used as QC samples but can be used as QAS samples. Originally, soil QA materials began existence as reference materials and are slowly evolving as important components of QA programs.

Performance evaluation materials[2,17] often are associated with an analytical program in which participants submit results to a central authority who "grades" the data either in comparison to the pooled results of all of the participants or against a "referee" laboratory in order to judge the overall performance or accuracy of the laboratory. Performance evaluation materials are, therefore, examples of QAS samples.

Whether the data is used on a real-time basis (QC) or at the end of a study (QAS), the overall effect of a QA sample is to evaluate measurement system performance. The sample may be used to evaluate a whole system, from sampling through data validation, or a part of the system; such as extraction efficiency.

An important issue for soil sampling and analytical QA is how closely soil QA samples represent the routine samples of interest. A QA sample should be similar to the routine samples for the analytical parameter in order for a true correlation to exist between the two. Analytes spiked onto potter's clay or sand probably do not accurately mimic environmental samples visually or analytically and, therefore, test only the recoverability of the analytes from the clay or sand in combination with the competence of the analysts. In the chemical analysis of natural soil samples, it is especially important that a QA sample be of a similar soil type as that of the samples being analyzed to eliminate the effects of various matrices effects on analytical measurements and final results.

This paper deals with three basic types of QA soil samples which are non-blind, single-blind, and double-blind soil QA samples. Non-blind QA samples are used for internal quality control and for calibration. Single- and double-blind QA samples are used in quality assessment and external quality control. All three types of blind QA materials have been successfully

utilized to control and evaluate laboratory measurements.[18,19]

Non-blind QA Samples

These samples are not blind to the analyst. The identity and reference values of the sample are known. Reference materials and laboratory control samples are examples of non-blind samples.

Single-blind QA Samples

Single-blind QA samples are used principally as a reference point in analyses, the data from which serve as a guide to acceptance or rejection of routine sample data. A single-blind QA sample is known to be a QA sample, but its composition is not known to the analyst. A performance evaluation material is an example of a single-blind QA sample.

Double-blind QA Samples

Double-blind QA samples are used as a basis for acceptance or rejection of routine sample data and for quality assessment. The difference between single- and double-blind QA samples is that the double-blind QA sample is intended to be indistinguishable from a routine sample. Visually, the QA sample resembles the routine sample in container type, number system, soil texture and soil color. Analytically, the QA sample resembles the routine sample in interferences, coanalytes, etc. This minimizes bias in processing the sample batch. A double-blind QA sample is even more difficult to compose or develop because, in addition to having the same or similar chemical make-up, the sample must appear to be of the same soil type. For example, if the soil being sampled for analysis is a Hagerstown silt loam (a fine textured medium brown soil with a neutral pH), an acidic red-colored sand would not be an appropriate double-blind sample. Spiked field samples and field duplicates are examples of double-blind QA samples. Manufactured double-blind QA materials are rare.

Use of Single-blind and Double-blind QA Samples

Quality assurance samples are used to detect bias and to estimate precision in the measurement system. The advantage of double-blind QA samples is that they are treated exactly like the routine samples in the analytical laboratory and hence should be exposed to the same types and levels of errors in the preparation and analytical processes.

Unfortunately, it is often difficult to employ double-blind QA samples for studies of environmental pollution. Difficulties in using double-blind QA samples usually arise for one of two reasons. The first reason is that the nature of the pollutant may make it impossible to carry out the drying, grinding, sieving, homogenizing, and subsampling (to obtain a laboratory sample) of routine samples outside the analytical laboratory. This series of preparatory steps is essential for obtaining homogeneous soil QA materials. Such treatment produces QA samples that look different from the routine samples, provided the routine samples did not go through the same process before entering the laboratory. The second most probable reason is that an appropriate soil QA material is not available, and there is insufficient time prior to field sampling to characterize the soil QA material for double-blind samples. It should be noted that no matter how many soil QA materials are available, it is unlikely that a soil QA material exists that is appropriate for double-blind samples unless the material actually comes from the site under investigation.

If it is not possible to employ double-blind QA samples in an investigation, an alternative procedure has been suggested based upon single-blind samples and additional field duplicate samples.[1] The additional field duplicate samples in this alternative procedure allow the estimation of total measurement error (i.e., the precision of the measurement system) and the estimation of the variance contributions of several of the possible sources of error. Depending on where they are incorporated into the sampling and analytical scheme, the single-blind samples provide means for detecting bias from sample handling, preparation, and analysis. Unfortunately, the single-blind QA samples may miss some of the bias in the laboratory, owing to special handling by the chemist, to which a double-blind sample would not have been subjected. A research study by Rumley[20] evaluated the effects of favorable treatment of samples and of alteration of results to reduce bias on indices of performance in external quality assessment (EQA) schemes. He concluded, in fact, that EQA schemes can be affected by giving favorable treatment to single-blind samples.

Since there will always be a need for single-blind soil QA samples, and the need will often involve situations requiring rapid response, it seems imperative that an extensive inventory of soil QA materials be prepared and maintained for future environmental pollution studies. Double-blind soil QA samples should be employed where practicable, and facilities should be available to produce such samples in an expeditious manner.

AVAILABILITY

The establishment and expansion of monitoring and enforcement programs by federal agencies requires the use of many QA samples. Federal agencies such as the U.S. EPA and the Food and Drug Administration (FDA) established repositories of QA materials out of the necessity to support their own programs. The private sector, although originally interested in producing standards for calibration of different instruments, produces QA samples in various media and for specific environmental programs (e.g., RCRA) in a limited variety.

Although a listing of many of the soil QA materials described that are available today (Table 1) may appear sizable, many analytes are not represented. At this time, the authors are unaware of any sources of soil QA materials for volatile organic analytes. The natural variability of soils, however, is the factor that makes a large number of QA materials necessary. The same factor limits the ability to manufacture sufficient materials to provide realistic and/or blind QA materials for all hazardous waste sites that are being investigated. This deficiency makes it difficult to plan and implement many soil sampling and analysis QA programs.

SOIL QA MATERIALS NEEDED

AGENCY NEEDS

Clearly there is a need for more sources of soil QA materials. This leads to certain questions. Which types are most often needed? Which materials should be manufactured first? A survey[21] of U.S. EPA officials shows that all 10 Regions share an interest in a national QA material program for Superfund analyses, primarily for use by the Contract Laboratory Program and by Potentially Responsible Parties (PRPs).

Although each Region has specific needs, there is some agreement on analytes. Most interest is in materials containing Target Compound List[21] analytes. Special requests include tetrachlorodibenzo-p-dioxin (TCDD) and pentachlorodibenzo-p-dioxin and -furan (PCDD/PCDF) isomers; explosives (RDX); benzene, toluene, and xylene (BTX), solvents; and polycyclic aromatic hydrocarbons (PAHs) in sediment. The number of QA materials needed per year and their concentrations vary among the Regions (Table 2).[21] One Regional official commented that site-specific QA materials are needed.[22] The value of the soil QA materials distributed by the EMSL-LV CLP Performance Evaluation Program has been proven,[12,17] but as demonstrated in Table 1, this program offers a limited variety of samples and analytes. The EMSL-LV program would need additional resources in order to be able to provide a wider variety of materials.[23]

INDUSTRIAL POLLUTANTS

Industrial organic chemicals presently comprise the highest volume of hazardous waste produced, followed by wastes from general chemical manufacturing, petroleum refining, and explosives (Table 3)[24]. According to the Comprehensive Environmental Response Compensation Liability (Act) Information Systems[25] database, the most abundant pollutants on the National Priority List (NPL) of Superfund sites are from the industrial and general organic chemicals industries, petroleum refining, and explosives industries (Table 3). The pollutants found most often on these NPL sites (Table 4) are Pb, As, Cd, Cr, Hg, Cu, and cyanides for inorganic pollutants, and trichloroethylene (TCE), other chlorinated solvents, and BTX for organic pollutants. The highest volumes of organic pollutant/waste are volatile organic compounds (VOCs), while heavy metals comprise the greatest volume of inorganic wastes. It would seem that soil QA samples containing the pollutants specified by the users (e.g., Regional users) and/or those most commonly found at the NPL sites should be the first to be produced.

SUGGESTED RESEARCH

Supplying Blind Soil QA Materials

At this time, preparing and stocking complete (adequate analytes) and realistic (double-blind as well as single-blind) soil QA materials is not feasible due to the tremendous natural variability of soils. On the other hand, as stated previously, variety of QA samples from present sources is limited (Table 1).

Two general approaches, that overlap somewhat in their philosophy, are presented for manufacturing both single-blind and double-blind QA materials. These are: industry-specific QA materials in which a limited number of soils are produced that contain analytes specific to polluting industries; and site-specific QA materials in which soils found at hazardous waste sites are prepared to contain analytes or analyte combinations commonly found at hazardous waste sites. Either approach would require a rigorous multi-laboratory characterization study. As one example, soils naturally rich in particular metals could be obtained and processed for either industry- or site-specific QA materials

representing mining industry wastes for sites with similar soil characteristics.

Industry-specific Materials

Using historical industry data as well as NPL data, information such as geographic location, contaminant types, and concentrations can be mapped and evaluated for any general geographic trends. This information can then be correlated with 10-15 general soil-types[26,27] to narrow the choices of industry-specific soil/analyte combinations. The next step would be to collect and homogenize the selected soils. During homogenization some of the soils would be spiked with contaminants for characterization and distribution. This would result in samples that could be used for non-, single-, and perhaps double-blind, blank, or contaminated soil QA materials. The materials could then be stored at distribution centers to fill user requests for various industry-generated hazardous waste sites.

Site-specific QA Materials

Relying on NPL site data in combination with geographically related soils, a set of site-specific soil QA samples could be developed. In this approach, the selected soils could be collected for spiking and processing, as described in the previous section; or, using site-specific soil/analyte combinations, the materials could be collected from actual hazardous waste sites, with blanks being obtained from nearby uncontaminated soils of similar composition. The artificially composed materials and the materials obtained from waste sites could be used during the investigation and remediation of sites having similar soils characteristics, or they could be stored and used throughout the study of the site from which they were obtained.

Site-specific QA materials have been successfully manufactured and used for treatability studies for similarly characterized sites,[28] as single-blind QA samples with routine samples,[17] and for integration of QA data (site comparison soils)[29] among several projects on a large (21 square mile) site for the duration of the site investigation and remediation.

A disadvantage in preparing site-specific soil QA materials is that often they cannot be used as double-blind samples because their visual characteristics may be altered by the processing that is employed to prepare QA materials. The site-specific approach is very successful, however, when the site is fairly dry[15] and sieving is not necessary.

CONCLUSION

Increased public interest in environmental issues has led to new legislation at both the state and federal levels. As a result of these laws, many contaminated sites have been or will be evaluated. A large number of these sites have been grossly contaminated by a variety of hazardous chemicals at different concentrations.

A parallel increase in the number of sites added to the National Priority List (NPL) and the number of contaminants regulated by RCRA and Superfund Amendment Reauthorization Act (SARA) (CERCLA) and other federal and state regulations demands a comprehensive suite of quality assurance samples[1] or a mechanism to produce such on short notice. The QA samples should represent the variety of contaminants at appropriate concentrations and natural soil characteristics to provide a true comparison to real world samples. The authors of this report recommend that the rationale document[1] described previously be consulted to determine whether the information and conclusions presented there pose serious problems for the investigator. If the quality of environmental data cannot be adequately assessed because suitable QA materials do not exist, then more effort clearly needs to be made to increase the supply of soil QA materials.

Future research should include a preliminary study comparing approaches for producing realistic soil QA materials. It is felt that such a study may show that the site-specific approach produces the most useful soil QA materials. A multi-laboratory pilot study would evaluate the advantages and disadvantages of each approach and should lead to a long-term plan for providing a supply of soil QA materials.[28,29]

NOTICE

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TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS*

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
Environmental Research Associates 5540 Marshall St. Arvada, CO 80002 USA 1-800-372-0122	Sludge	Certified QC standards in a sludge matrix for volatile (Benzene & TCE), semi-volatiles (5 BNA), pesticides/ PCB, and metal analysis (11 metals)	Volatiles (5-500 µg/kg) Semi-volatiles (300-30,000 µg/kg) Pesticides/PCBs (10-10,000 µg/kg) Trace metals (1-5,000 mg/kg)	40 CFR 503
	CLP-priority pollutant in soil	Certified QC standards in soil matrix for Superfund volatiles (6 to 8 VOCs), semi-volatiles, trace metals, and cyanide analysis	Volatiles (5-500 µg/kg; Sealed ampoule containing VOCs in methanol to be spiked into 10 g of soil) Semi-volatiles (300-30,000 µg/kg) Pesticides/PCBs (10-10,000 µg/kg) Trace metals (1-5,000 mg/kg)	Evaluation of laboratory performance - especially for CLP-type analysis
	Hydrocarbon fuel in soil	Standards of gasoline, No. 2 diesel, heating oil, and crude oil in a soil matrix	20 g QAS containing unleaded gasoline (5-500 mg/kg) No. 2 diesel fuel, heating oil or crude oil (10-5,000 mg/kg)	Evaluation of specific analysis for Underground Storage Tanks (UST program)
	Total petroleum hydrocarbons (TPH) in soil	Standardized 50 g QC soil samples, one specifically designed for analysis of TPH in soil in the presence of fatty acids in screw top bottles	Standard 1 - 50 g (100-2000 mg/kg) level Standard 2 - the presence of fatty acids (100-2000 mg/kg)	UST program
	Benzene, toluene, ethyl benzene and xylene (BTEX) in water/soil	QC set containing two standard concentrates and one soil matrix	Ampulated 5-500 µg/kg in CH_3OH to be spiked onto 10 g soil	UST program

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
Fisher Scientific 711 Forbes Avenue Pittsburgh, PA 15219 USA (412) 562-8300	Solid waste	Real world samples, homogenized for consistency and tested for accuracy	Fly ash (4 metals)	SW 846
			Waste water treatment media (3 metals)	Water treatment facilities
			Diatomaceous earth filter cake (4 metals)	SW 846
			Circuit board coating sludge (5 metals)	Waste from electronic industries
			Electroplating tank bottoms (5 metals)	Waste from electroplating
			Raw sludge, chrome plating process (4 metals)	Waste from electroplating
			Incinerated sludge (5 metals)	Waste from incinerators
			Municipal incinerator ash (8 TCLP metals, 4-4000 ppm)	SW 846, Methods 3050, 6010
			PAH-contaminated soil (14 PAH and PCPs, 20-1200 ppm)	SW 846, Methods 3540, 3550
			Custom Orders	As required

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
National Institute of Standards and Technology Chemistry Bldg. B-311 Gaithersburg, MD 20899 USA 302-975-6776	Ore, minerals, and refractories	QC reference materials for critically important material balance in mining and metallurgical industries	Copper ores (5 metals, 0.03 ppm to 0.84%) Fluorospar (CaF_2) (97.4 to 98.8%) Iron ores (Fe, 58 to 90.8%) Bauxite ores (Al, 21.1 to 28.8%)	Mining and metallurgical processing
	Solid organics	QA materials for analysis of materials for constituent of interest	Powdered lead-based paint (Pb, 12%) Trace mercury in coal (Hg, 0.13 µg/g) Lead in refinery fuel (5 varieties, 11.0 to 780.0 µg/g)	Lead-based paint analysis Heavy metals in fuel

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
National Institute of Standards and Technology Chemistry Bldg. B-311 Gaithersburg, MD 20899 USA 302-975-6776	Trace elements	Trace elements in solid matrices (12 to 42 elements)	Urban particulate (1.0-860 µg/g) Coal - bituminous (0.1-100 µg/g) Coal - fly ash, 4 varieties (0.2-200 µg/g) Coal - subbituminous (0.1-20 µg/g) Estuarine sediment (0.5-375 µg/g) Buffalo River sediment (0.1-555 µg/g)	Evaluation of laboratory performance especially for analysis of trace elements in variety of matrices
	Urban dust	Urban dust QA materials for analysis of organic constituents	10 g	Air pollution
	Diesel particulate matter	QA materials for analysis of diesel particulate matter and its organic constituents	100 mg/ampoules	Air pollution
	PAH in solid matrices	QA materials with variety of PAHs on solid matrices	6 varieties, 1.0-4000 µg/g	SW 846 or similar analytical programs
	Polychlorinated biphenyls in sediments	QA materials of sediments contaminated by PCBs	In preparation	SW 846 or similar analytical programs
	Organics in marine sediments	QA materials made of marine sediment contaminated by organics	In preparation	General

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
Canada Centre for Mineral and Energy Technology 555 Booth Street Ottawa, Canada K1A 0G1	Soil Samples SO-1, SO-2, SO-3, SO-4	Compositional Reference Materials	Clayey soil, sandy podzolic B horizon with a high organic content, a calcareous till, and a chernozemic A horizon	General analytical and earth science for agricultural, forestry, and environmental applications, especially for mining and metallurgical operations.
United States Geological Survey Geochemistry Branch P.O. Box 25046 MS 973 Denver Federal Center Denver, CO 80225	GXR-1-6	Jasperoid soils, Cu millhead tailings, B horizon soil	Chemical and physical soil and mineral properties	General analtyical and earth science for agricultural, forestry, and environmental applications, especially for mining and metallurgical operations.
U.S. Environmental Protection Agency RREL, Releases Control Branch Edison, NJ 08837-3079 USA 201-321-4372	Synthetic Soil Matrix/I	30% clay, 25% silt, 20% sand, 20% topsoil, 5% gravel High organic, low metal	Organic: 400-8200 mg/kg Metal: 10-450 mg/kg	Soil treatability studies
	Synthetic Soil Matrix/II	Low organic, low metal	Organic: 40-820 mg/kg Metal: 10-450 mg/kg	Soil treatability studies

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
U.S. Environmental Protection Agency RREL, Releases Control Branch Edison, NJ 08837-3079 USA 201-321-4372	Synthetic Soil Matrix/III	Low organic, high metal	Organic: 40-820 mg/kg Metal: 500-22,500 mg/kg	Soil treatability studies
	Synthetic Soil Matrix/IV	High organic, high metal	Organic: 40-8200 mg/kg Metal: 500-22,500 mg/kg	Soil treatability studies
U.S. Environmental Protection Agency EMSL-LV, QAD P.O. Box 93478 Las Vegas, NV 89193-3478 702-798-2114 FTS 545-2214	Dioxin performance evaluation materials	Real World samples contaminated by dioxin and/ or selected matrices fortified by dioxin	Kiln ash, XAD Resin, filter paper, florisil, clay, sand (20 ppt to 6 ppb) TCDD/PCDF soil Times Beach soil Times Beach & PCDD/PCDF soil Times Beach & Region 9 soil	SW 840, 8280
	Base-neutral-acid PEMs	Sand fortified with selected BNAs	Low level BNA (400 ppb) Medium level BNA (15 ppm) High level BNA (75 ppm) Mixed level BNA	SW 846, 8250, 8270
U.S. Environmental Protection Agency EMSL-LV, QAD P.O. Box 93478 Las Vegas, NV 89193-3478 702-798-2114 FTS 545-2214	Pesticide PEMs	Real world samples contaminated with toxaphene and other pesticides or selected soil fortified by selected pesticides & PCBs	Toxaphene soil Pesticide soil 1 (4-40 µg/kg) Pesticide soil 2 (4-40 µg/kg) Pesticide soil 3 (30-100 µg/kg) + PCB 1016 Pesticide soil 4 (30-60 µg/kg) + PCB 1266	SW 846, 8080

TABLE 1. LIST OF GOVERNMENT AND PRIVATE SOURCES FOR SOIL/SOLID QA MATERIALS (Continued)

SUPPLIER	QA MATERIAL	DESCRIPTION	TYPE & CONCENTRATION RANGE	APPLICATION
U.S. Environmental Protection Agency EMSL-LV, QAD P.O. Box 93478 Las Vegas, NV 89193-3478 702-798-2114 FTS 545-2214	Inorganic PEMs	Selected soil samples fortified with metals and cyanide	LCS metals (1 ppm-200,000 ppm) LCS, cyanide (4-8 ppm)	SW 846, 6010

* Information contained in this table was obtained in September 1990 and may not include some sources of QA materials despite the authors' efforts to be accurate and complete.

DISCLAIMER: Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE 2. SOIL AND WATER PE SAMPLES NEEDED BY THE 10 REGIONS OF THE U.S. EPA[21].

Region	Analytes	Levels	# PE samples/year
I	VOA, BNA, PEST/PCB soil blanks for VOA and BNA Dioxin	same as CLP PE no detectable levels isomer specific; not only 2,3,7,8	100/type/year
II	Unspecified	Unspecified	100, or if replace MS/MSD[+] 1/50 samples
III	*TCE 25 ppb toluene vinyl chloride phenols napthalene pentachlorophenol	 100 ppb 100 ppb 100 ppb 50 ppb 100 ppb	
IV	2 or 3 mixes for each fraction; e.g. 5 analytes 7 analytes 3 analytes (determine in workgroup)	 2 x (CRQL)** 5 x (CRQL) 10 x (CRQL)	unknown
V	*VOA and BNA from CLP-TCL PEST/PCBs Metals VOA and BNA	~ 1.5 ppb ~CRQL ~CRQL ~CRQL	15-20 15-20 15-20 15-20
VI	case by case; not routine enough to predict levels or analytes PCBs Pest/Herb PCP TCE and solvents dioxin congeners, tetrachloro-specific isomers	 100-80,000 ppm (soil) 300-10,000 ppm (soil) 300-30,000 ppm (oily matrix) low ppb (water)	up to 100 if convenient and flexible schedule
VII	Complete TCL (grouped aromatics, PAH, etc.) EDB RDX explosives TCDD only PCDD/PCDF chloroform, carbon tetrachloride	Low (10 x CRQL) Med (50 x CRQL) 100 ppt; 1 ppb 1 ppb 1 ppb; 5 ppb; 10 ppb (soil) 10 ppt (water) 10 ppb (soil) 20 ppb	200 water, 200 soil 50 20 1500 soil 50 water 50
VIII	BTX chlorinated hydrocarbons VOA and BNA Heavy metals	wide variety high for high soils; low for drinking water	~30; contractors would like 2
IX	include most common and possibly some more difficult compounds	asbestos needed but don't expect it in this effort	50-75/matrix/analyte set
X	PAH (sediment)	low and high (within DOT regulatory limits)	if replace MS/MSD, 1 per data set

[+]Matrix spike/Matrix spike duplicate

*Soil samples not requested.

**Contract required quantitation limit

TABLE 3. VOLUME OF WASTE GENERATED BY INDUSTRIAL ACTIVITIES PER YEAR[24].

Standard Industrial Classification	Category	Hazardous Waste Volume, Millions of metric tons
2869	Industrial organic chemicals	60-80
2800	General chemical manufacturing	40-50
2911	Petroleum refining	20-30
2892	Explosives	10-15
2821	Plastic materials/resins	6-10
4953	Refuse systems (commercial TSDR* facility)	5-8
2879	Agricultural chemicals	5-8
2865	Cyclic crudes/intermediates	5-8
2816	Inorganic pigments	3.5-5
2812	Alkalis/chlorine	2.5-4.5

* Transportation, storage, disposal, or recycling

TABLE 4. MOST FREQUENTLY REPORTED SUBSTANCES AT 546 NPL SITES[25].

Rank	Substance	Percent of Sites
1	Trichloroethylene	33
2	Lead	30
3	Toluene	28
4	Benzene	26
5	Polychlorinated biphenyls (PCBs)	22
6	Chloroform	20
7	Tetrachloroethylene	16
8	Phenol	15
9	Arsenic	15
10	Cadmium	15
11	Chromium	15
12	1,1,1-Trichloroethane	14
13	Zinc and compounds	14
14	Ethylbenzene	13
15	Xylene	13
16	Methylene chloride	12
17	Trans-1,2-Dichloroethylene	11
18	Mercury	10
19	Copper and compounds	9
20	Cyanides (soluble salts)	8
21	Vinyl chloride	8
22	1,2-Dichloroethane	8
23	Chlorobenzene	8
24	1,1-Dichloroethane	8
25	Carbon tetrachloride	7

DISCUSSION

JANINE ARVIZU: Have you considered as one of your options for preparation of these materials, reconstruction of some simulated soils from stockpiles of individual soil constituents (clays and gravels) and so forth? Based on compositional analysis of the soils, would you be able to reconstruct QA materials on a site-specific basis?

AMY CROSS-SMIECINSKI: Yes, we have considered this possibility and have tried to locate large stockpiles of various types of soils. Most of the sources of soils that we have found are not extensive. They're small volumes and the people who distribute them are apprehensive about sending out large quantities. They are used mostly for a routine soil sample analysis.

JANINE ARVIZU: I'm curious as to how you would envision addressing the problem of accurately dealing with active soils. (e.g., biologically active soils or natural soils that have absorptive properties) and being able to accurately determine the recovery of analytes from those types of materials?

AMY CROSS-SMIECINSKI: In another study we have in the poster session, we have looked into various types of soil, specifically volatile organic preservatives, to prevent those kinds of degradations and activities. But then it's something that would be a real problem for any type of soil QA material.

LLEW WILLIAMS: I might just comment on something we've been wanting to try to see if we can get better representative spiking into QA materials. I think this has always been a concern that spiked materials frequently don't reflect in recoveries for instance. The same analytes, if they were naturally in a waste material, we may get fifteen percent (15%) recovery, we spike them and then we get ninety percent (90%) back.

One of the things that we're looking into right now and some of you who have the facilities might want to play around with it a little bit, too, is looking at the concept of using super critical fluid to put analytes back into matrices, rather than taking them out. If the concept is a good one to reach down into the pores and draw analytes out of a matrix, it's possible to be able to release the pressure and put analytes deeply into a matrix in a way that they may better assimilate natural materials.

JANINE ARVIZU: Your concerns about double blind QA samples for soils, I think are really legitimate. Have you considered the introduction of single blind QA samples with every analytical batch as an alternative to having a double blind? Would it serve some of the same purposes?

AMY CROSS-SMIECINSKI: We believe it does and it has. Single blind QA samples have been used this way for some time, particularly in the dioxin program. But we feel that the double blind QA samples, although they're very hard to manufacture, would be the most realistic type of soil QA samples at this point.

EVALUATION OF EMISSION SOURCES AND HAZARDOUS WASTE SITES USING PORTABLE CHROMATOGRAPHS

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ABSTRACT

Portable gas chromatographs (PGC) capable of direct detection of ambient concentrations of toxic organic vapors in air were operated in field studies while simultaneous data were taken for comparison by the Canister/TO-14 Method. Samples were obtained downwind of Superfund hazardous waste sites, highways, chemical plants, and in locations where there was concern about odors or nasal/respiratory irritation. In some cases two PGCs equipped identically were used side-by-side or upwind/downwind. In others, different columns were used side-by-side to analyze a larger group of compounds. Reasonable agreement between methods was found, even though sampling techniques were not equivalent. Such agreement suggests that both methods were free of sampling errors, and that the data were substantially accurate.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Toxic organic compounds are usually present in ambient air at such low levels (typically about one ppB) that they cannot be analyzed without preconcentration. In the TO-14 Method, six-liter air samples are collected in passivated canisters and stored pending analysis. Just prior to analysis they are cryogenically preconcentrated (1). Use of a portable gas chromatograph (PGC) equipped with a photoionization detector (PID) sensitive enough to detect organic compounds at sub-ppB levels without preconcentration offers an alternative sample collection method which produces data on-the-spot in near real-time.

PID detectors are no longer novel. In 1984-5 Verner (2) and Driscoll (3) reviewed more than a decade of PID use in gas chromatography. There have been several reports since 1980 describing analyses of airborne organic vapors with them. However, none of the instruments were portable, and sample preconcentration was always required because those PIDs were not significantly more sensitive than other kinds of detectors (4-8). Then Leveson and coworkers developed a 10.6 electron-volt PID of significantly greater sensitivity and incorporated it into a PGC (9). The light source was an electrodeless discharge tube which was excited by a radio-frequency oscillator to produce an intense emission line. The chromatograph was claimed to detect benzene without preconcentration at 0.1 ppB (10-13). However, the lamp is restricted to low-temperature operation because heating it would decrease sensitivity by broadening the emission line. For Leveson's PGC (Photovac Model 10A10), Berkley estimated a benzene detection limit equivalent to 0.03 ppB. The smallest sample actually analyzed, one microliter containing 1.6 picogram of benzene, produ-

ced a 2.3 volt-second peak at maximum gain. A linear response to benzene was observed over a wide concentration range (0.5 to 130 ppB), and injections as large as one milliliter could be made without significant loss of chromatographic resolution. Similar sensitivity to other aromatic compounds and to chloroalkenes was also observed (14). Such an instrument obviously should be useful for air monitoring, but few reports of it have appeared. Lipsky analyzed vinyl chloride from landfills (15), and Hawthorne analyzed indoor air in a "research house" (16). Jerpe estimated a benzene detection limit of 20 picograms using a Model 10A10 PGC to which an external capillary column and constant-volume sample loop had been connected (17). Users of the Model 10A10 PGC experienced difficulty with battery endurance, baseline drift, and on-site data interpretation. These problems were mostly resolved by the later series of Model 10S- PGCs. Since PGCs can be more easily transported than large numbers of canisters, they more readily produce large volumes of data in the field. Their disadvantages are that (a) at present they are limited to low resolution chromatography, (b) they identify, by retention time only, the limited number of compounds which they can detect at low ppB levels, and (c) they require a skilled operator.

It is difficult to be certain that preconcentrated samples are not being spoiled by sampling errors. Although sample integrity during storage in passivated canisters has been demonstrated in the absence of highly reactive compounds (18), artifact formation can be caused, for example, by HCl (19). We have evaluated PGCs in both laboratory and field operation (20, 21). Because PGCs are not affected by breakthrough of analytes from a preconcentration trap, by chemical reactions between collected compounds, or by sample degradation during storage, use of them in parallel with the Canister/TO-14 Method could identify such problems, should they ever occur, if the two methods could be shown to consistently produce similar results under field conditions. That requires much parallel use over a long period of time at a variety of sites under different ambient conditions using many kinds of operating parameters. Herein are reported an accumulation of comparative data obtained during the past two years.

EXPERIMENTAL

Spherical 6-liter electropolished canisters (SIS, Incorporated) were used to collect air samples and store PGC calibration standards. Canisters were cleaned by heating to 90°C while evacuating through a liquid nitrogen trap to a final pressure below 10 micrometers (mercury equivalent) for two hours. Sampling for direct comparison of canister and PGC data was done by holding a canister with its inlet less than 10 centimeters from the end of the PGC probe and opening the valve to fill it during the time the PGC sample pump was running. Another method of comparison was to perform consecutive PGC analyses while time-integrated canister samples were being collected. For time-integrated measurements, evacuated canisters were fitted with pre-calibrated mechanical flow controllers, and air was sampled at 25 milliliters/minute for two hours. Air samples collected in canisters were transported to a laboratory, cryogenically preconcentrated, and analyzed using a modified Hewlett-Packard Model 5880A gas chromatograph equipped with flame ionization and electron capture detectors. A Hewlett-Packard Model 5970A mass selective detector was used for some samples. Calibration was based on 41 organic compounds cited in the Canister/TO-14 Method (1).

Microprocessor-controlled PGCs (Photovac Model 10S70) were used. They were equipped with constant-temperature column enclosures and 0.53 millimeter ID X 10 meter fused-silica wall-coated open-tubular (WCOT) columns, a 1.67 meter section of which was backflushable precolumn. Chemically-bonded stationary liquid phases were used, either CPSil5CB or CPSil19CB (Chrompak). A KCl/Alumina porous-layer open-tubular (PLOT) column of the same size and configuration was used for extremely volatile compounds. Ultrazero air (less than 0.1 ppM carbon) was the carrier gas. An IBM-compatible laptop computer, using vendor-provided software via an RS-232 interface, controlled chromatograph operation and data storage. Chromatographic peaks were identified and quantitated using retention times and response factors stored in nonvolatile memory of the PGC microprocessor. The calibration library was created by analyzing mixtures of analytes (10 ppB) produced by flow-dilution of commercially-prepared standards as described above. Compounds with ioniza-

tion potentials greater than 10.6 electron-volts were not detected by PGCs at ambient (below 10 ppB) levels. Before beginning to sample, a stable baseline was observed, and the library was recalibrated with a single-compound standard (approximately 10 ppB) which had been certified by GC/FID analysis. Chlorobenzene or tetrachloroethylene were used as calibrants with the WCOT columns, and vinylidene chloride with the PLOT column. During sampling, automatic recalibration was performed every 4 or 5 runs using the single compound standard, after which the microprocessor corrected the retention time and response factor for the calibrant, then corrected proportionally the retention times and response factors of other compounds. Samples were taken every 15 minutes. Air was drawn into the sample probe (3 meters long X 2 millimeter ID stainless steel tubing) for 45 to 60 seconds. Then the sample was injected for 7 to 15 seconds, after which the sample loop was removed from carrier flow to minimize peak tailing. The precolumn was backflushed by the carrier stream except while calibrated compounds were passing through it. Calibration runs differed from sample runs only in that the loop received calibration mixture instead of an air sample. PGCs were sheltered from drafts and direct sunlight inside a vehicle or building, and a stainless steel sample probe was extended through a window or a sampling port. External rechargable 12-volt batteries (Johnson Controls GC12800 or PP12120 Gel-Cell, and Sears Die-Hard Marine) were used to supply power.

RESULTS AND DISCUSSION

In comparing Canister and PGC data it is important to remember that samples collected by the two methods are not equivalent. A PGC analyzes only one of 50 to 70 milliliters of air which enter the probe during sampling, whereas a representative sample of the entire six liters collected by the canister is analyzed. If the air is well-mixed and devoid of reactive or corrosive materials, then canister and PGC data should resemble each other, and generally do. However, if a heterogeneous plume is sampled, or if highly reactive materials enter the canister, then PGC and canister data could differ significantly even though the "same" air was sampled.

Complaints about episodes of stench at Marcus Hook, PA were investigated at the request of EPA Region III. A PGC was operated in a van at several sites, and canister samples were taken for comparison. The results are shown in TABLE 1. The PGC twice failed to recognize small benzene peaks which eluted in the tail of the large initial peak. The CPSil5CB column eluted compounds so close together that resumption of backflush always interfered with some peak, no matter when it occurred. In this case toluene was missed. Trichloroethylene, reported by the PGC, was never found in the canisters. That peak was undoubtedly due to some other compound which had a similar retention time. For other compounds, agreement between the two methods was reasonable.

TABLE 2 shows samples taken at hazardous waste sites near Wilmington and New Castle, Delaware. Concentrations at the Superfund remediation sites were low, typical of sub-ppB background levels in remote areas, showing that buried waste was not emitting significant quantities of these compounds into the air. Relative agreement between PGC and canister data seemed to improve with increasing concentration. PGC data for tetrachloroethylene at the waste lagoon were not reported because of a persistent coeluting peak. Samples taken by both methods near the waste incineration plant show toluene and higher homologues at significant levels. High levels of benzene and chlorobenzene were found by both methods downwind of the Standard Chlorine plant. For compounds found by both methods, agreement was reasonable over a wide range of concentrations.

Under Project 02.01-12 of the US-USSR Environmental Agreement, samples were taken at a roadside site about 12 kilometers from Vilnius, Lithuania. Two PGCs were operated while time-integrated canister samples were collected. A mobile laboratory stood about 20 meters from the highway on ground about 2 meters below it. Daytime traffic volume was moderate-to-heavy without stop-and-go congestion and subject to a 100 km per hour speed limit. No industrial activity was visible in the immediate vicinity. Two identically equipped PGC's were compared side-by-side and then upwind/downwind. During side-by-side operation inside the mobile laboratory, the sample probes extended to about 18 meters from the roadway and one meter above it. TABLE 3 compares colocated

and upwind/downwind PGC analyses with time-integrated canister data. During colocated sampling canisters were placed 3 and 10 meters downwind of the highway. Sampling was done during nonturbulent movement of air across the site and while traffic density was fairly constant. Average levels of benzene, toluene, ethylbenzene, *m,p*-xylene (reported as one compound) and *o*-xylene found by the PGC's were in reasonable agreement with data from the canisters. PGC data for toluene, and sometimes *m,p*-xylene, exceeded average concentrations found in the 10 meter canisters, even though the PGCs were farther from the highway. This discrepancy may have occurred because the PGCs often sampled the plumes of passing vehicles. When the PGCs were deployed across the highway from each other, PGC-1 was inside a van parked 12 meters downwind while PGC-2 remained upwind in the mobile laboratory. Canisters were again placed 3 and 10 meters downwind of the highway. Scheduling constraints allowed only a half hour of PGC sampling to be compared to the canisters, but downwind PGC results agreed substantially with canister data.

At a Superfund remediation site in northwest Georgia, airborne emissions produced strong odor but contained low levels of compounds which could be detected by the PIDs. Two PGCs equipped with CPSil19CB columns were operated side-by-side while canister samples were taken for comparison. Data are shown in TABLE 4. Toluene and xylenes were consistently seen by both methods at similar levels. Some styrene was also seen. These compounds probably came from trucks and earth-movers on the site. The CPSil19CB columns provided better resolution than CPSil5CB columns, but benzene peaks smaller than one ppB were missed because the PGC peak-recognition algorithm could not find them on the tail of the large initial peak.

Compounds which can be analyzed without concentration by a PGC are those to which the PID is sensitive and which can be separated from each other by an isothermal column at low temperature (50°C maximum). The number of compounds which can be analyzed can be increased by operating two PGCs side-by-side with different columns. An example is shown in TABLE 5. The site was about 40 meters downwind of a dry cleaning plant. PGC-1 was equipped with a KCl/Alumina PLOT column and used to analyze vinyl chloride and vinylidene chloride. Since the PLOT column had very low bleed, the PGC could be operated at maximum gain (1000). PGC-2 equipped with a CPSil5CB column was calibrated for the usual list of compounds. Traces of vinyl chloride and vinylidene chloride were found by PGC-1 but not found in the canisters. These concentrations were below detection limit (approximately 0.2 ppB) for the Canister/TO-14 Method. PGC detection limits for vinyl chloride and vinylidene chloride were 0.005 and 0.010 ppB, the amounts which would have produced 5 millivolt-second peaks. The integration algorithm does not process smaller peaks. Canister and PGC data showed tetrachloroethylene at elevated concentrations. They did not agree closely, probably because the plume was poorly mixed. To measure the extent of agreement between PGC and canister data, a criterion for evaluation is needed. The absolute difference between results was chosen because it does not change drastically with concentration. For each compound, the averages of absolute differences are shown in TABLE 6. For the CPSil5CB column these differences (from data in TABLES 1, 2, and 5) range approximately from 1 to 2 ppB. Apparently, absolute differences do increase slightly with increasing concentration. Supposing they did not, then at about 100 ppB, relative differences would be 5%. At 10 ppB they would be approximately 10%, and at one ppB, 100%. A difference of 100% seems large, but suppose one method reported one ppB of toluene while the other reported two ppB. That difference would arouse little concern; the data would be considered similar because both results are "small". Detection limits for the Canister/TO-14 Method (about 0.2 ppB) prevent making such comparisons at significantly lower concentrations. For data taken with CPSil19CB columns (TABLE 4), agreement was much better, because those columns retain compounds longer and resolve them better, so peaks are more likely to be identified and integrated properly. Agreement for benzene and styrene was poorer than for other compounds because benzene was lost in the tail of the initial peak on every run, while styrene was crowded by an artifact peak produced by column bleed. PGC performance could most readily be improved by using a column with better resolution and less bleed, perhaps a thicker-phase CPSil5CB, which would pro-

vide better resolution of early-eluting compounds and sufficient space between later peaks to accommodate the minute-long baseline disturbance which erupts when backflush resumes. Improvement of resolution will ultimately be limited by flow system configuration. Another advantage of using a column with less bleed would be that operation at higher gain could result in lower detection limits.

CONCLUSIONS

Portable gas chromatographs can rapidly produce reasonable estimates of ambient background concentrations of many volatile nonpolar and semi-polar organic air pollutants which ionize below 10.6 electron-volts. Because they process data immediately, they are useful for evaluation of hazardous waste sites, chemical spills, and other sources of airborne organic vapors. PGC data generally agree well with data from the Canister/TO-14 Method, which provides further indication that the latter is generally valid for sampling atmospheres not contaminated with highly reactive compounds, even when analyses are delayed. Combined Canister/PGC analyses should be used at uncharacterized sites or where highly reactive compounds are suspected. Positive interferences could affect either PGC or canister data, but negative interferences might be less likely to influence PGCs because they do not store or preconcentrate samples. Furthermore, when analyses using different sampling methodologies produce similar results, a preponderance of evidence is created that sampling errors did not occur and that data are substantially correct. Comparison of canister and PGC sampling should be extended to include additional classes of compounds, especially polar compounds.

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TABLE 1. MOBILE PGC AND CANISTER SAMPLING AT MARCUS HOOK, PENNSYLVANIA

April 25, 1990. PGC in van with probe one meter above roof on upwind side. CPSil5CB column. Concentrations are parts per billion by volume.

	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Chlorobenzene	Ethylbenzene	m,p-Xylene	o-Xylene	Styrene
Market Street at Railroad Overpass. 77°C.									
PGC	ND	ND	*	4.90	0.53	ND	ND	ND	ND
CAN	6.8	ND	15.9	0.1	ND	1.4	6.1	ND	1.9
PGC	4.86	2.18	*	ND	0.13	ND	2.82	ND	0.36
CAN+	7.7	ND	15.6	0.1	ND	2.3	7.5	1.4	2.5
PGC	6.59	2.20	*	ND	ND	0.47	7.14	ND	ND
CAN+	10.2	ND	20.1	0.1	ND	3.4	13.0	ND	4.1
Rt. 13 at Trailer Park Street, Trainer, PA. 77°C.									
PGC	ND	ND	*	ND	ND	0.03	0.84	ND	ND
CAN	1.6	ND	3.7	0.4	ND	0.5	1.8	ND	0.8
Railroad Station SW Parking Lot. 77°C.									
PGC	4.83	1.99	*	ND	ND	ND	0.63	ND	ND
CAN+	4.7	ND	7.6	0.6	ND	1.0	3.4	ND	1.7

\+ An appreciable concentration of hydrocarbons (not calibrated) was observed in the canister sample.
* Toluene detection by PGC prevented by incorrect placement of valve time.
ND Not detected. Peak was absent or smaller than 5 millivolt-second.

TABLE 2. PGC AND CANISTER DATA AT HAZARDOUS WASTE SITES IN NORTHERN DELAWARE

April, 1989. Samples taken at Superfund hazardous waste sites. PGC was mounted in a van with probe one meter above roof on upwind side. CPSil5CB column. Concentrations are parts per billion by volume.

	Benzene	Tri-chloro-ethylene	Toluene	Tetra-chloro-ethylene	Chloro-benzene	Ethyl-benzene	m,p-Xylene	Styrene	o-Xylene
April 5, 1989 Grantham Lane									
* PGC	0.59	ND	ND	INT	0.60	ND	ND	ND	ND
CAN	0.93	ND	1.00	<0.15	ND	ND	0.62	ND	0.38
Army Creek									
* PGC	0.39	ND	ND	INT	0.54	ND	0.28	ND	0.05
CAN	0.75	ND	0.69	<0.15	ND	<0.15	0.34	ND	0.18
Delaware Sand & Gravel									
* PGC	ND	ND	ND	INT	0.59	ND	0.12	0.11	ND
CAN	0.45	ND	0.27	ND	<0.15	ND	<0.15	ND	0.18
April 6, 1989 Halby Waste Lagoon									
PGC	ND	ND	2.78	INT	1.61	0.52	0.64	ND	1.30
CAN	1.00	ND	2.37	<0.15	ND	0.47	1.09	ND	0.43
PGC	ND	ND	2.00	INT	0.22	0.27	0.62	ND	0.04
CAN	0.50	ND	1.90	0.36	ND	0.20	0.60	ND	0.23
Pigeon Point Waste Disposal Plant									
PGC	ND	2.39	11.91	INT	0.71	1.60	5.37	2.83	0.77
CAN	0.54	0.63	8.84	0.63	ND	1.23	4.12	0.51	1.10
Standard Chlorine of Delaware Plant									
PGC	15.95	ND	0.69	INT	46.44	ND	0.14	ND	0.27
CAN	14.69	ND	0.57	ND	40.77	0.15	0.40	ND	0.13

ND Not detected. Peak was absent or smaller than 5 millivolt-second.
INT Persistent interference at this retention time.
* Landfill under Superfund remediation.

TABLE 3. COLOCATED AND UPWIND/DOWNWIND PGC AND CANISTER OPERATION IN USSR

Vilnius June 1989. Colocated: PGCs in mobile laboratory. Probes 2.5 cm apart 18 m from highway. Canisters sited on same side of road as PGCs and filled continuously between 1631 and 1815. Data not shown if either PGC recalibrating. Upwind/downwind: PGC-1 in van 12 meters downwind of roadway with probe extended 1.5 meters above roof. PGC-2 in mobile laboratory. Canisters downwind of road and filled continuously between 1100 and 1300. CPSil19CB columns. Concentrations are parts per billion by volume.

Start Time	Benzene		Toluene		Ethyl-benzene		m,p-Xylene		o-Xylene	
COLOCATED DATA June 1, 1989										
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1631	0.8	0.8	2.5	2.8	ND	ND	0.5	ND	ND	0.4
1701	1.3	1.0	2.7	2.7	ND	ND	0.7	ND	ND	0.1
1716	0.6	0.7	2.1	2.1	ND	ND	0.7	ND	ND	0.1
1731	1.1	1.0	2.4	2.2	ND	ND	0.9	ND	ND	ND
1801	0.7	0.8	2.3	2.6	ND	ND	0.5	ND	ND	ND
Average PGC values during the canister sampling period										
	0.9	0.8	2.4	2.5	0.0	0.0	0.7	0.0	0.0	0.1
Canister sample values (distance from roadway in meters)										
	(3)	(10)	(3)	(10)	(3)	(10)	(3)	(10)	(3)	(10)
	2.1	1.1	3.1	1.3	0.4	0.2	1.2	0.5	0.5	0.2
UPWIND/DOWNWIND DATA June 2, 1989										
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1229	1.3		4.5		ND		2.5		ND	
1244		6.3		2.0		ND		ND		ND
1259	3.3	0.4	7.4	1.3	ND	ND	3.1	ND	ND	ND
Average portable chromatograph values during the canister sampling period										
	2.3	3.3	5.9	1.6	0.0	0.0	2.8	0.0	0.0	0.0
Canister sample values (distance from roadway in meters)										
	(3)	(10)	(3)	(10)	(3)	(10)	(3)	(10)	(3)	(10)
	2.1	1.1	3.1	1.3	0.4	0.2	1.2	0.5	0.5	0.2

ND Not detected. Peak was absent or smaller than 5 millivolt-second.

TABLE 4. SIDE-BY-SIDE PGC AND CANISTER DATA AT LAFAYETTE, GEORGIA

June 6, 1990. Shaver's Farm Superfund Site. PGCs in van were moved to several sites. CPSil19CB columns. Concentrations are parts per billion by volume.

	Benzene	Tri-chloro-ethylene	Toluene	Tetra-chloro-ethylene	Chloro-benzene	Ethyl-benzene	m,p-Xylene	o-Xylene	Styrene
PGC-1	ND	ND	1.10	ND	ND	0.67	1.31	0.12	*
PGC-2	ND	ND	1.75	ND	ND	0.62	1.84	ND	18.03
CAN	0.7	ND	1.0	0.1	ND	1.0	1.6	0.8	5.9
PGC-1	ND	ND	0.99	ND	ND	0.46	0.28	ND	*
PGC-2	ND	ND	0.18	ND	ND	0.69	0.58	ND	13.68
CAN	0.3	ND	0.7	0.2	ND	0.8	0.8	0.4	4.5
PGC-1	ND	ND	0.59	ND	ND	ND	ND	ND	*
PGC-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
CAN	0.1	ND	0.4	ND	ND	0.2	0.4	0.2	0.2
PGC-1	ND	ND	0.32	ND	ND	ND	0.04	ND	*
PGC-2	ND	ND	0.10	ND	ND	ND	0.07	ND	ND
CAN	3.0	ND	0.2	ND	ND	0.1	0.2	0.2	0.2
PGC-1	ND	ND	0.08	ND	ND	ND	ND	ND	*
PGC-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
CAN	0.1	ND	0.1	ND	ND	ND	ND	0.1	ND
PGC-1	ND	ND	0.19	ND	ND	ND	ND	ND	*
PGC-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
CAN	0.1	ND	0.3	ND	ND	0.2	0.4	0.3	0.4

* PGC-1 was not calibrated for styrene because of a persistent interfering peak probably caused by column deterioration.

ND Not detected. Peak was absent or smaller than 5 millivolt-second.

TABLE 5. TANDEM PGC DATA AND CANISTER DATA IN RESEARCH TRIANGLE PARK, NORTH CAROLINA

March 23, 1990. PGC-1 analyzed vinyl chloride and 1,1-dichloroethylene with KCl/Alumina PLOT column. PGC-2 analyzed other compounds with a CPSil5CB column. PGCs in car with probes 1.5 meters above the on upwind side, 40 meters downwind of dry-cleaning plant. Concentrations are parts per billion by volume.

	Vinyl-chloride	1,1-Di-chloro-ethylene	Benzene	Toluene	Tetra-chloro-ethylene	m,p-Xylene	Styrene	o-Xylene
PGC	0.01	0.02	ND	ND	1.41	ND	ND	ND
CAN	ND	ND	0.68	0.56	3.38	0.35	0.20	0.20
PGC	ND	0.01	ND	ND	4.09	ND	ND	ND
CAN	ND	ND	0.76	0.62	3.15	0.29	ND	< 0.20

ND Not detected. Peak was absent or smaller than 5 millivolt-second.

TABLE 6. AVERAGE ABSOLUTE DIFFERENCES BETWEEN PGC AND CANISTER DATA

Absolute values of differences between PGC and canister results for each compound were averaged. CPSil5CB data taken from TABLES 1, 2, and 5. CPSil19CB data taken from TABLE 6, in which two PGC values for each analysis were averaged. CPSil5CB is methylsiiicone. CPSil19CB is 7% cyanopropyl-silicone, 7% phenylsilicone, 85% methylsilicone, and 1% vinylpolysiloxane. Phase thicknesses 2 micrometers. Differences have dimensions of parts per billion by volume.

	Column	
Compound	CPSil5CB	CPSil19CB
Benzene	1.49	0.72
Trichloroethylene	2.03	*
Toluene	0.76	0.15
Tetrachloroethylene	1.27	0.05
Chlorobenzene	1.17	*
Ethylbenzene	0.97	0.20
m,p-Xylene	1.69	0.30
o-Xylene	0.40	0.31
Styrene	1.53	3.69

* No data were available for these compounds.

DISCUSSION

EDWARD FURTAUGH: We also have a Photovac 10S70. I used it in a smoking lounge and at a gain of 100, there was a monster peak occurring near the retention time of toluene. Any suggestions what it could have been? The Photovac people that I've talked to haven't been able to shed much light on it.

RICHARD BERKLEY: Indoor air is a pretty tough thing to deal with. You normally see ambient background levels of things like toluene as a result of single photon absorptions. In indoor air you can have ppm concentrations so you can see things which are ionized in double photon absorptions. You can, for example, calibrate things like carbon tetrachloride and chloroform, which you can't see at all at ambient background levels. So, in indoor air all bets are off, and I have seen some horrendous things in indoor air which are probably relatively high levels of things that the instrument normally can't see. If it didn't have the retention time of toluene, and if you were using a constant temperature column accessory the chances are very good that it was not toluene. It may be a much larger level of something else.

TOM SPITTLER: We just did an air study of our building in Boston using the Photovac. And we found 1 to 2 ppb of benzene and toluene in every place because it's a very well ventilated building. But in the smoking room we found about 100 ppb of toluene and about 50 of benzene. There wasn't any question, the retention times matched beautifully. We took samples back and confirmed them on GC/MS. You get benzene and toluene in all smoking rooms. I'm not sure why your peak wasn't exactly there, but I bet anything that's what it was. A question though: you were using canisters and the Photovac with what? Occasional sampling or regular sampling? How often did you sample with the Photovac in order to cover the period of time you were drawing the canister sample?

RICHARD BERKLEY: In most cases what I did was take a canister grab sample by holding the canister within ten centimeters of the tip of the Photovac intake and opening the can so that it filled during the same time, during the minute or so that the Photovac pump was running. These samples are necessarily nonequivalent. In the canister you get six liters, and you take a representative sample of that to analyze it. The Photovac takes a milliliter or something that happened to be flying through at the moment when it decided to inject. These are not equivalent, but if the same air is being sampled they ought to resemble each other.

TOM SPITTLER: Yes, I agree. I think it's really a nice correlation.

RICHARD BERKLEY: So, in all cases expect variances while taking those grab samples. Variances were seen with two-hour integrated canister samples, and we were taking Photovac runs during the time.

TOM SPITTLER: You just averaged them then?

RICHARD BERKLEY: Well, the canister samples were shown as dotted and dashed lines because they were the time-integrated samples. If you could go back and compare those slides, you'd find that all those dotted and dashed lines were at the same level on all of those slides. We couldn't quite figure out how to show the continuity there.

TOM SPITTLER: No, I thought it was really nice data. This afternoon a couple of guys from the Regional Lab up in Boston are going to show some Photovac versus canister standards and calibrated by different techniques. They are actually directly comparable samples, and you see the same basic kind of correlation. It may be a little tighter now because they're sampling exactly the same way and they're sampling the same known mixture of air.

RICHARD BERKLEY: Something I forgot to mention and it'll be important to some people, we are using canisters to hold our calibration standards, and we're preparing the standards the same way we prepare the standards for the method that is used to analyze the canisters. There is no independence on that point. These two methods are locked together, and if we make a mistake on one, we make a mistake on the other. What's independent here is sampling methodology, and I should have said that.

JOSEPH EVANS: My question pertains to detection limits. I notice that you're down measuring at very low levels (1, 2 ppb). Your worst agreement was at those levels. When you got to the higher levels you had much better agreement. And I was wondering about how close you were to your detection limits for the two different methods?

RICHARD BERKLEY: Well, there are two limits to talk about here. One of them is detection limit, and for single photon ionizations, compounds that ionize well below 10 eV, such as benzene, its homologs and the chloroethylenes. We measured detection limits by extrapolation, three times the baseline noise, using an old 10A10 with a gain turned all the way up, and it appeared that the absolute detection limit was somewhere in the neighborhood of 18 femtograms. That would translate out to down in the neighborhood of 1/100 ppb in a 1 mL sample. That's just a detection limit. The instrument in fact will refuse to process any peak that is smaller than five millivolt seconds. And of course, when we did that detection limit we were only extrapolating — our smallest sample was 1.6 picograms, and it produced a peak of about 2.3 volt seconds. We were no where near this extrapolated detection limit with any sample we actually delivered to the instrument. So, we're just guessing. But, we do have a substantial basis to guess that a 5 millivolt second peak is way above that. And all you have to do if you want to really get tough about what the detection limit is, is to run a sample on a blank library, then shift to a calibrated library and calculate how much it would take to make a five millivolt second peak, assuming linear response.

JOSEPH EVANS: What levels were your calibration standards?

RICHARD BERKLEY: We generally try to use between 10 and 20 ppb. If something is very convenient to prepare like chlorobenzene or tetrachloroethylene, we like to use one of them on one instrument and the other one on the other instrument, because there is some tendency, if the calibration gas valve is a little bit weak, to have some carryover contamination, usually no more than 0.5 ppb. You do need to look at that for your standard, whatever your standard compound is.

JOSEPH EVANS: You were actually measuring below your lowest calibration standard?

RICHARD BERKLEY: We're using a single point calibrations. We did a lot of work on this thing early on and found that we were getting pretty consistent linear responses from as low a sample as we could inject all the way up to higher than we could inject.

HIGH SPEED GAS CHROMATOGRAPHY FOR AIR MONITORING

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Abstract

Gas chromatography has the potential to be a much faster method of separation than is usually realized. If column operating conditions are optimized for speed and injection band width is minimized, some simple separations can be completed in a few seconds. In the work described here the system was evaluated using common organics including alkanes, aromatics, alcohols, ketones and chlorinated hydrocarbons. Quantitative trapping and reinjection was achieved for all tested compounds. Limits of detection (LOD) for many compounds, based on a 1 cm^3 gas sample, were less than 1 ppb, but for one carbon-chlorocarbons the LOD when using a flame ionization detector was inadequate. By using the cold trap inlet with a low dead volume detector and a high speed electrometer, the efficiency available from commercial capillary columns can be better utilized and retention times for some routine separations may be reduced to a few seconds.

Introduction

Gas chromatography (GC) is often used for routine, repetitive analysis of simple mixtures. For some of these applications, the use of 2 to 5 m capillary columns operated at linear velocities of 100 to 200 cm/s offers the possibility of greatly decreased analysis times. This potential for high speed analysis has been documented in the literature (1-7). Under optimal conditions, a 0.25 mm i.d. column should be capable of achieving 5000 to 7000 effective plates with retention times of 5 to 10 seconds (4,8). Although this number of plates is low compared to most capillary systems, it is comparable to the number of plates achieved by many packed column systems with retention times of several minutes or more. Therefore, some routine GC separations that are currently performed using packed columns or non-optimized open tubular columns could be performed much faster with a capillary system that is optimized for speed.

While the theoretical potential of capillary columns for high speed analysis is well known, limitations in commercially available equipment, especially inlet systems, have prevented general application of high speed techniques. With most commercial instruments, the major

factors that limit analysis speed are the width of the initial band produced by the inlet system and the response time of the electrometer. Efficient separation with retention times of 5 to 10 seconds and a column diameter of 0.25 mm requires an initial band width of about 20 ms or less and an electrometer response time of about 5 ms. For purposes of comparison, most capillary GC systems produce injection band widths of 50 to 500 ms and feature electrometer response times of 150 ms or longer.

In response to the requirement for narrow injection bands, a number of experimental inlets have been described (5, 9-13). Our group has described a prototype cold trap that was used as a vapor collection device and which may also serve as a focusing system for rapid analysis of simple mixtures (14-15). The design reported by our group, which expanded on the innovative work of Hopkins and Pretorius (16), featured a cold trap that was cooled by a continuous flow of cold nitrogen, and was resistively heated using a current pulse. This design was a marked improvement over that reported earlier, which had a number of unrecognized serious flaws that prevented reliable and/or quantitative operation (17-18). More recently, van Es et al described a fast GC system that utilized a similar inlet (19). In their design, a 50 micron capillary column was used for the separation.

Experimental Section

The design and operation of the cold trap is given in detail elsewhere (14,15), and is shown schematically in Figure 1.

Operating conditions and chromatographic equipment. All chromatograms were collected isothermally at column temperatures of 35 to 60 ^{o}C using a 5 m long, 0.25 mm i.d. fused silica column with a 0.1 micron bonded methyl silicone stationary phase (Quadrex). The carrier gas was hydrogen, which was supplied at a flow rate of 2.5 to 3 ml/min to produce linear velocities of 85 to 102 cm/s. The injector and detector were heated to 225 ^{o}C. A flame ionization detector (FID) was used in all experiments. To minimize the effective dead volume, the column was moved close to the base of the flame. Both a Varian 3700 or an HNU 301 GC were used.

For trap recovery studies, test mixtures were prepared either without solvent or in high purity carbon disulfide provided by The Dow Chemical Company. The injection volume was 2.5 uL in all cases and the split ratio ranged from about 50:1 to 500:1 depending on the sample concentration. For vapor studies, samples were injected in humidified or laboratory air in volumes of 0.025-1.0 cm^3.

Results and Discussion

Design Considerations. A number of design considerations were found to be important in determining the durability and performance of the system. The choice of trap material and dimensions affects durability and reinjection performance. An ideal material would have high electrical resistivity, low chemical activity, a low coefficient of thermal expansion, would be highly malleable and would not work harden. A number of materials, including stainless steel, nickel, platinum, Monel 400, and an alloy of thirty per cent copper - seventy per cent nickel were evaluated for use as trap tubes. The work reported here was done using a trap made of Monel 400. Stainless steel, which was used in some early studies (17, 18), is the least desirable choice because of its tendency to work harden and become brittle. For a trap made of hard-tempered Monel 400 with an internal diameter of 0.25 mm, a wall thickness of 0.18 mm provided a good combination of strength and performance.

Trapping and Reinjection Efficiency. Cold traps have been used in GC for many years (19-23). Since the short, open tubular trap used in these experiments may be less efficient than some other designs (23), a careful evaluation of trapping efficiency was necessary.

In order to test trapping and reinjection efficiency, samples were injected without using the cold trap and average peak areas were calculated for each compound. In addition to comparing peak areas obtained with and without trapping, the FID response was monitored during the entire process to allow any breakthrough of the sample to be detected. At temperatures of -100 ^{o}C or colder, each of the tested compounds was quantitatively trapped and reinjected. Peak area reproducibility for all compounds was very good with coefficients of variation ranging from 1 to 5 per cent, or less in all cases in which trapping was used.

Compounds tested were (given in order of increasing boiling point): isoprene, pentane, dichloromethane, acrolein,chloroform,methanol, hexane, carbon tetrachloride, acrylonitrile, 2-butanone,benzene,propanol, heptane, i-octane, toluene, n-butanol, tetrachloroethylene, octane, m- & o-xylene, nonane, 4-ethyltoluene, and 1,3-dichlorobenzene. Detailed results are given elsewhere (15). Trapping efficiency was also measured for 1% solutions of aromatics prepared in carbon disulfide. The trapping efficiencies obtained in those experiments were not significantly different than those measured without solvent. These materials can be effectively trapped and reinjected at temperatures of -100 ^{o}C. However, trapping behavior is not easily predicted on the basis of boiling point or freezing point, and in most cases an effective temperature must be experimentally determined for each type of sample. Highly volatile materials, which may be gases at room temperature, and low volatility materials, which may be difficult to revaporize, have not yet been tested and may be difficult to trap and reinject with this system.

Limit of Detection (LOD). For monitoring volatile organics in ambient or workplace air, the LOD of the method must be very low. As of early November, 1990, the LOD's for pentane, hexane, heptane, octane, benzene, toluene, xylene, ethylbenzene, 4-ethyltoluene, 1,3,5-/1,2,4-trimethylbenzenes, and chlorobenzene have been measured and been shown to be in the range of 0.2 - 5 ppb, with the most recent results all being <1.0 ppb. (The drop in LOD has occurred as a result of improved methodology as work has proceeded over the past few months. There has not been time to re-do some of the earlier work.)

All of these values were determined based on an injection of a maximum of 1 cm^3 of air, and the use of an FID. The LOD was calculated based on a definition of three times the standard deviation of the noise.

One of the major factors contributing to the reduced LOD was the optimization of the custom-designed, high speed electrometer supplied for this project by HNU Co. A filter setting of 12 Hz was found to be optimal for GC peaks in the retention time range of 5-10 seconds.

Note that these LOD's are not achievable for one carbon-halocarbons. LOD's in the sub-20 ppb range for certain halocarbons will only be achievable with the use of an electron capture detector (ECD). Unfortunately, an ECD has, of necessity, a certain internal volume that may significantly spread peaks, and reduce the advantage of the Fast-GC method. This may require assays to be performed on a 30-60 second basis, rather than on a 5-10 second basis.

In addition, it is important to remember that the Fast-GC technique trades chromatographic resolution for speed. Although the cost of this trade is reduced by tuning the column for high speed, low retention time use (8,14), the separation of components of complex mixtures may not always be possible.

Further, the limitations imposed by the use of an isothermal GC method (necessitated by the short analysis times) limit the ability to monitor compounds of widely differing boiling point simultaneously. While this might be overcome by flow-programming methods, the extent to which such strategies will allow effective ambient air monitoring is unknown at this time.

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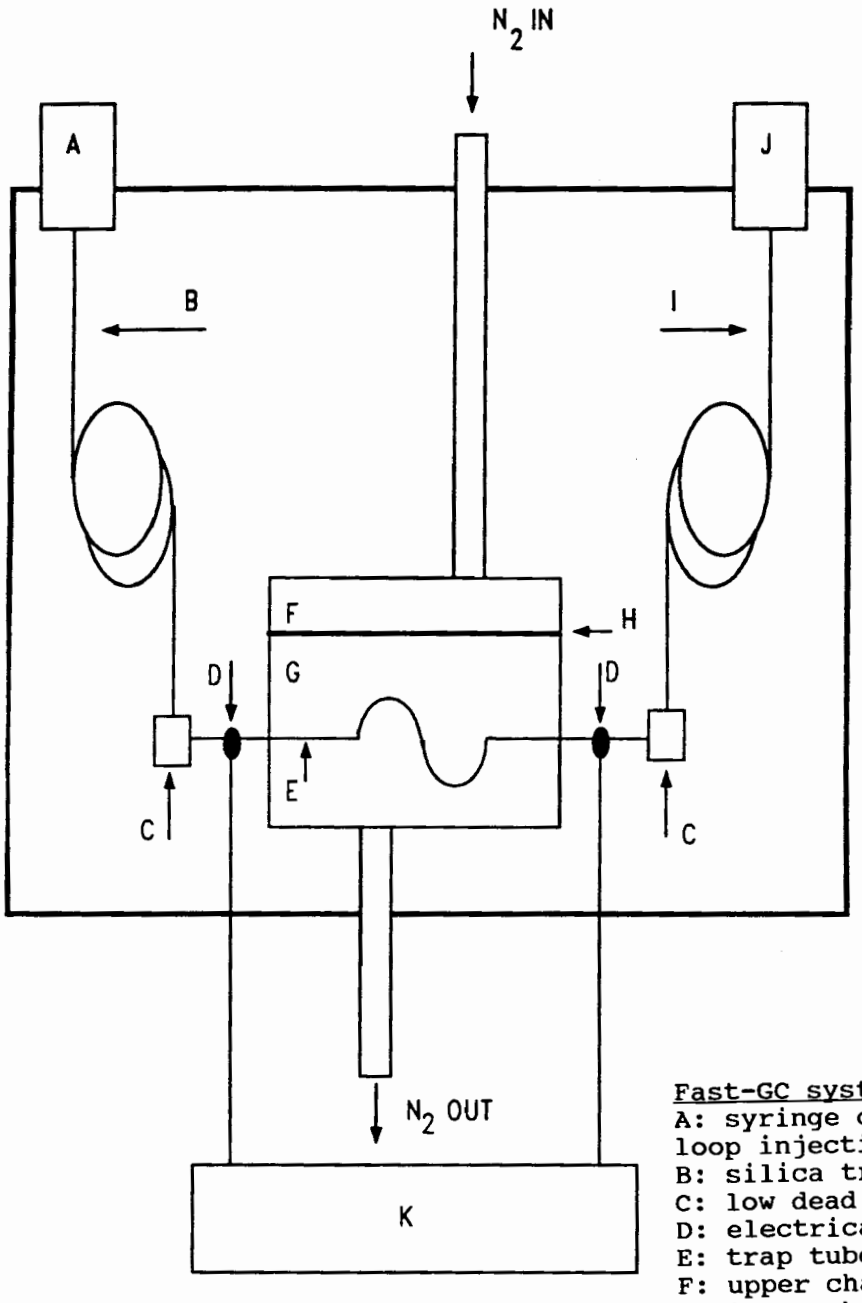

Figure 1

Fast-GC system:
A: syringe or gas sampling loop injection port;
B: silica transfer line;
C: low dead volume unions;
D: electrical contacts;
E: trap tube;
F: upper chamber cold trap;
G: lower chamber cold trap;
H: baffle;
I: capillary column
J: flame ion. detector;
K: capacitor power supply

DISCUSSION

HANK WOHLTJEN: How much energy did your capacitive discharge heater use?

STEVEN LEVINE: It's running about 30 to 70 volts discharge with a few tens of amps.

HANK WOHLTJEN: How big are the capacitors? Are they a tenth of a farad or something like that?

STEVEN LEVINE: All the details of the design is in that paper in Analytical Chemistry.

HANK WOHLTJEN: You mentioned electric cooling of the trap. What do you think you'd use for that, a refrigerator or a thermal electric?

STEVEN LEVINE: It would have to be a thermoelectric cooler. We are investigating that at this moment.

JOHN SNYDER: I was curious as to the diameter of the columns you're using.

STEVEN LEVINE: They're just 0.25 mm columns. They're very traditional columns. They're not megabore. They're not ultra small.

JOHN SNYDER: You also spoke about the dead volume in the detectors. Are you modifying traditional detectors or are you making your own detectors?

STEVEN LEVINE: We have a 90 μl dead volume ECD from HNU Systems at this point that we're working with. We feel that size is probably too big.

SCREENING VOLATILE ORGANICS BY DIRECT SAMPLING ION TRAP AND GLOW DISCHARGE MASS SPECTROMETRY*

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ABSTRACT

Two different types of direct sampling mass spectrometers are currently being evaluated in our laboratory for use as rapid screening tools for volatile organics in a wide range of environmental matrices. These include a commercially available ITMS ion trap mass spectrometer and a specially designed tandem source glow discharge quadrupole mass spectrometer. Both of these instruments are equipped with versatile sampling interfaces which enable direct monitoring of volatile organics at part-per-billion (ppb) levels in air, water, and soil samples. Direct sampling mass spectrometry does not utilize chromatographic or other separation steps prior to admission of samples into the analyzer. Instead, individual compounds are measured using one or more of the following methods: spectral subtraction, selective chemical ionization, and tandem mass spectrometry (MS/MS). For air monitoring applications, an active "sniffer" probe is used to achieve instantaneous response. Water and soil samples are analyzed by means of high speed direct purge into the mass spectrometer. Both instruments provide a range of ionization options for added selectivity and the ITMS can also provide high efficiency collision induced dissociation MS/MS for target compound analysis. Detection limits and response factors have been determined for a large number volatile organics in air, water, and a number of different soil types.

INTRODUCTION

Direct sampling mass spectrometry for the measurement of trace levels of volatile organics in environmental matrices has a wide range of important field screening applications. These include the measurement of volatiles in waters, soils, oily wastes, stack emissions, and ambient air, among others. In addition, real-time "sniffing" capability provides a convenient means of detecting soil gas emissions, leaking waste containers, and probing the atmosphere in enclosed storage facilities.

Because of their small size, relative simplicity, ruggedness, and low power consumption, conventional quadrupole mass spectrometers and quadrupole ion trap mass spectrometers are especially attractive for transportable field screening applications. In fact, several commercial quadrupole based instruments are currently available for field monitoring applications and recently, several different research groups have been developing and demonstrating transportable ion trap mass spectrometers for on-site GC/MS applications (1-3).

This paper describes the use of an ion trap mass spectrometer and a tandem source glow discharge mass spectrometer for the direct measurement of ppb levels of volatile organics in air, water, and soil. Because these instruments do not use chromatographic separation prior to admitting a sample into the mass spectrometer, the response time is virtually instantaneous and accurate quantification of target analytes can be accomplished in less than 2 minutes. Although the tandem source quadrupole mass spectrometer is somewhat limited in its ability to handle complex samples, the ion trap mass spectrometer has the capability of selective ion storage and multiple stages of collision induced dissociation for much greater specificity.

Laboratory-based instruments are currently being used to develop and validate methods for direct air monitoring and the screening of water, soil and waste samples. A transportable ion trap mass spectrometer for field use is under construction in our laboratory and will be initially tested in 6-9 months.

EXPERIMENTAL

Instrumentation

Ion Trap Mass Spectrometer

All ion trap experiments were performed with a Finnigan MAT Corporation ITMS ion trap mass spectrometer. Our instrument is equipped with a specially designed vacuum chamber which is electropolished on the inside and pumped to high vacuum with two air cooled 330 L/sec turbomolecular pumps. The vacuum chamber and analyzer cell are maintained at a constant temperature of 120° C by means of infrared heating lamps which help to minimize the adsorption of contaminants on the analyzer surfaces. This instrument is also equipped with the necessary hardware and software to perform electron impact (EI) and chemical ionization (CI), as well as selective ion ejection, and collision induced dissociation multiple-step (tandem) mass spectrometry experiments (MS/MS). Control of the instrument and data acquisition are performed with an IBM AT compatible computer using software provided by the manufacturer.

The standard chromatographic interface provided with the ITMS instrument has been replaced with a custom designed interface developed in our laboratory. This interface consists of a short length (14 inches) of 110 micron ID uncoated fused silica capillary tubing which is maintained at atmospheric pressure at one end and high vacuum at the other end. The high vacuum end of the capillary is inserted directly into the ITMS analyzer cell and the atmospheric pressure end is connected to a quick-coupling device which allows rapid switching of sampling modules for different monitoring applications. The gas flow rate through the capillary restrictor is approximately 0.5-1.0 mL/min. Because the samples are introduced directly into the ion trap cell, the manifold pressure is maintained at a lower pressure. This is believed to help reduce deterioration of the electron filament and the electron multiplier. For example, even when sampling water-saturated air for extended periods of time, the electron filament lifetime has been approximately 6 months and the multiplier lifetime has been in excess of 12 months.

ITMS Air Sampling Probe

For direct air monitoring experiments, a special sampling system has been developed as shown by the diagram in Figure 1. This system consists of an 1/4 inch OD teflon transfer line which is connected at one end to the air sample generation system and at the other end to a sampling "cross" arrangement which allows helium to be mixed with the air sample prior to entering the ITMS. The helium is necessary as a buffer gas in the ITMS to collisionally cool ions, thus reducing loss of ions from the trap and improving the overall performance. A pulsed valve is used to meter helium into the air stream providing approximately an order of magnitude increase in sensitivity relative to a fixed-ratio, continuous mixing of helium with the air. A vent port also located on the inlet "cross" of the sampling system allows the gas stream to be continuously sampled at a high flow rate, thus decreasing the response time for the mass spectrometer. The other port of the inlet "cross" is connected to a short section of uncoated fused silica megabore capillary which is used as an "open/split" interface with the ITMS by inserting 1 inch of the microbore capillary restrictor into the other end of the megabore tubing. Approximately 2 L/min of air is drawn through the megabore tubing by means of a small sampling pump; however, a metering valve located between the pump and the splitter can be used to reduce the pumping speed if desired. This combination of active pumping and the use of the open/split capillary interface minimizes the dead volume in the inlet system leading to a response time of only a few seconds.

Purge Device for Water and Soil samples

For the measurement of volatile organics in water and soil samples (slurries), the air sampling probe is simply replaced with a high speed needle sparge purge device as shown in Figure 2. This device accepts standard 40 mL VOA vials which mount directly on the needle sparger. A pressure regulator and a precision needle valve control the flow of helium purge gas through the sample and the purged components exit through a 10 inch length of megabore capillary tubing. Normal helium flow rates vary from 100 to 200 mL/min which efficiently purges the volatile components from a room temperature sample in less than 5 minutes. The purge device connects directly with the capillary restrictor interface in an open-split configuration with a split ratio of approximately 100:1. The bulk of the sample is diverted to the vent port. As an added feature for screening applications, the vent port is capable of accepting resin cartridges for trapping of components that would normally be vented. This enables the collection of an archived sample which may be sent back to a central laboratory for confirmatory analysis by GC/MS.

Tandem Source Quadrupole Mass Spectrometer

The tandem-source quadrupole mass spectrometer (TSMS) is a prototype instrument constructed using an EXTREL C-50 quadrupole mass spectrometer as the basic system. This instrument was configured with 3/4" diameter rods for high transmission efficiency and a 300 watt RF power supply for a maximum mass range of 500 amu. Control of the instrument is provided by a Dell 325 computer using software written in our laboratory. An axial EI source was purchased with this instrument for testing purposes and for generating conventional 70 eV electron impact spectra.

In order to produce a versatile instrument for environmental monitoring applications, the configuration of the standard C-50 mass spectrometer was extensively

modified. In addition to the axial EI source which was purchased with the spectrometer, a glow discharge ionization source was designed and constructed for this instrument. This source is housed in a differentially pumped vacuum chamber which is separated from the rest of the mass spectrometer by a 1.5 mm diameter vacuum conductance limit as shown in Figure 3. The glow discharge source is typically maintained at a pressure of 0.25 torr while the analyzer is maintained at 2×10^{-5} torr. Ions generated by glow discharge ionization pass through a lens assembly into the high vacuum portion of the instrument where they enter the lens assembly of the axial EI source and are subsequently focussed into the mass analyzer.

Air samples can be introduced into the tandem source quadrupole mass spectrometer by two different methods, either through the differentially pumped glow discharge source chamber, or directly into the electron impact source by means of a simple capillary restrictor. Both inlet systems have been designed so that they are directly compatible with the same sampling devices used with the ion trap mass spectrometer. Thus, essentially the same apparatus and experimental conditions are used for direct purging of water and soil samples regardless of the mass spectrometer used. The only difference is the ability of the glow discharge ionizer to sample air directly without the need for the air sampling pump and open/split interface used with the ITMS.

Dynamic Sample Generator

A dynamic sample generation apparatus is used to produce known concentrations of volatile organic analytes in an air stream. This apparatus was used for the determination of instrumental detection limits for real-time air monitoring experiments. It basically consists of a variable speed syringe pump and a dilution air manifold. The syringe pump continuously meters small amounts of organic compounds into a controlled stream of air. Concentrations of the analytes can be easily varied by adjusting the speed (metering rate) of the syringe pump and/or by changing the flow rate of dilution air through the manifold. Turbulent mixing of the organic compounds and the dilution air occurs in the manifold line which provides a homogeneous concentration at the sampling ports.

Components of the dynamic sample generator include a Razel Instruments model A-99 syringe pump equipped with a 5 mL syringe, a 100 psi air supply line equipped with an on/off toggle valve and a precision metering valve, a 1.5 m x 6 mm Teflon line (dilution manifold), and two 1/4 inch Swagelock sampling ports. The apparatus produces continuous and stable generation of organic concentrations in air and also allows rapid changes in concentration without having to wait excessively to reach a steady-state concentration.

Air containing the desired concentration of individual organic compounds is typically generated by metering a (1:1) water/methanol solution containing approximately 400 ug/mL of the organic compound into the dilution air stream using the syringe pump. The flow rate of the syringe pump can be continuously varied from 8.47×10^{-4} mL/min to 0.0503 mL/min. The dilution air flow is typically adjusted for a rate of 25 L/min through the manifold. As this air flows rapidly past the syringe pump needle, it quickly vaporizes the volatile organics and the solvent. Liquid flow from the syringe, however, must be maintained low enough to prevent condensation in the system. By knowing the concentration of the organic in the liquid solution, the flow rate out of the syringe, and the flow rate of the dilution air, the concentration of the organic compounds in the air can be readily calculated. This assumes that there is minimal adsorption of analytes on the walls of the manifold and complete vaporization of the liquid into the dilution air.

Operating Conditions

Ion Trap Mass Spectrometer

Most of the ion trap data presented in this paper was generated using electron impact ionization conditions. Scan functions for the acquisition of mass spectra were written using the scan function editor program supplied with the commercial software. Typically, for optimum sensitivity the electron ionization time was 50 msec. Low mass cut-off was 60 amu, preventing the storage of ions due to water and air. The mass scan range was approximately 50 to 200 amu which enabled the detection of major ions for each of the volatile organic compounds. In order to improve the signal-to-noise ratio, 16-25 microscans were averaged per displayed scan. Axial modulation was used for all experiments in order to achieve optimum instrument performance. Helium buffer gas was admitted into the system exclusively through the sample transfer line.

Tandem Source Quadrupole Mass Spectrometer

The glow discharge ionization source is specifically designed for high sensitivity direct air monitoring applications. Air is admitted into the ionization region through a metering valve at a flow rate of 0.5-1.0 standard mL/min while a 160 L/min roughing pump maintains the pressure in the ionizer at a constant 0.25 torr. Coaxial ionization electrodes are used for the discharge and consist of a 1 cm diameter x 2 cm long hollow cathode with a 20 gauge wire anode. A potential difference of approximately 600 volts is sufficient to strike and maintain a discharge in the source. Ionization of organic compounds in this source is the result of ion molecule reactions which produce proton transfer and charge exchange reaction products. Conditions within the glow discharge source can be adjusted to optimize either proton transfer or charge exchange reactions. The proton transfer reactions provide high sensitivity for compounds which have proton affinities greater than that of water (which is the primary proton

transfer reagent). Charge exchange on the other hand, is a much more universal ionization method and produces fragmentation spectra which are similar to electron impact ionization spectra. By operating the glow discharge source at low pressures, the formation of water cluster ions which often hamper API mass spectrometers is nearly eliminated, improving sensitivity and decreasing the complexity of the spectra.

Direct sampling using the electron impact ionization source of the quadrupole mass spectrometer is accomplished by means of a 1 meter length of 110 micron ID uncoated fused silica capillary tubing. A simple on/off valve between the capillary and the source allows the restrictor to be isolated when not in use. The conditions in the ionizer include an electron current of 0.5 to 1.0 milliamps and an electron energy of 17 to 20 eV. The use of lower electron energies helps to minimize fragmentation, thus concentrating ion current in fewer ions.

Samples and Chemicals

Individual samples of 31 different volatile organic compounds from the USEPA Target Compound List were obtained from Ultra Scientific Company as solutions of the neat compound dissolved in methanol at a concentration of 10,000 ppm. Solutions for use in the dynamic sample generation system were prepared from the methanol stock solutions using ultra-pure water and spectroscopic grade methanol. In order to verify the proper calibration and performance of the dynamic sample generation system, certified standards of volatile organics in nitrogen were purchased from Scott Specialty Gases.

Water samples were prepared using distilled water containing 0.15 g/L of sodium chloride and 0.17 g/L of sodium sulfate. A series of concentrations of individual volatile organics from approximately 1 ppb to 200 ppb in water was prepared by injecting a known concentration of a methanol solution into water and then carefully pipetting the water standard into a 40 mL pre-cleaned VOA vial. The vials were capped with Teflon lined septa until used. Most samples were prepared at approximately pH 7; however, samples of benzene, trichloroethylene, and tetrachloroethylene were also prepared at pH 2 and pH 10.

A total of 5 different soil samples were examined as part of this study including 2 soils provided by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), 2 local soils, and a potting soil. These represent a range of soil types including clay, sand, and high humic content. The soil samples were prepared by injecting a pre-weighed 5 gram sample of soil in a 40 mL VOA vial with a known quantity of the volatile organic in methanol and allowing it to sit for a short period of time. Slurries of the soil samples for direct purge experiments were prepared by adding 25 mL of water to the sample and allowing them to sit for at least 1 hour prior to analysis.

RESULTS AND DISCUSSION

Volatile Organics in Air

The primary objective of the air monitoring study was to optimize the experimental conditions and determine the real-time detection limits for a representative sample of volatile organic pollutants. This sensitivity assessment was performed using standard electron impact ionization on both the tandem source quadrupole mass spectrometer and the ITMS. This enables comparison of our results with other mass spectrometer systems which are commercially available and use electron impact ionization. For all ITMS experiments, the electron ionization time was 50 msec. Mass scan ranges were selected as appropriate for each compound although the lower mass cut-off was normally at least 40 amu or higher. This prevented water, nitrogen, and oxygen ions from being stored in the ion trap simultaneously with the analyte ions, thus minimizing the effects of space charge and unwanted ion-molecule reactions. Future studies will involve a comparison of sensitivities for chemical ionization and electron impact ionization.

Using the ITMS instrument, sensitivities for the 31 volatile organics were determined. However, pumping problems with the tandem source quadrupole mass spectrometer restricted experiments to the determination of detection limits for only 3 compounds: benzene, trichloroethylene, and tetrachloroethylene. For both instruments, response curves (instrument response vs. concentration in air) were prepared for each of the compounds studied. The range of concentrations examined was generally between 4 and 200 ppb. A typical experiment involved the acquisition of a background level signal, followed by the acquisition of spectra for a series of decreasing concentrations in air generated with the dynamic sample generator. Instrument response vs. time produced a "stair-step" curve as the concentration of organic was reduced to successively lower levels. Each concentration level was maintained for several minutes to ensure that a steady state concentration was reached before further reducing the level.

Ion Trap Mass Spectrometer

An electron impact mass spectrum of a mixture of volatile organics in air is shown in Figure 4. This mixture contained carbon disulfide, benzene, chloroform, toluene, and ethyl benzene at concentrations of approximately 1 to 10 ppm. As shown in this figure, space-charge-induced peak broadening and mass shifting are not significant.

A typical "stair-step" air monitoring response curve acquired with the ITMS is shown in Figure 5. This is a

reconstructed plot of the ion current for m/z 83 as"seen" by the ITMS instrument vs. time for a sample of chloroform in air. As the concentration of the chloroform was decreased to lower values over a period of time, the response of the ITMS decreased proportionally. This same type of plot can be generated in real-time continuous monitoring applications, allowing changes in the concentration to be readily visualized. As shown in Figure 5, the response time of the ITMS to changes in concentration was very fast (less than 15 seconds) and the time required for the sample generator to reach steady state at a new concentration was typically less than 3 minutes.

In addition to the continuous plotting of the ITMS total ion response, it is also possible to monitor the actual mass spectrum in real time in order to detect changes in specific ion intensities. This is especially useful whenever multiple components are present in a sample. All of the information which is generated in real-time may be stored on a hard disk as a temporal series of mass spectra, allowing response curves for any ion in the mass range to be reconstructed, plotted, and integrated. An example of a post-processed mass spectrum of chloroform in air is shown in Figure 6.

An important feature of the response curves generated with the ITMS is the pseudo-sinusoidal waveform superimposed on the curve. This is not actually noise, but is actually an effect due to the pulsed valve addition of helium into the air stream. Maxima correspond to the optimum helium/air ratio and minima correspond to the least effective helium/air ratio. By synchronizing the pulsing of the helium valve with the acquisition of the spectral scans, this effect should be nearly eliminated.

The experimentally determined detection limits for the 31 volatile organic compounds in air are presented in Table 1. As shown in this table, the detection limits are generally in the low ppb range which is comparable to the sensitivity of some commercially available API mass spectrometers. Exceptions to this include bromoform, chloroethane, and chloromethane. However, because chloromethane and chloroethane are extremely volatile (boilding points of 24°C and +12.3°C, respectively), it is likely that these compounds were lost during preparation of the standard. Bromoform, on the other hand, is less volatile than most of the compounds examined, with a boiling point of +150.5°C. Bromoform probably condenses on the walls of the vapor generating system at room temperature and never reaches the ITMS inlet. With proper sample preparation techniques and a shorter, heated sampling line, detection limits for chloromethane, chloroethane, and bromoform would probably be more comparable to the other compounds studied. This is a reasonable assumption since these compounds are chemically very similar to other halogenated hydrocarbons that have been successfully measured and would be expected to have similar ionization efficiencies under electron impact ionization conditions.

The detection limits which are reported for volatile organics in air, were calculated using the RMS (root mean square) variation in the signal measured with no sample present (a blank). This is an accurate determination of the analytical detection limit and represents the lowest concentration of a compound in air that can reliably be observed with the current sampling interface and ITMS operating parameters. For these calculations, the lowest reliably measured signal is defined as the average of the blank signal plus three times the RMS variation in this signal. From the lowest reliably measured signal, the detection limit can be calculated from a calibration curve relating signal to concentration. Linear least squares calibration curves were constructed for the 31 volatile organics studied. Due to space charging effects encountered with a few compounds, a quadratic model was necessary to describe a better fit for the data.

Tandem Source Quadrupole Mass Spectrometer

Detection limits for benzene, trichloroethylene, and tetrachloroethylene in air were also determined using the tandem source quadrupole mass spectrometer. Various concentrations of the individual compounds were generated using the dynamic sample generator as previously described. One signal averaged mass spectrum (n=36) was acquired and stored for each concentration. Signal averaged background samples were also acquired and subtracted from the mass spectra of the actual samples. Experimental difficulties arising from a high hydrocarbon background in the instrument complicated these low-level analyses. The background problem was due to backstreaming of diffusion pump oil and condensation on the ionization source.

Linear regressions of the data were calculated and both data and regression were plotted for each compound. Due to the nature of the signal averaging experiments, an accurate detection limit could not be determined for the three compounds using the same RMS noise calculation method as the ITMS. Rather, the detection limit was determined by calculating the standard deviation of the linear regression plot and then determining the concentration at which the signal is equal to the standard deviation[4] as shown in Figure 7. The regression curve for benzene in air is shown in Figure 8 and the calculated detection limit was determined to be approximately 11 ppb. Based on the linear regression curves for trichloroethylene and tetrachloroethylene, detection limits for these compounds were determined to be approximately 42 and 29 ppb respectively.

Although the electron impact ionization was used predominantly for this study, earlier experiments with the glow discharge ionization source indicate that the detection limits are very similar to or slightly better than those

achievable with the electron impact ionization source. In fact, the tandem source configuration of the quadrupole mass spectrometer is unique and provides extra versatility in terms of sample introduction and ionization options relative to a conventional electron impact ionization quadrupole. For example, air may be sampled and ionized directly with the glow discharge source or it may be sampled through a capillary restrictor and ionized with the axial electron impact ionization source. Since both ionization sources are simultaneously installed on the spectrometer, switching between ionization modes or sample inlet systems is a simple matter of opening the appropriate valve and turning on the electronics for the selected source.

The advantages of the glow discharge source relative to the electron impact ionization source are that it is more rugged for long term operation, the response time is virtually instantaneous, and the source is very tolerant of high oxygen and water saturated atmospheres. Primary advantages of the axial electron impact ionization source are ease of operation and the ability to produce library searchable mass spectra. A major problem with the electron impact source is that the filament assembly is very susceptible to oxidation and burn-out if exposed to large amounts of oxygen or water. For example, when performing direct air monitoring experiments with the electron impact source, the filament must be replaced every 3 to 4 weeks.

Volatile Organics in Water and Soil

The sample handling apparatus and methods for the determination of volatile organics in water and soil slurries are identical for both the ITMS and the TSMS experiments. Volatile organics are purged from a water or soil slurry directly into the mass spectrometer without any preconcentration such as trapping on a resin cartridge. In the simplest case, conventional electron impact ionization spectra are continuously acquired over a mass range of approximately 40-200 amu in order to observe the response for ions corresponding to the purged volatile organics. As shown in Figure 9, the purge profiles for a particular ion can be reconstructed as a plot of response versus purge time. At a helium purge flow of 200 mL/min, purging is normally 90% or more complete after 3 minutes. The area beneath a purge profile correlates well with the concentration of the analytes in the sample as shown in Figure 10. Quantification is accomplished simply by integrating the area of a reconstructed purge profile for the ions corresponding to the target analytes. A typical calibration curve for benzene in water from 1 to 100 ppb is shown in Figure 11. Using carefully prepared standards, correlation coefficients of better than 0.998 are possible. Quantitative reproducibiltiy of less than 10% at the 95% confidence level can also be achieved for water samples without the use of internal standards.

A series of experiments were conducted in which the detection limits, relative response factors, and standard spectra were generated for a series of volatile organics in water. In addition, studies with benzene, trichloroethylene, and tetrachloroethylene were also conducted in order to examine the effects of pH and soil type on the purge efficiency of water samples and soil slurries relative to solutions of volatile organics in pH-7 water. Data for these samples were acquired simultaneously using both the ITMS and the TSMS instruments in order to compare detection limits and quantification accuracy.

The detection limits for 21 different volatile organics in pH-7 water using the ITMS and electron impact ionization are shown in Table 2. These range from approximately 3 ppb for benzene to approximately 60 ppb for dichloroethane and appear to be routinely achievable using the direct purge method. For comparison, the detection limits for compounds purged into the TSMS are also typically less than 200 ppb, although they are generally not quite as good as can be achieved with the ITMS. Accurate detection limits for acetone, 2-butanone, and 4-methyl-2-pentanone have not yet been established due to much lower purge efficiencies.

The matrix effect experiments which were conducted for benzene, trichloroethylene, and tetrachloroethylene appeared to show essentially the same purge efficiency at pH-2, pH-7, and pH-10. Similar results for these compounds were also obtained for a potting soil leachate with a high humic content. These results suggest that accurate quantification may be achieved without the need for extensive sample preparation or the use of internal standards for many water samples. An exception to this may be water samples which contain a high surfactant concentration, although comparative data have not yet been generated.

As opposed to the water samples, differences in the purge efficiencies for volatile organics in soil slurries are more pronounced. As shown in Table 3, the relative purge efficiency for benzene, trichloroethylene, and tetrachloroethylene ranges from approximately 25% to 90% relative to pH-7 water. The least efficient purging was from the soils which had a high clay content and the most efficient purging was from soils having the highest sand content. Although the general trend exhibited by these results is probably reasonable, the actual purge efficiencies are probably better than the data indicate. For example, comparative purge profiles for benzene, trichloroethylene, and tetrachloroethylene in pH-7 water and a potting soil slurry are very similar as shown in Figure 12.

Apparent differences in purge efficiency most likely reflect inefficient stirring and sample purging using a single needle sparger. Further studies have also shown that there was probably significant loss of volatiles from the soil

samples during the preparation step using our soil spiking procedure. Improvements in the purging of soils samples could probably be achieved by simultaneously stirring samples to ensure more homogeneous sparging. Further, the use of an internal standard would be useful to help minimize quantitative errors due to differences in purge efficiency.

CONCLUSIONS

The results of these studies have demonstrated the feasibility of using direct sampling mass spectrometry for the real-time detection of trace organic compounds in air, water, and soils. Detection limits for both the tandem source quadrupole mass spectrometer and the ion trap mass spectrometer are generally in the range of 5 to 200 ppb for water and soil samples without any sample preparation or preconcentration. The detection limits for volatile organics in air using the ITMS range from approximately 1 to 45 ppb for the 31 volatiles studied which is approximately 1,000 times lower than the threshold limit values (TLV's) for these compounds. These detection limits are comparable to those that can be achieved with API mass spectrometers. Detection limits for the compounds studied using the TSMS are slightly worse than those obtained with the ITMS; however, they also are well below the published TLV's. This suggests that the ITMS or TSMS could indeed be useful for field monitoring of stack emissions and soil gas emissions at hazardous waste sites.

Although it is not likely that significant improvements can be made in the detection limits achieved with the TSMS, modification and optimization of the sampling interface for the ITMS will probably result in even better detection limits than reported in this document. In addition, the ITMS instrument also has the capability of chemical ionization which can be used to selectively enhance certain target analytes relative to other compounds in a sample stream.

Both the TSMS and ITMS have excellent detection limits for volatile organic compounds in air, water, and soil; however, experience with the two different mass spectrometer systems suggests that the ion trap mass spectrometer overall is a more useful instrument for continuous air monitoring. Specifically, the ITMS is highly reliable, easier to operate, and more stable than the tandem source quadrupole mass spectrometer. Further, the ion trap mass spectrometer has the capabilities of controlled chemical ionization, selective ion storage, and collision induced dissociation (CID) tandem mass spectrometry (MS/MS). These features are especially important in helping to identify individual components in a complex sample, especially since no chromatographic separations are performed on the sample prior to entering the mass spectrometer. Without these features, the TSMS is restricted to monitoring samples that typically have fewer than 10-15 components. Finally, due to the simplicity of the ion trap analyzer assembly, this type of instrumentation lends itself to downsizing, portability, and remote operation better than the TSMS.

While the results of this study have been quite successful and demonstrate the potential of the instrumentation for screening of environmental samples, much work remains. Especially important is the development of methods for the identification and quantification of compounds in complex mixtures. This work will involve a thorough examination of chemical ionization reactions, the generation of MS/MS spectra of commonly encountered organic pollutants and potential interferences, and the development of computer programs to process this information in real time.

ACKNOWLEDGEMENT

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Table 1

Detection Limits for Volatile Organics in Air using Direct Sampling ITMS

Compound	Detection Limit (ppb)
1,1,1-Trichloroethane	2
1,1,2,2-Tetrachloroethane	3
1,1,2-Trichloroethane	20
1,1-Dichloroethane	16
1,1-Dichloroethene	6
1,2-Dichloroethene	3
1,2-Dichloropropane	45
2-Butanone	48
4-Methyl-2-Pentanone	17
Acetone	22
Benzene	5
Bromodichloromethane	4
Bromoform	> 80
Bromomethane	>280
Carbon Disulfide	25
Carbon Tetrachloride	16
Chlorobenzene	2
Chloroethane	>209
Chloroform	3
Chloromethane	>268
Cis-1,3-Dichloropropene	6
Dibromochloromethane	12
Ethylbenzene	2
Methylene Chloride	12
Tetrachloroethylene	8
Toluene	3
Trans-1,3-Dichloropropene	7
Vinyl Acetate	44
Vinyl Chloride	5
O-Xylene	4

Table 2

Detection Limits for Volatile Organics in pH-7 Water using Direct Purge ITMS

Compound	Detection Limit (ppb)
1,1,1-Trichloroethane	12
1,1,2,2-Tetrachloroethane	28
1,1,2-Trichloroethane	18
1,1-Dichloroethene	33
1,2-Dichloroethane	27
1,2-Dichloroethene	21
Benzene	3
Bromoform	15
Carbon Disulfide	18
Carbon Tetrachloride	16
Chlorobenzene	5
Chloroform	20
Cis-1,3-Dichloropropene	6
Ethylbenzene	4
Methylene Chloride	60
Styrene	5
Tetrachloroethylene	5
Toluene	4
Trans-1,3-Dichloropropene	15
Vinyl Chloride	5
Xylenes (total)	4

Table 3

Purge Efficiency of Volatile Organics in Soil Slurries Relative to pH-7 Water

		Relative Purge Efficiency (%)		
Soil Sample	Soil Type	Benzene	Trichloroethylene	Tetrachloroethylene
THAMA 1	Clay	29	20	19
THAMA 2	Sand/Clay	51	48	46
Local 1	Sand/Clay	61	45	61
Local 2	Sand/Clay/Humic	46	42	42
Potting	Sand/Humic	91	77	53

ITMS DIRECT AIR INLET

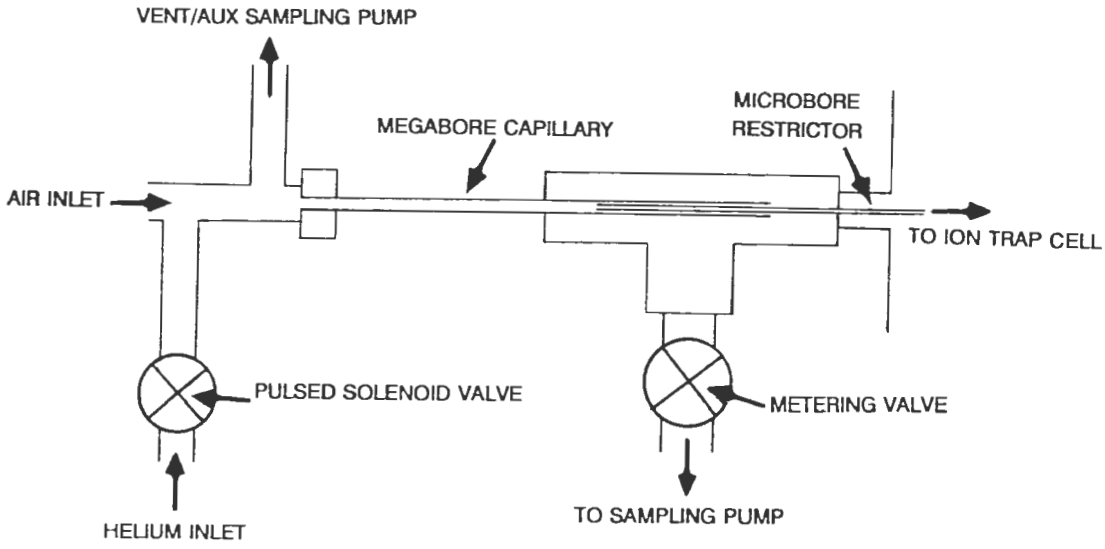

Figure 1 Air sampling interface for ITMS.

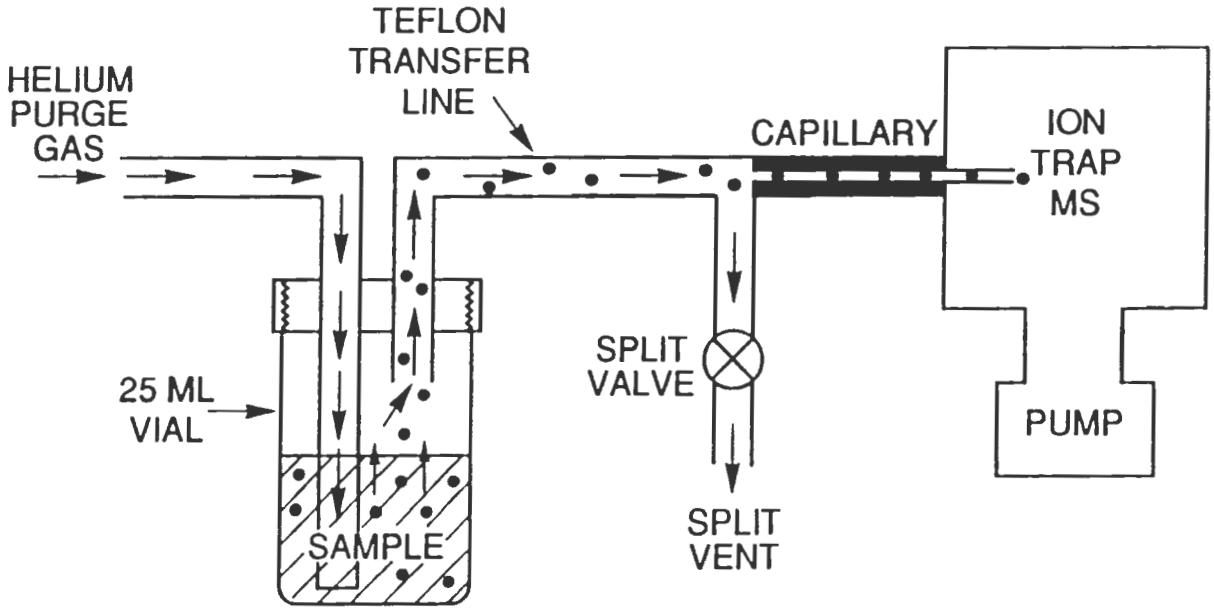

Figure 2 Device used for direct purge of volatiles from water and soil samples.

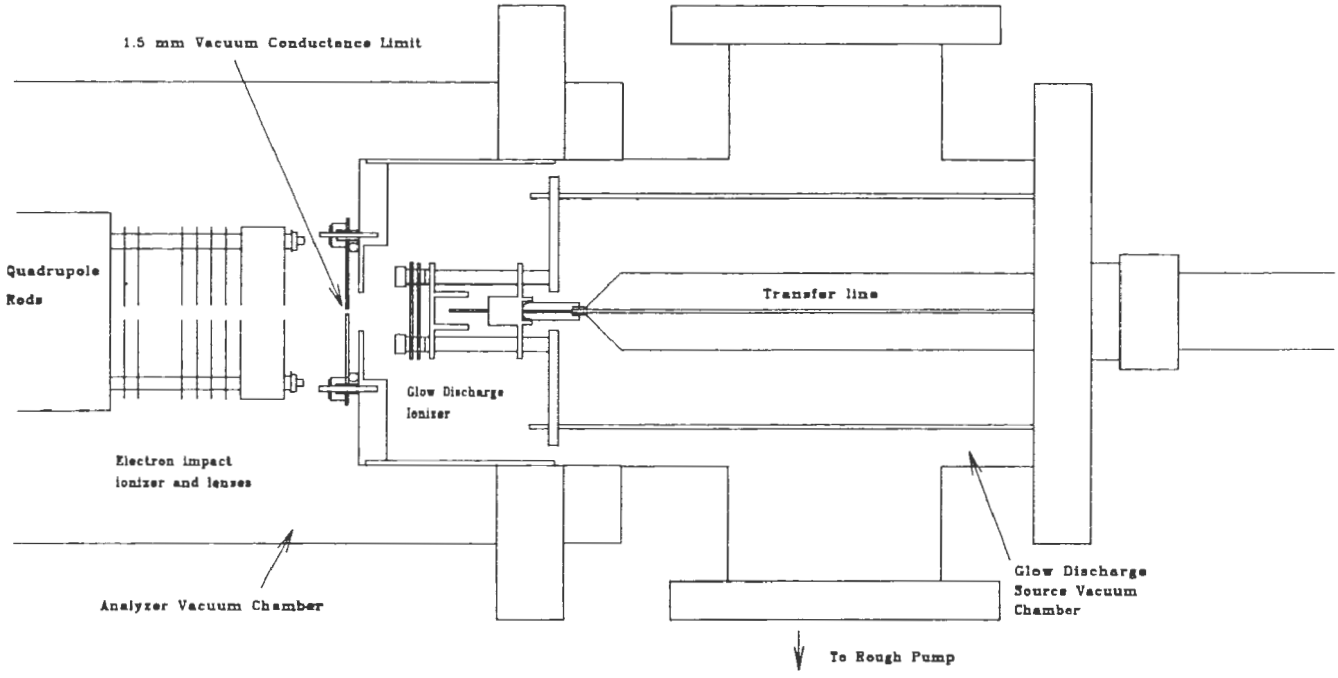

Figure 3 Diagram of the tandem source quadrupole mass spectrometer.

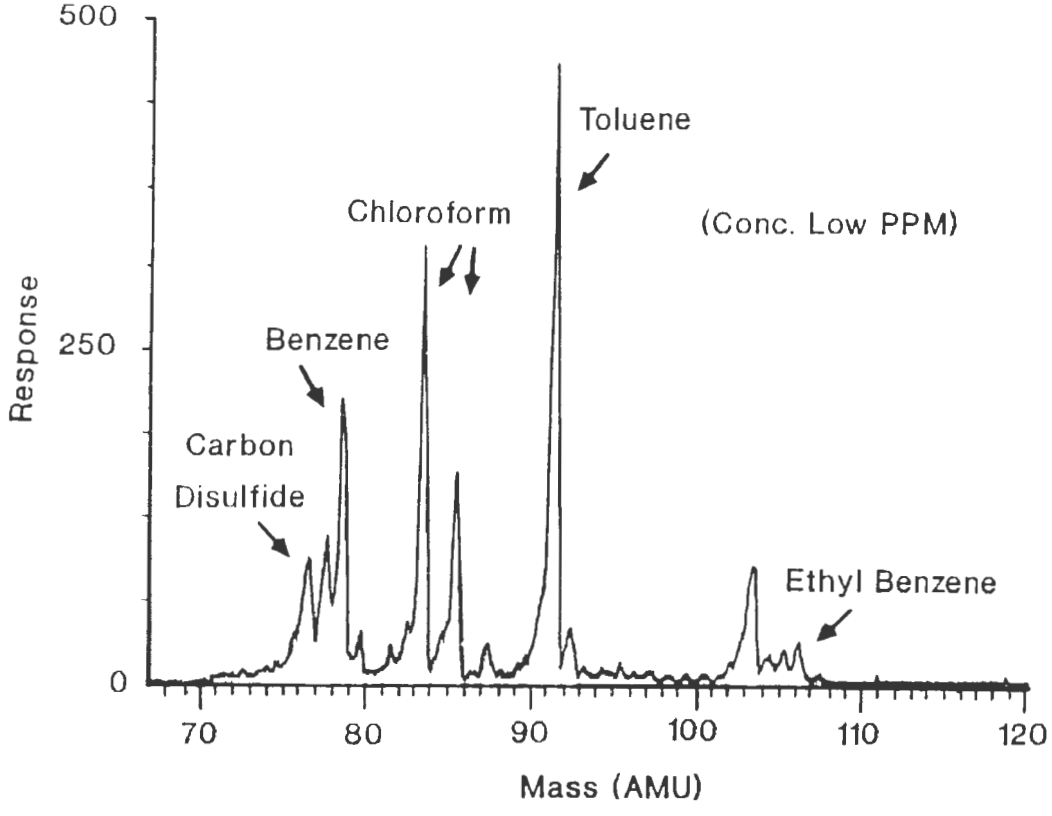

Figure 4 ITMS electron impact mass spectrum of ppm levels of VOCs in air.

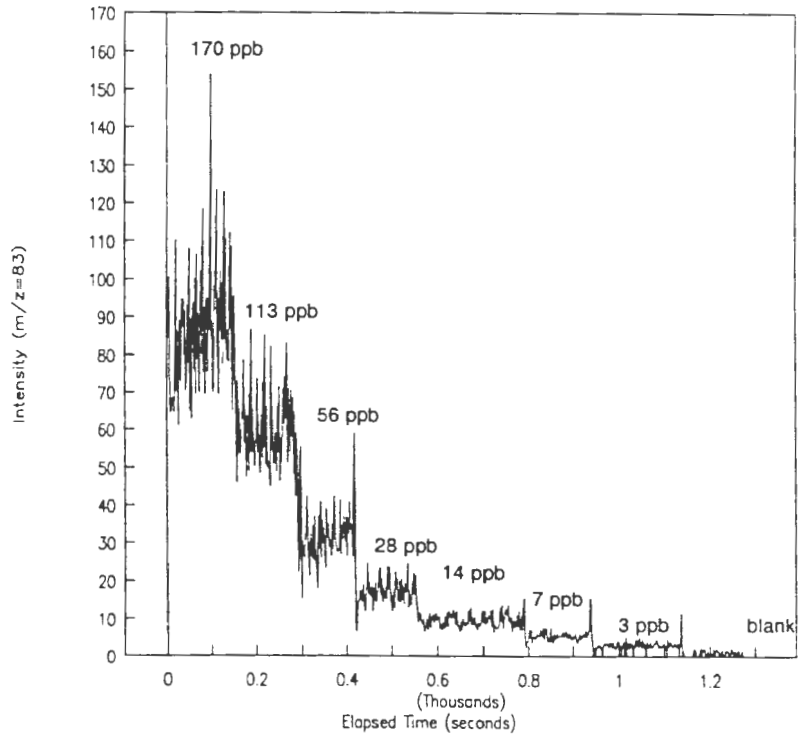

Figure 5 ITMS response for m/z 83 at various concentrations of chloroform in air.

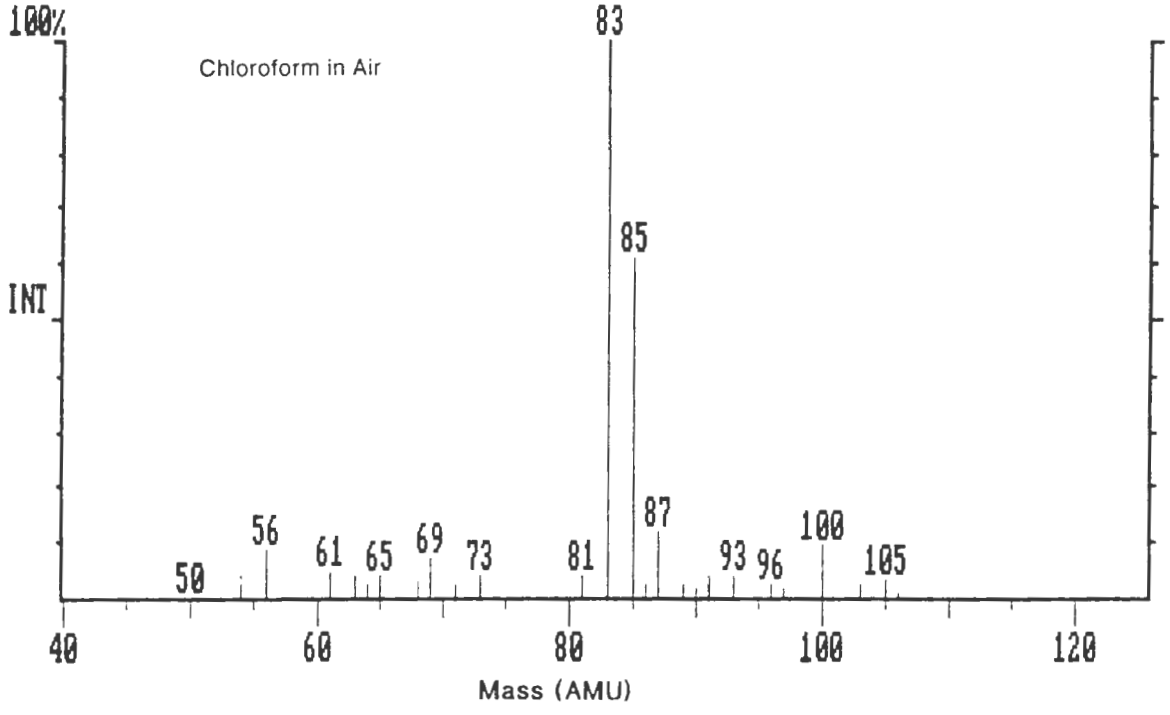

Figure 6 ITMS post processed mass spectrum of chloroform in air.

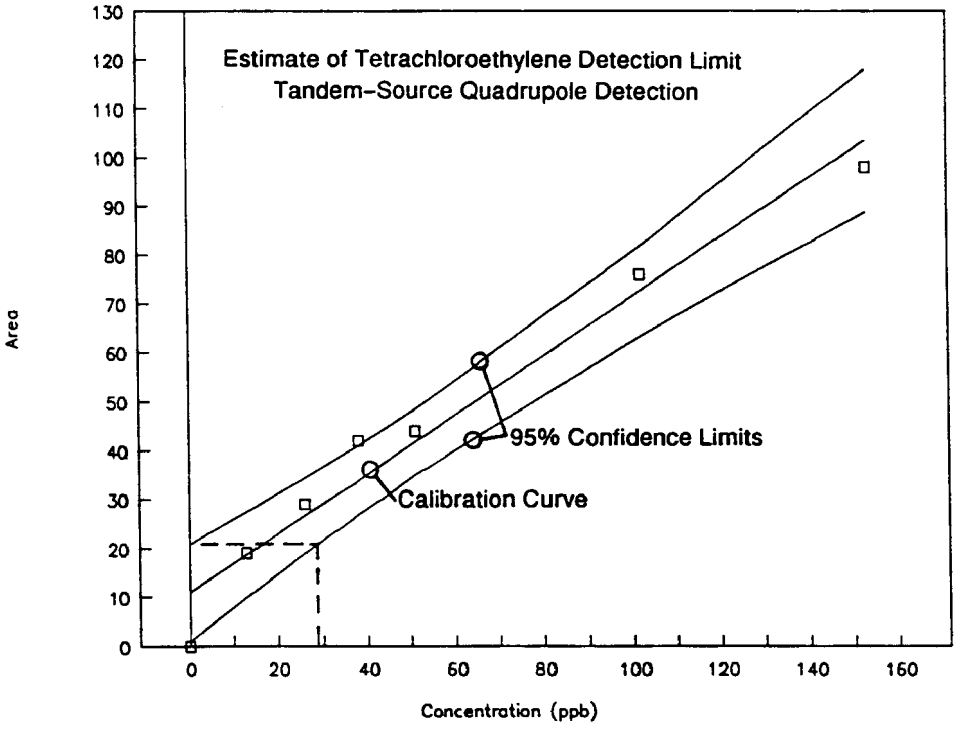

Figure 7 Graphical determination of detection limits for the TSMS instrument.

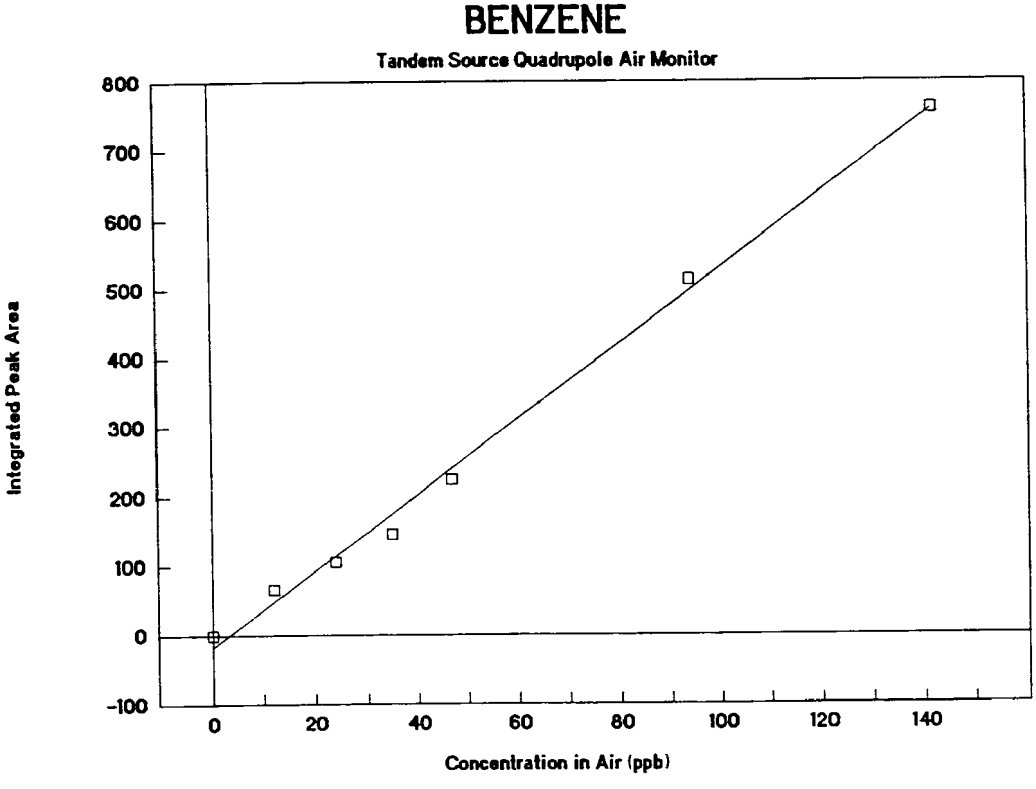

Figure 8 Linear regression curve for benzene in air using the TSMS instrument.

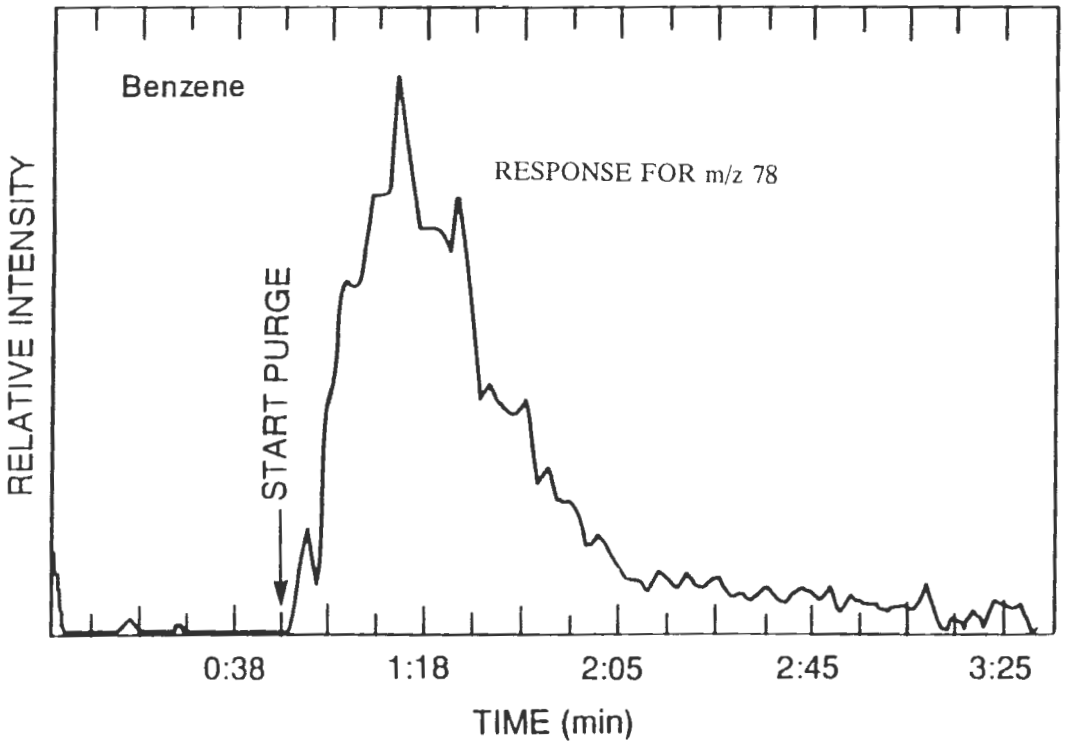

Figure 9 Reconstructed purge profile for 100 ppb of benzene in water.

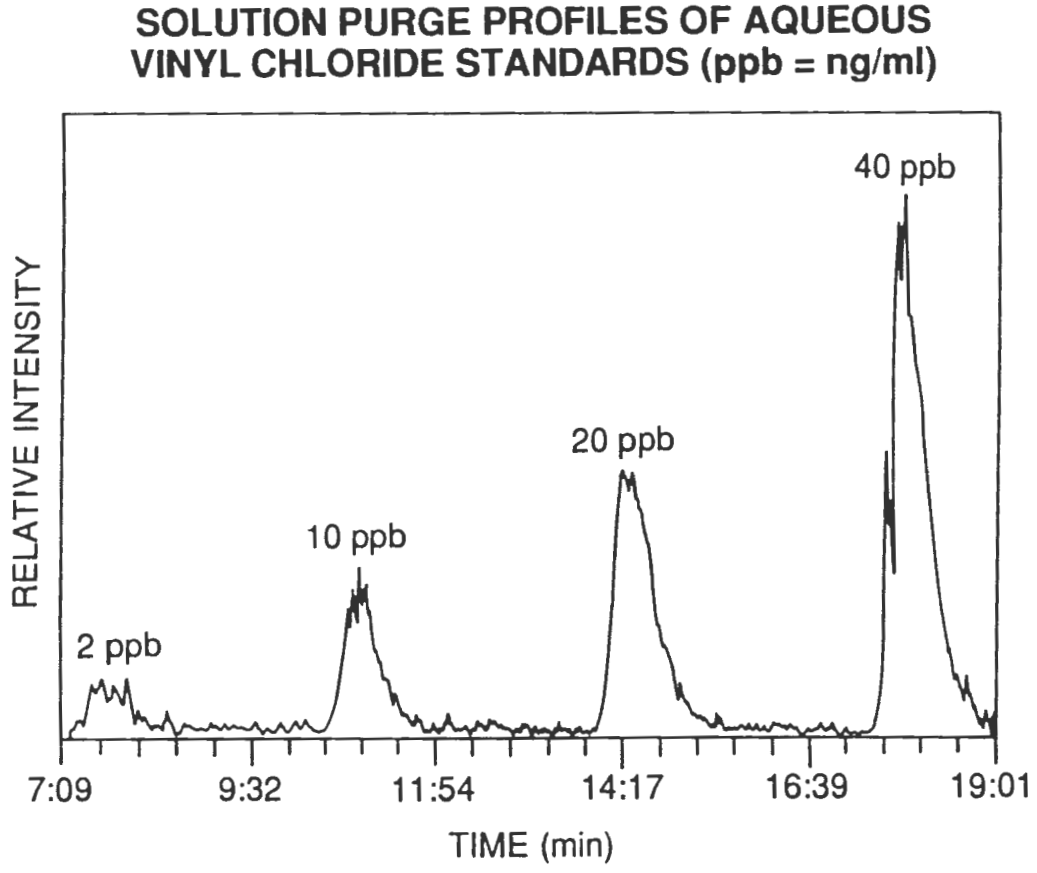

Figure 10 Direct purge profiles for 4 different concentration of vinyl chloride in water.

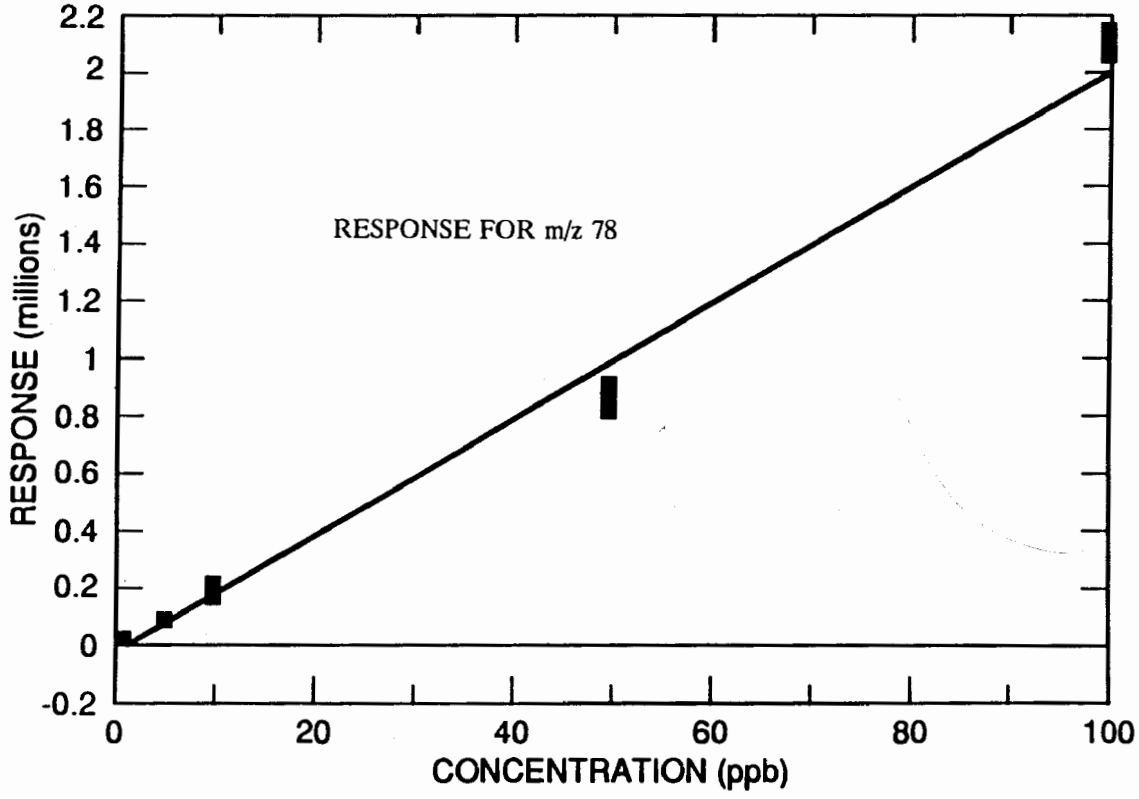

Figure 11 Response curve from 1 to 100 ppb for direct purge of benzene from water.

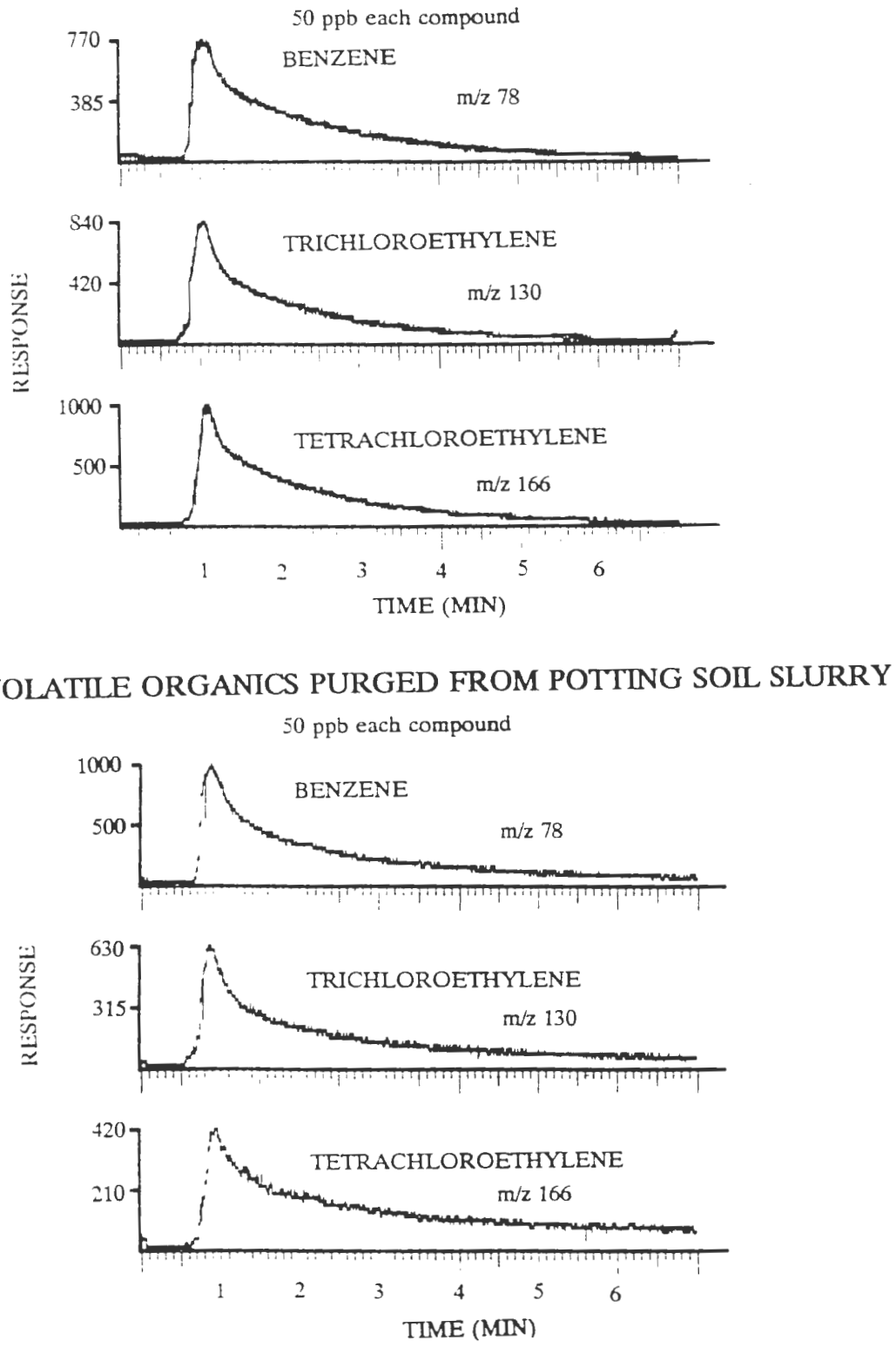

Figure 12 Comparison of VOC purge profiles for pH-7 water and potting soil.

DEVELOPMENT AND TESTING OF A MAN-PORTABLE GAS CHROMATOGRAPHY/MASS SPECTROMETRY SYSTEM FOR AIR MONITORING

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ABSTRACT

A fully man-portable, GC/MS system based on the combination of an automated vapor sample inlet, a "transfer-line" gas chromatography module and a modified Hewlett Packard model 5971A quadrupole MS system is described. The current prototype weighs approx. 70-75 lbs and uses 150-200 W of battery power. The mass spectrometer and computer are carried in front of the operator by means of a shoulder harness whereas battery pack, carrier gas supply and roughing vacuum system are carried as a backpack. Air samples can be analyzed using a special automated air sampling inlet. The man-portable GC/MS system is designed to be supported by a vehicle transportable "docking station".

BACKGROUND

In situations involving severely contaminated hazardous waste sites, industrial accidents or natural disasters, as well as special military or law enforcement operations, mobile laboratories may be of little use because of limited site access, restrictions due to contamination or terrain constraints. Under such conditions, man-portable analytical instruments may offer the only acceptable means of carrying out on-site analyses.

Obviously, man-portability puts severe constraints on weight, size and power requirements as well as on ruggedness and user-friendliness. Consequently, the man-portability requirement may also function as a convenient benchmark for the development of analytical equipment for a variety of special operational environments ranging from remotely operated devices (e.g., robotic vehicles, drones or probes) space stations and operating rooms. All of the above environments require a high degree of miniaturization, reliability and ease of operation.

The past decade has witnessed impressive progress in miniaturization of mass spectrometric systems. Besides a broad range of commercially available benchtop instruments, including the Hewlett Packard MSD (Mass Selective Detector) and Finnigan MAT ITD (Ion Trap Detector), several specialized MS instruments have been developed for applications where transportability is a prime requirement. Well known examples include the Bruker Franzen MM1 system, originally developed for military applications involving chemical agent detection, and the Viking Spectratrak system primarily designed for environmental applications.

As shown in Figure 1 most commercially available miniaturized systems are characterized by a combination of relatively low weight (typically 100-300 lbs, excluding power source) and modest power requirements (600-1800 W range). In spite of these marked advances in system miniaturization, however, man-portability and some of the other abovedescribed applications require even more stringent size, weight and power limitations.

This prompted us to undertake a study aimed at obtaining maximum power and weight reduction using the Hewlett Packard MSD as a starting point. Although the project is still under continuing development, some preliminary results and conclusions are starting to take shape, as will be discussed in the following paragraphs.

SYSTEM DESIGN CONCEPTS

An overview of the selection criteria for the main system modules and components is given in Table I.

Automated Vapor Sampling Inlet Module

Transfer line gas chromatography (TLGC) is defined here as a form of GC in which the column connects two environments, viz. an atmospheric environment at ambient pressure and the vacuum environment of the MS ion source region. In other words, column inlet and outlet pressures are more or less fixed and, consequently, optimization of column flow requires suitable adaptation of column length and/or diameter. This sets TLGC apart from the more widely used short column gas chromatography (SCGC) technique in which column inlet pressures can usually be adjusted while column length is kept below 5 meters or so.

Although most TLGC applications reported thus far do use short to very short column lengths, optimum GC conditions for a 500 μm i.d., ambient inlet transfer line columns connected to a vacuum detector (e.g., MS) may dictate column lengths in the 50-100 m range (see Figure 2). In view of the abovedescribed distinctive differences between TLGC and SCGC we feel justified in adding yet another term to the already baffling jargon of the chromatographer.

When sampling condensable and potentially labile vapors from air, the main challenge is to avoid compound losses through irreversible adsorption and/or decomposition in the transfer line section. To this end, a novel, automated vapor sampling method was recently designed at the University of Utah Center for Micro Analysis & Reaction Chemistry (1,2). The most characteristic property of this sampling method, illustrated in Figure 3, is the absence of any valves or other mechanical obstructions in the path of the molecules between the ambient environment and the ion source. Only quartz walls and/or surfaces coated with inert stationary phases (e.g., poly-dimethylsilicones) are seen by sample molecules on their way to the ion source.

A second advantage of the new sampling technique is the potentially very short switching time. Sampling times as short as 60 msec have been used already (2) and 20 msec or less may be achievable in the near future. This enables "injection" of a narrow sample plug into the TLGC column, thereby minimizing peak broadening due to sample injection and allowing repeat GC analyses at 6-60 sec intervals (3). All air flows in the inlet are sustained by means of a Graseby Ionics miniaturized dual air pump (max. capacity 2 x 500 ml/min, max power consumption 1 W) whereas rapid switching of air flows is performed with a Skinner micro valve (5 msec response time).

Transfer Line Gas Chromatography Module

The GC oven module consists of a simple heated aluminum cylinder which houses the capillary GC column, e.g., a 29 cm long, 50 μm i.d. fused silica capillary coated with a 0.2 μm thick layer of poly-dimethylsilicone (DB5) and providing a continuous He flow of approx. .02 ml/min.

At present the oven is used in isothermal mode only. A temperature programming option as described by Arnold et al. (4), which would allow a broader range of compounds to be analyzed in a single GC run and also help protect the column from oxidative degradation, has not yet been implemented in the present prototype. A direct consequence of the rapid GC run time is the need for very high temperature programming rates, e.g, 10-20 C/sec. This requires significantly larger power supplies than necessary for isothermal operation.

A small (2 ft^3) compressed gas cylinder with flow controller provides more than 36 hours of He or N_2 carrier gas flow. The theoretical relationship between inner column diameter, max. resolving power, column length and retention time is depicted in Figure 2. Obviously, the use of a 50 μm i.d. column (primarily selected to keep gas flows as low as possible) has the advantage of allowing very rapid separations, although limiting maximum achievable resolving power.

Quadrupole MS Module

A Hewlett Packard Model 5971 MSD (Mass Selective Detector) was modified extensively in order to reduce system weight and power requirements and increase overall manoeuverability. The original housing was completely discarded and the relative positions of the electronic boards were changed to enable convenient operation of the air sampling inlet. The new configuration is shown in Figures 4 and 5. Most importantly, the original AC and DC power supplies were removed and replaced by a battery powered 12 V DC supply with DC/DC converters for the various DC voltages required for mass spectrometer, computer and sampling inlet operation. Total power consumption of the modified MS system was determined to be 43 W (see Table I).

Vacuum System

The vacuum system of the HP model 5971 MSD was completely reconfigured to provide operating pressures in the 10^{-4}-10^{-5} torr range while minimizing roughing vacuum requirements. The original 60 l/sec diffusion

pump was exchanged for an Alcatel Model 5010 MDP (Molecular Drag Pump) with a max. pumping speed of 8 sec^{-1} for N_2 and a roughing vacuum requirement of $\leq$ 30 millibar. This enabled us to replace the original rotary pump (power requirement approx. 160 watts; weight 14 lbs) with a simple vacuum buffer capable of maintaining a roughing vacuum of better than 10 millibar for up to 12 hours at the specified GC column flows. The vacuum assembly configuration can be seen also in Figs. 4 and 5.

Micro Computer Module

A Toshiba model 5200, 20 Mhz, 80386 lap top is used to control all GC/MS functions by means of a standard PC interface and software available from Hewlett Packard. In addition the PC system controls the operation of the air sampling inlet. The only modification of the Toshiba 5200 consisted of removing the built-in, relatively heavy DC and AC power supplies and connecting the unit directly to the specially constructed DC power supply shown in Figures 4 and 5.

SYSTEM INTEGRATION

Mechanically, the various components described thus far were integrated by means of a specially designed shoulder harness and backpack frame, as shown in Figure 5. The aluminum backpack frame carries the two batteries as well as the vacuum reservoir whereas the entire mass spectrometry assembly with MDP and PC is suspended from the shoulder straps and stabilized by two hip straps. Due to the difficulty of typing in detailed computer commands during field use, especially when wearing gloves, a beach ball type mouse was installed to enable direct communication with a single (gloved) hand. Alternatively, one could envisage the use of a built-in PC computer card (without display screen or keyboard) remotely controlled by a second, more completely outfitted PC using standard PC software such as Carbon Copy® or PC Anywhere®.

The most simple remote control option would be to use an umbilical cord carrying a twisted pair cable in addition to AC power. The latter option would eliminate the heavy (28 lb) battery pack, thus resulting in greatly reduced overall size and weight. Finally, as also shown in Figure 4, a special transportable "docking station" (still under construction) enables vacuum system regeneration, battery recharging and carrier gas refills at 6-10 hour intervals.

PRELIMINARY TEST DATA

TLGC/MS curves generated with a 100 cm long, 100 µm i.d. capillary column, coated with 0.25 µm polydimethylsilicone (DB5, Supelco) while sampling a mixture of 10 ppm vapor components in air for 1 sec at 30 sec intervals are shown in Figure 6. Obviously, a highly useful level of chromatographic separation is achieved with the very short transfer line. Also the narrow peak shapes (half height width $\leq$ 1 sec) illustrate the efficiency of the rapid sampling air inlet. Overall peak height reproducibility (approx. $\pm$ 10%) is influenced by the limited resolution of the sampling time due to manual operation.

From the selected ion profile (tropylium fragment ion at m/z 91) in Figure 6 the minimum detectable concentration in direct air sampling mode appears to be approx. 1 ppm. Although this is 1-2 orders less than the minimum concentrations detected by means of ion trap type MS systems when using the automated vapor sampling inlet (2), the MSD system has not yet been fully optimized for operation under the present vacuum and flow conditions. However, since it may be anticipated that some of the most promising applications will require detection limits in the lower ppb range, a suitable adsorption/desorption module is currently under development in our laboratory.

Figure 7 illustrates the performance of the automated air sampling TLGC/MSD system with polar compounds under similar experimental conditions as in Figure 6. Note the rapid separation of a mixture of ketones into its components and the relatively minor degree of peak tailing due to the heated, all quartz vapor sampling inlet.

Finally, Figure 8 shows selected ion chromatograms for several chemical agent simulants, demonstrating the fast, repetitive (17 sec interval) analysis capability of the short (29 cm) narrow bore (50 µm i.d.) capillary column used while maintaining adequate chromatographic resolution.

Although it is tempting to envisage the use of man-portable GC/MS instruments for military reconnaissance purposes, e.g., when venturing into contaminated regions with high levels of background interferents, it should be pointed out here that the current sensitivity of the MSD based TLGC/MS system is insufficient for such applications. Partially, this is due to the relatively low sample mass flow through the narrow bore capillary columns used. In principle, this could be corrected by closing up the MSD ion source thereby increasing the residence time

of the vapor molecules in the source which would result in increased ionization efficiencies.

Additionally, the use of rapid absorption/desorption methods for sample preconcentration should be considered. Assuming a 10 second absorption interval at 10 times normal flow, followed by a 1 second desorption interval at normal flow, it should be possible to obtain a 100 times enrichment factor without sacrificing analysis speed. Basically, the 10-15 seconds necessary for chromatographic separation is then being used to collect and preconcentrate the next sample.

Finally, we are investigating the use of rapid (10-20 C/sec) temperature programmed heating in order to broaden the range of compounds that can be analyzed in a single chromatographic run. The feasibility of this approach has been demonstrated by Arnold et al. (4). A second, important advantage of rapid temperature programming is that the initial "air peak" passes through the column at low temperature, thereby considerably reducing the likelihood of oxidative degradation of the column. This then allows programmed heating of the column to high temperatures (e.g., 300 C) thus enabling separation and detection of large polar molecules such as underivatized trichothecenes, as demonstrated by McClennen et al. (5). Many commercially available, air sampling mass spectrometry and ion mobility spectrometry systems use silicone membrane interfaces, thereby the detection of large, polar compounds.

CONCLUSIONS

The feasibility of constructing a fully man-portable "transfer line" GC/MS system with automated vapor sampling capability has been demonstrated. In its present form, the system weighs 72 pounds, consumes 160 W of electrical power and can operate continuously for 6-10 hours. Application of novel battery technologies, further integration of the microcomputer module and use of alternative vacuum pumping strategies is expected to reduce overall system weight to less than 50 lbs. Without vapor preconcentration, practical detection limits appear to be in the low ppm range. Development of rapid temperature programming capabilities is being considered in order to facilitate detection of relatively nonvolatile species and to increase the range of compounds that can be analyzed in a single run. The ultralow power and weight requirements of the technique would seem to offer promise for a broad spectrum of field applications ranging from hazardous waste sites and industrial or natural disaster areas to reconnaissance drones, space stations, interplantary probes and autonomous vehicular robots.

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TABLE I: PRIMARY SYSTEM COMPONENT SELECTION CRITERIA

- o Automated Vapor Sampling Inlet Module
  - -- fully automated
  - -- only inert quartz and fused silica materials
  - -- ultrashort sample "injection" pulse
- o Transfer Line GC Module
  - -- interferent rejection
  - -- rapid analysis capability
- o Hewlett Packard 5971A Mass Selective Detector
  - -- low power requirements (43 W)
  - -- lightweight (7 kg)
- o Alcatel 5010 Molecular Drag Pump
  - -- low power consumption (17 W)
  - -- high backing pressure up to 40 mbar (no backing pump needed)
  - -- light weight (2.35 kg)
- o Toshiba 5200, 20 mhz, 386 Computer
  - -- low power consumption (40 W)
  - -- high speed, capable of running existing MSD software

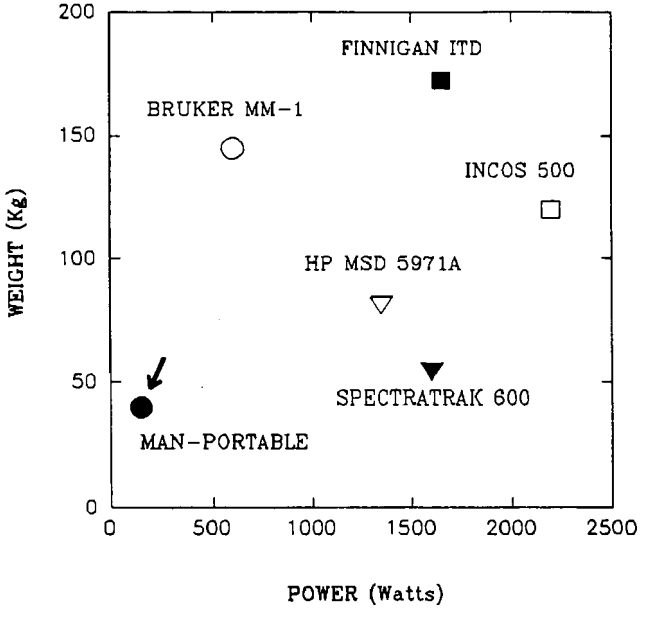

Figure 1. Power requirements and weights of typical miniaturized GC/MS systems (note that man-portable system includes power and carrier gas sources).

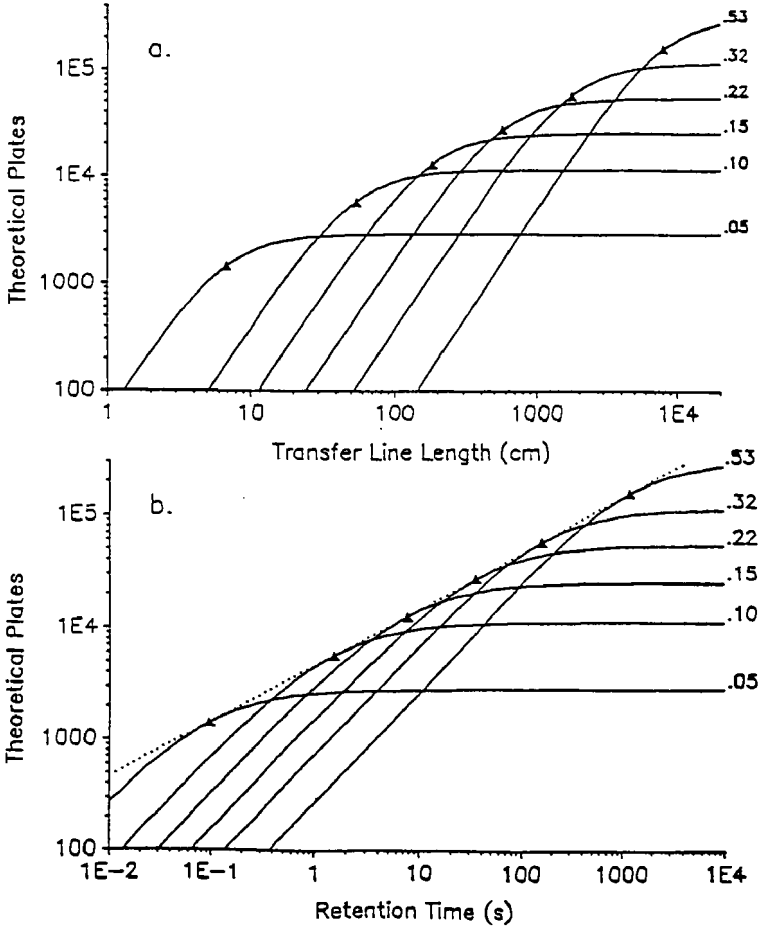

Figure 2. Theoretical relationships between internal column diameter (in μm), maximum achievable resolving power, column length and retention time for a compound with capacity factor k=5.0. (Triangles indicate points of minimum plate height operation.)

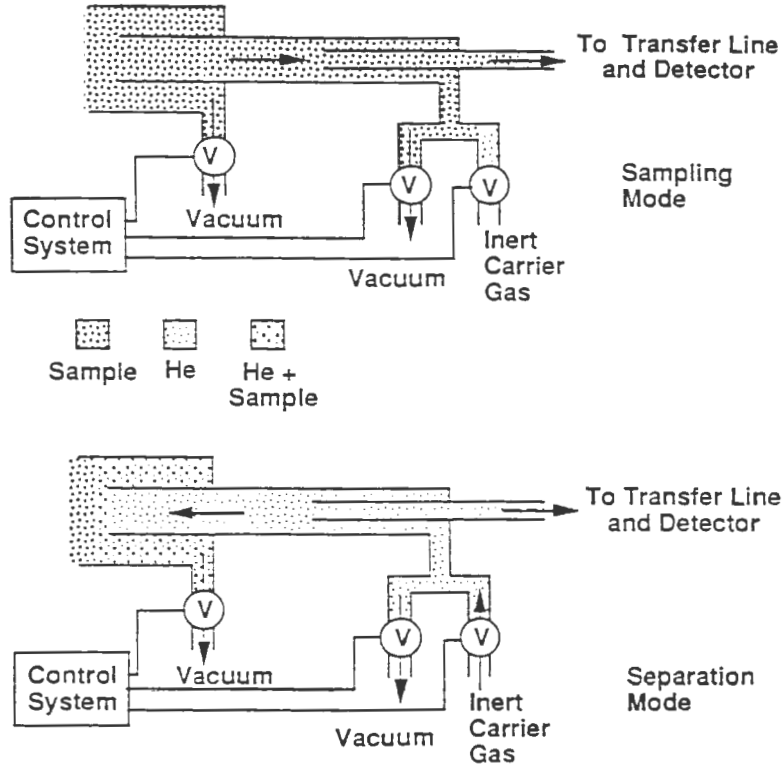

Figure 3. Operating principle of automated vapor sampling inlet developed at University of Utah (US patent no. 4,970,905).

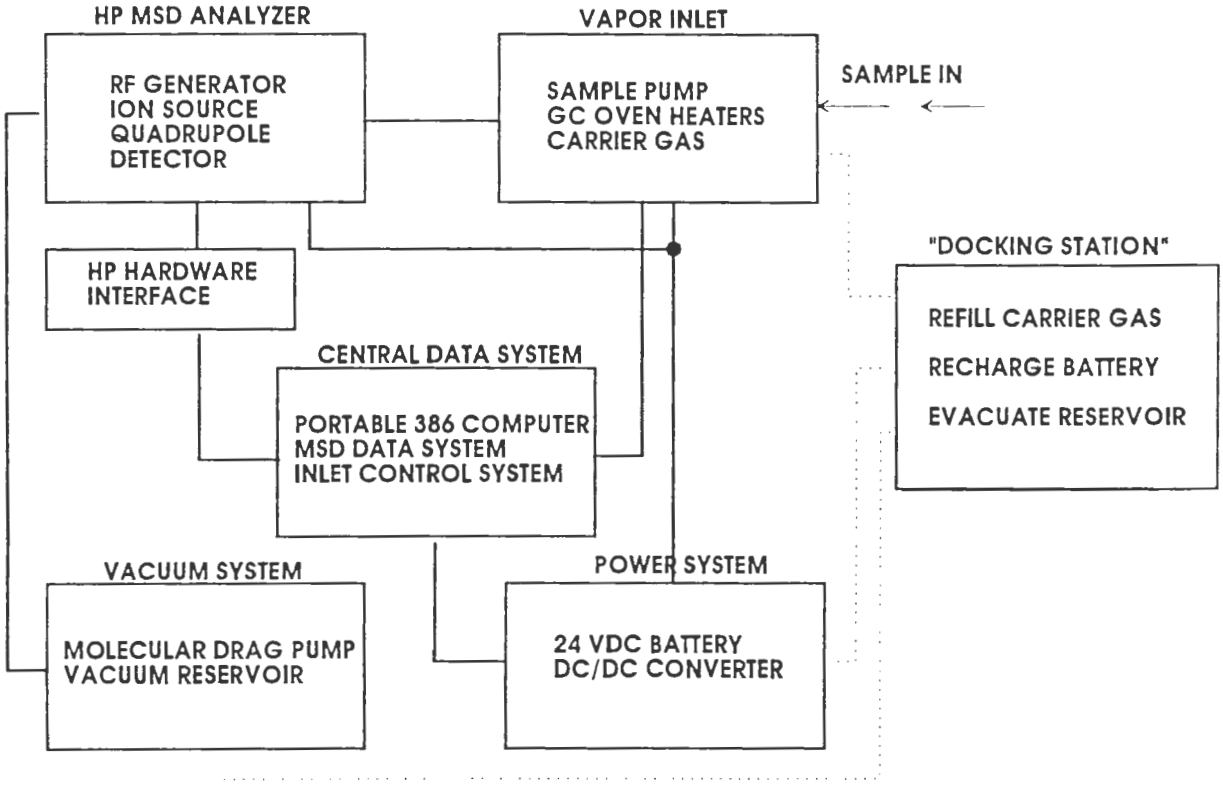

Figure 4. Block diagram of man-portable GC/MS system and docking station interface.

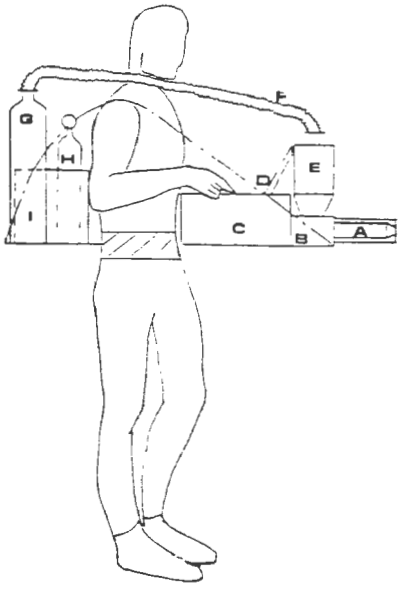

Figure 5. Schematic outline of GC/MS man-portable system with operator. A) vapor inlet/transfer line GC column; B) MSD analyzer; C) control electronics; D) portable 386 computer; E) molecular drag pump; F) vacuum hose; G) vacuum reservoir; H) carrier gas, and I) 24VDC battery.

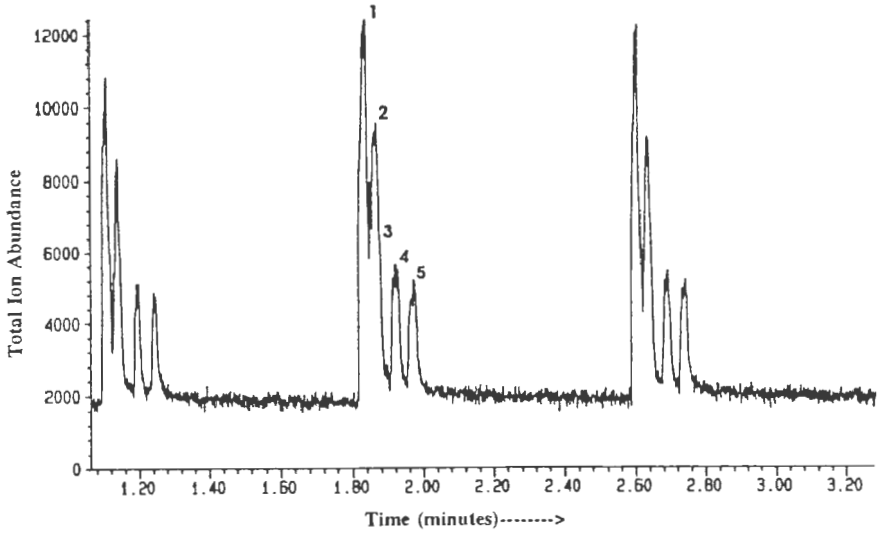

Figure 6. Selected ion chromatogram profile of an alkylbenzene mixture at m/z 91 obtained by TLGC/MS using the automated vapor sampling inlet in combination with a 100 cm long, 100 μm i.d., DB5 coated fused silica capillary column. (1) toluene; (2) ethyl benzene; (3) m-xylene; (4) o-xylene. Approximate vapor concentrations: 10 ppm. Arrows indicate air sampling events at 30 second intervals. Note that o-xylene (peak 4) elutes after the next sampling event.

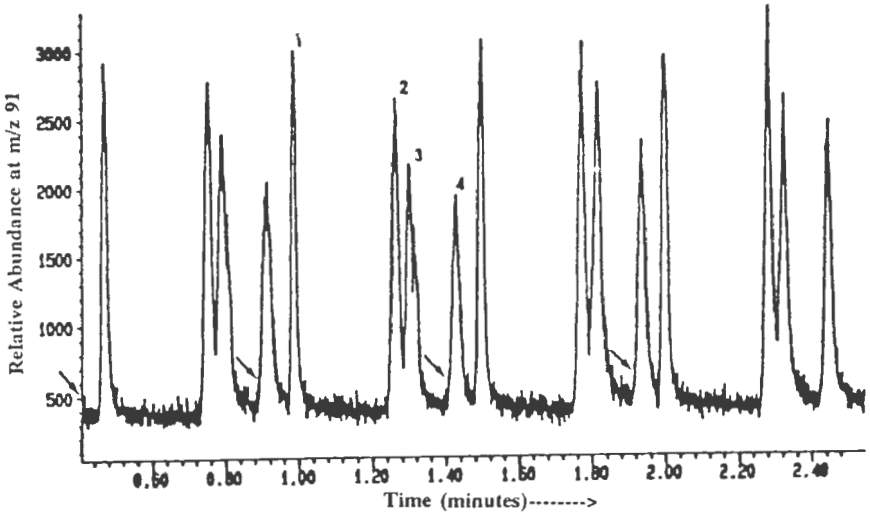

Figure 7. Total ion chromatogram (TIC) for a mixture of 4 ketones. 1) acetone; 2) methyl ethyl ketone; 3) ethyl acetate; 4) 3-pentanone; 5) methyl iso-butyl ketone.

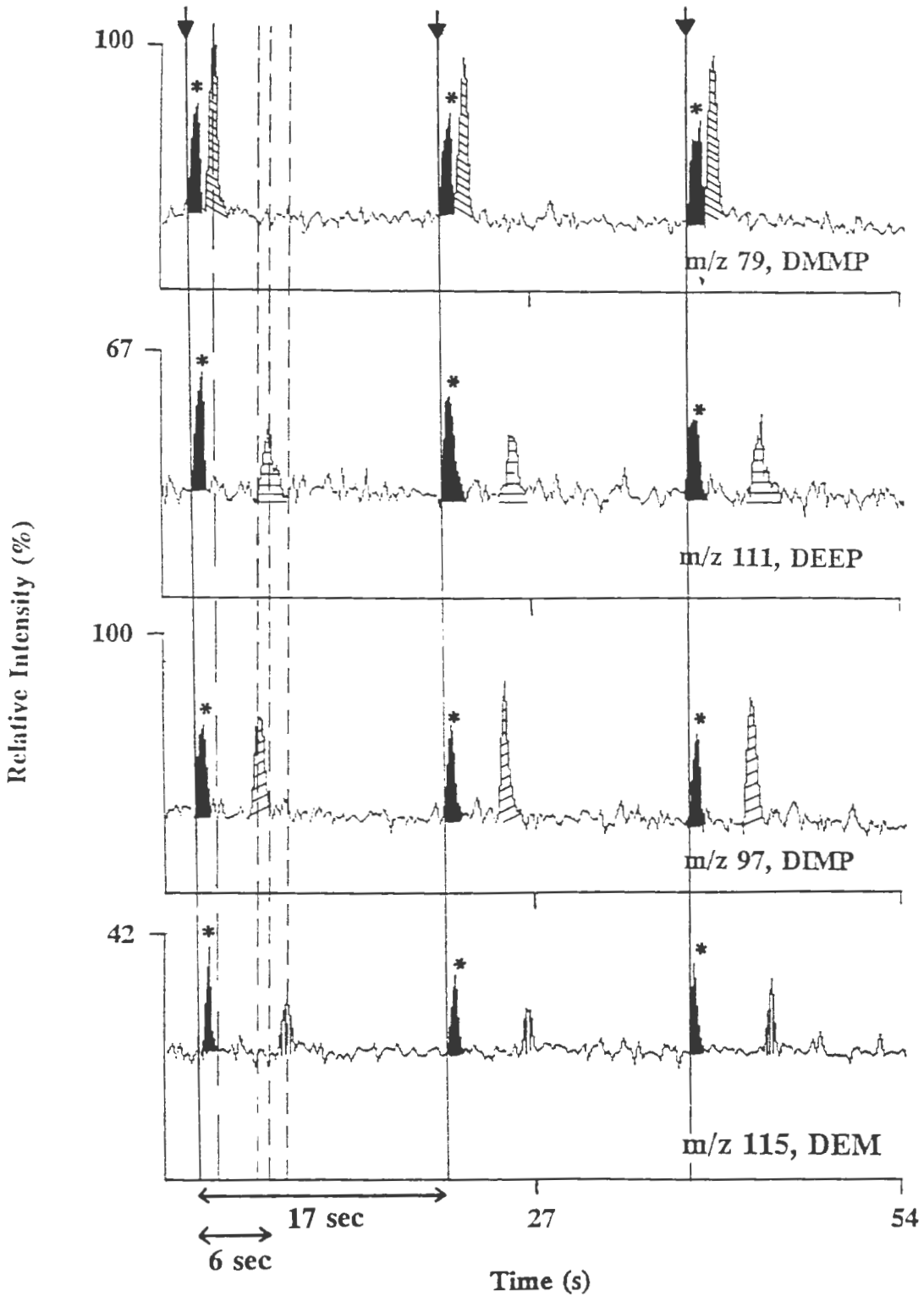

Figure 8. Selected ion chromatograms of 4 chemical agent simulants (DMMP=dimethyl methyl phosphonate, DEEP=diethyl ethyl phosphonate, DIMP=diisopropyl methyl phosphonate, DEM=diethyl malonate). Arrows indicate air sampling points (17 sec interval). Note separation of all 4 simulants within 6 sec. Star symbol (*) indicates "pseudo" peak due to effect of eluting air on MS system.

DISCUSSION

RALPH SULLIVAN: With these high flow rate systems, how did you go about calibrating it and how do you introduce the gas to it to know what you have in the system?

HENK MEUZELAAR: You make diluted air — the flow rate doesn't have to be above 100 mL per minute, or even 50 per minute. So, if you have a dilution system that can give you that kind of output, you can just calibrate it with a calibrated dilution system.

AUDIENCE PARTICIPANT: Could you repeat that?

HENK MEUZELAAR: All right. What I said is the high flow of the outer tube, the first sampling tube, can be as little as 50 or 100 mL per minute. So, if you have a vapor dilution system that can give you a couple hundred mL output you can do a loose coupling for such a system and get very good results. If you have a vapor dilution system that just puts out a few mL per minute it would be more difficult to do that. You could do it from a bag if you could fill a bag and keep it at atmospheric pressure for several minutes, you could obtain a sample without changing the pressure or the concentration in the bag.

BILL McCLENNY: I was wondering what the prospects would be for using some type of preconcentration that involved a cold trap, using thermo electric cooling or something of that sort, and what that would add to the power requirements for this unit?

HENK MEUZELAAR: I think almost any type of absorption, desorption, or preconcentration by any method I know that would keep the high response characteristic intact, would certainly require power because you would have to desorb for a relatively short period of time. And the only way to make gain is to absorb for let's say 60 seconds and flush desorb in one or two seconds. That's going to require power. We are currently looking at a number of different methods. The power requirement is just needed, for a second, or maybe even less than that. I think it's a doable thing, but it certainly will add to the power requirement.

ON-SITE MULTIMEDIA ANALYZERS: ADVANCED SAMPLE PROCESSING WITH ON-LINE ANALYSIS

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ABSTRACT

The need for on-site chemical analysis of air, water, and soils has led to development of two highly automated prototype instruments in the field of trace organic analysis: EPyA, the Environmental Pyroprobe Analyzer and CHAMP, the Chemical Hazards Automated MultiProcessor. In the EPyA unit, a purge and trap module permits routine determination of target chemicals in water and hazardous wastes. A thermal desorption module permits controlled thermal desorption of air sampling cartridges, as well as dynamic headspace/pyrolysis analyses of solids. CHAMP is based on supercritical fluid extraction (SFE) with liquid CO_2 mobile fluid for solid samples in amounts from milligrams to over several grams in six individually heated extractors. Specialty interfaces, such as TRANSCAP, provide on-line analysis by chromatographic and/or spectral detectors.

Both benchtop, microprocessor-based systems are newly designed for in-field operation, as well as laboratory or plant sites. Highly automated instruments such as EPyA and CHAMP operating with external expertise provided by artificial intelligence (AI) software, illustrate the Integrated Intelligent Instrument (I^3) approach which is focused on multimedia analyses for hazardous materials.

INTRODUCTION

Advantages of precision, accuracy, and reproducibility are realized with the use of automated instruments to perform thermal and nonthermal sample processing with on-line chromatographic and/or spectral analyzers. New engineering designs are required to bring this analytical power on-site to the field, mobile lab, or plant to provide rapid, validated information to analysts. Two prototype analytical systems are described to meet these needs; the Environmental Pyroprobe Analyzer, EPyA (1) and CHAMP, the Chemical Hazards Automated MultiProcessor (2). The prototypes are designed for compactness with integrated specialty separation and/or detector units that are important to the hazardous waste field for on-site use. Figure 1(a,b) shows the benchtop units, each about 2'x2'x3' and weighing ca. eighty pounds. The purpose of this report is to describe the ongoing development of specialty instrumentation that is based on proven analytical methodologies in trace organic analysis.

I. Thermal Sample Processing - EPyA

The thermal analyzer system, EPyA, is the result of over fifteen years of engineering design and manufacture of microprocessor-based instrumentation used throughout the world for trace organic analysis of vapors, liquids and solids. Studies in the 70's and

80's developed purge and trap modules for water analyses and thermal desorption methods for rapid analyses of air sampling cartridges that contained treated charcoals, porous polymers, Ambersorb, Tenax, etc. (3a). Figure 2 shows a test air mixture with 40 ppb levels of typical solvents (benzene, toluene, chloro-benzene, heptane, o-dichlorobenzene, and dodecane) sampled for 90 sec at 0.5 mL/min on a Tenax sorbent bed (100 mg) which was then thermally desorbed for GC/FID analysis (3b-e). Figure 3 shows an analysis conducted for gasoline/fuels using a cryofocusing concentrator module and on-line capillary GC/FID detection (4). Figure 4a,b,c give results from other studies (4) using remote air sampling cartridges for analyses of outside air, laboratory air, and paint shop air (all 500 ml samples) with GC/FID analysis.

Recently, the thermal desorption/cyrotrapping module was used in trace particulate analysis of a microencapsulated pesticide, Diazinon, in an air sampling cartridge with on-line analysis by GC-MS (5) (Figure 5). A corresponding dynamic headspace/pyrolysis method using the Pyroprobe Pt coil pyrolyzer on a few micrograms of a microencapsulated sample also provided trace detection and identification of the Diazinon core, which gives a parent ion at m/z 304 and a base peak at m/z 179. Clearly, thermal desorption, rather than CS_2 solvent stripping, proved to be the optimum analytical method which is now used throughout the world in the industrial R&D, forensic, and environmental fields. However, some thermally sensitive samples required additional effort for reliable analyses. A more effective method than solvent extraction was needed, both for analyzing thermally labile materials, as well as to eliminate solvent wastes. The traditional Soxhlet solvent extraction method has further disadvantages of hour or day-long extraction times and off-line, more labor intensive, multistep analyses for complex environmental samples.

II. The Nonthermal Sample Processing Analyzer - CHAMP

The nonthermal multiple sample processing system, CHAMP, using supercritical fluid (SF) technology (6) permits the conduct of trace organic analysis on diverse samples, including cartridge sorbent beds (7), soils, coals, or hazardous waste solids. Six individually heated sample extractors may contain up to five grams or more of material to be treated near or at supercritical fluid conditions in the 2, 4, or 6 mL extractor vessels.

Automated SF extraction (SFE)-capillary GC analysis of gasoline from charcoal filters may be routinely analyzed with either single or multiple SFE units. Analytes requiring well-established capillary GC methods use the automated SFE system configured for GC separation. Alternatively, in Figure 6, the SFE-SFC analysis is shown of a phosphonate chemical in soil (ca. 500 mg) with detection by FID at estimated ppb levels. The SFE was conducted at 3000 psi, 100°C with CO_2, which is a nontoxic, safe and inexpensive mobile fluid. The SFC was conducted with a Nucleosil CN microbore column at 120°C and pressure programming from 2000 to 6000 psi at 300 psi/min with a FID unit.

As with the thermal processing analyzer, EPyA, it is necessary to have a variety of detection systems for adequate analytical sensitivity and specificity. The SFE process has been used with FID, ultra-violet and mid-infrared (ir) spectrometers using fiber optic monitors (FOM) (6,8). Figure 7 represents the recent on-line SFE-SFC analysis of a polyolefin/naphthalene mixture. An ion trap MS detector (ITD) was used to detect the molecular ion from naphthalene (m/z = 128) (9). Other detectors show similar potential for trace on-line analyses with highly specific and sensitive responses to hazardous/toxic substances, e.g., fluorescence/uv with fiber optic technology and advanced data analysis with applied AI (10). Both EPyA and CHAMP incorporate new design engineering features that emphasize compact, transportable systems. Sample processing, integrated with separation and

detection units are controlled by microprocessors with programmable, interactive software. External AI software will provide guidance in the use of the total system.

III. Applied Artificial Intelligence - Expert System Networks

The I^3 approach combines data generation using highly automated modular/interfaced systems with external intelligence for development, data analysis, interpretation and validation. Development of a proprietary expert system network for SF technology, MicroEXMAT, has been reported using CCS SF hardware and methods (11). Currently, a multivariate experimental design based on a Box-Behnken central composite is linked explicitly in the network via an expert system, EXBOXB. Further integration of MicroEXMAT into a full laboratory information management system (LIMS) was also outlined previously (12). Applications to EPyA and CHAMP are being developed. The recent ACS Symposium on expert systems applied to the environmental field (13) indicates the growing importance of AI in analytical chemistry.

IV. Summary

Newly designed instrumentation for multimedia (air, water, solids) environmental trace organic analysis is described for on-site applications. The automated prototype units feature advanced sample processing with interfaces for on-line analyses with chromatographic and/or spectral detectors. Thermal sample processing is provided by EPyA, including modules for purge and trap/thermal desorption, dynamic headspace, and pyrolysis. Nonthermal multi-sample processing is conducted with CHAMP based on supercritical fluid extraction and specialty interface units. Analyses of low ppb levels of vapors, aerosols/particulates, gasoline, and soils illustrate the proven capabilities of the integrated modular systems. A developing expert system network, MicroEXMAT, encodes expertise to guide analysts in analytical strategy, instrumental configurations, and method development for the proposed on-site analyzers.

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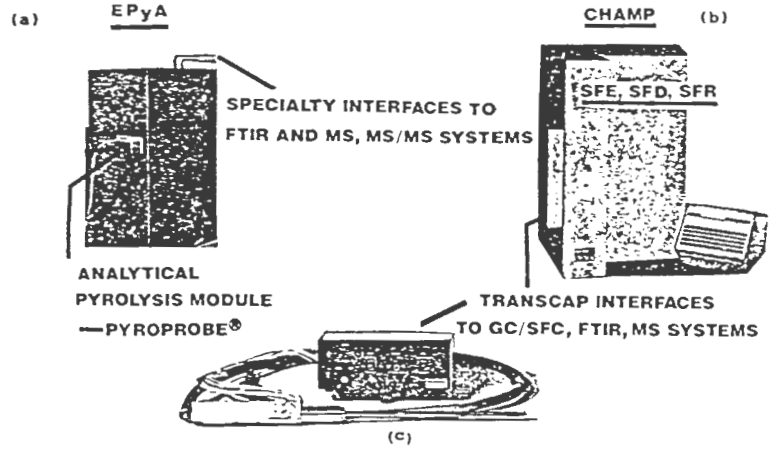

Figure 1. (a) EPyA, the Environmental Pyroprobe Analyzer
(b) CHAMP, the Chemical Hazards Automated MultiProcessor
(c) TRANSCAP Interface to Finnigan TSQ MS/MS

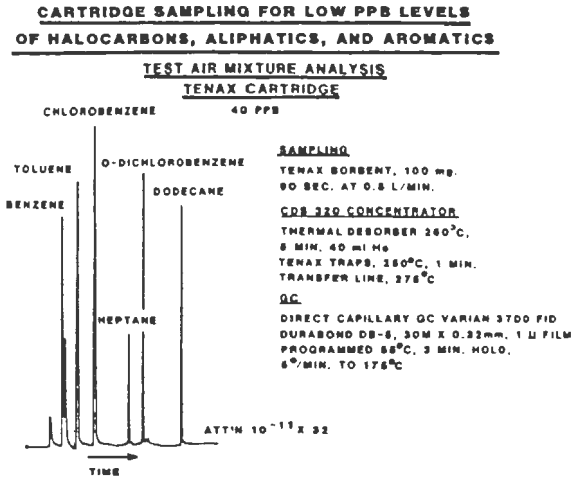

Figure 2. Cartridge Sampling for Low PPB Levels of Halocarbons, Aliphatics, and Aromatics in Air with Thermal Desorber Module

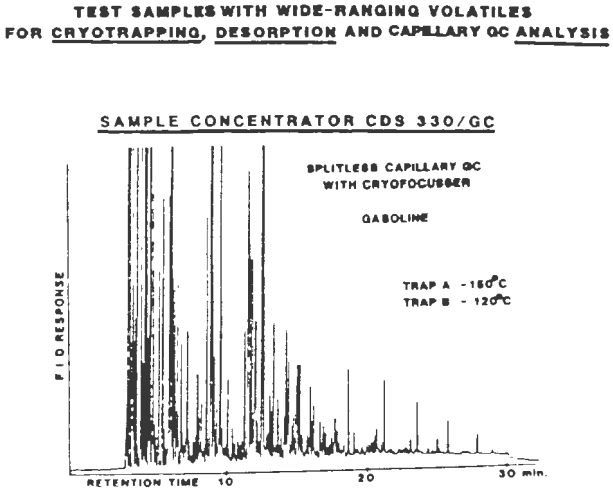

Figure 3. Gasoline and Diesel Fuel Test Mixture Analyzed with Cryotrapping, Thermal Desorption, and Capillary GC/FID System

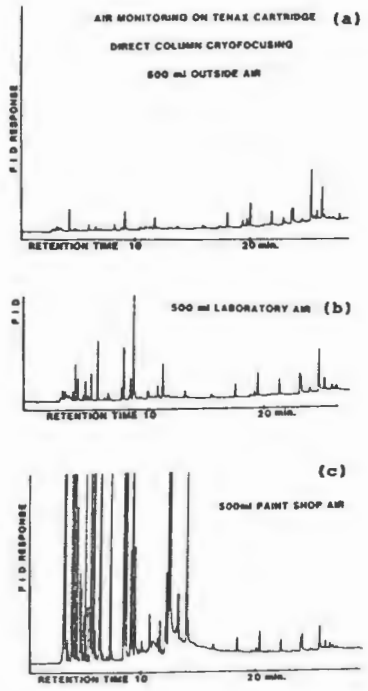

Figure 4. Air Monitoring on Tenax Cartridge with Direct Column Cryofocusing, 500 ml Sample
(a) Outside Air, (b) Lab Air, (c) Paint Shop Air

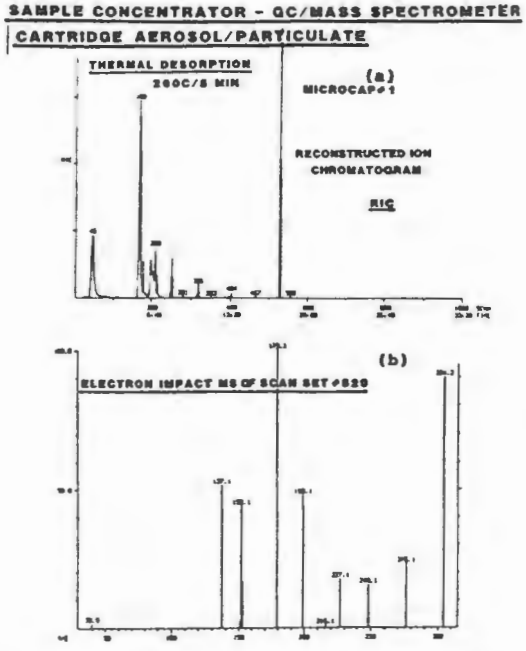

Figure 5. (a) Reconstructed Ion Chromatogram of Cartridge Aerosol/Particulate. Thermal Degradation (260°C/5 min) GC-MS Analysis of Microcap #1
(b) Electron Impact MS of Scanset #529

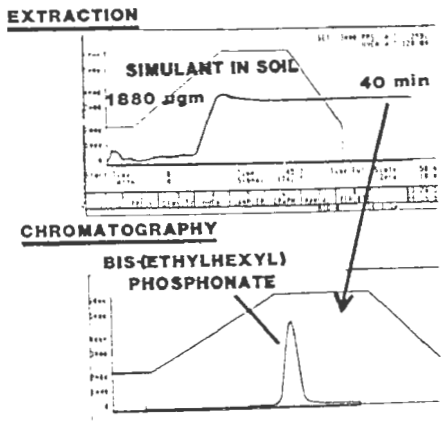

Figure 6. Supercritical Fluid Extraction-Chromatography (SFE-SFC/FID) of Bis-(Ethylhexyl)phosphonate, 3000 psi CO_2 Mobile Fluid

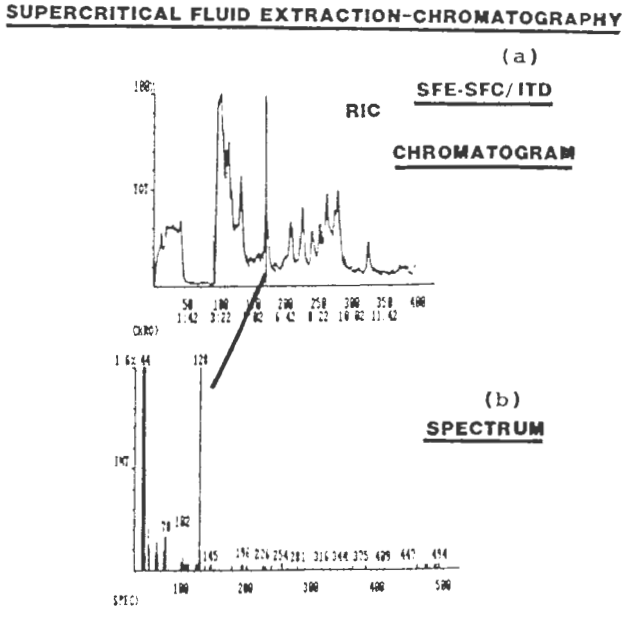

Figure 7. SFE-SFC Interfaced to Ion Trap Detector (ITD) of Polyolefin Mixture with Naphthalene
(a) Reconstructed Chromatogram
(b) Mass Spectrum, m/z 128

USING A FID-BASED ORGANIC VAPOR ANALYZER IN CONJUNCTION WITH GC/MS SUMMA CANISTER ANALYSES TO ASSESS THE IMPACT OF LANDFILL GASSES FROM A SUPERFUND SITE ON THE INDOOR AIR QUALITY OF AN ADJACENT COMMERCIAL PROPERTY

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The ERT was tasked to access the degree that VOCs, which may have been co-migrating with methane from a Superfund site, were affecting the indoor air quality of a shopping mall. Of particular concern to the Region was the fact that the mall had actually been built on top of the site prior to its being added to the NPL. The actual assessment used a combination of both field screening methods and fixed laboratory methods to gather two separate sets of data: one set on the landfill gases and the other set on the air inside the mall. OVA, Explosivity, and HNU readings from all of the landfill vent were used to select the vents from which the Summa canisters would be taken for GC/MS and permanent gas analyses. Concurrent with Summa sampling, the inside of the mall was screened using an OVA - particularly at all of the likely entry points for subsurface gases.

The analytical results were interpreted as follows: The Summa results were used to determine the "worst case" ratio of target compound to methane observed in the vent gases. These values were then multiplied by the worst OVA readings observed in the vicinity of a likely soil gas entry point in order to predict the highest possible concentration of VOCs that could have been present due to co-migration with the methane from the landfill. These "worst case" predictions clearly indicated that there was not an apparent long-term health risk due to VOC migration from the landfill.

FIELD ANALYTICAL SUPPORT PROJECT (FASP) USE TO PROVIDE DATA FOR CHARACTERIZATION OF HAZARDOUS WASTE SITES FOR NOMINATION TO THE NATIONAL PRIORITIES LIST (NPL): ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AND PENTACHLOROPHENOL (PCP)

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ABSTRACT

The path from initial discovery of a site as potentially contaminated to its inclusion on the National Priorities List (NPL) requires numerous activities, most importantly the identification and quantitation of hazardous wastes or contaminants associated with the site and the surrounding area. New guidance for NPL nomination places greater emphasis on accurate determination of the areal and volumetric extent of contamination during the site assessment phase of work. Under this guidance, extensive sampling is a prerequisite for characterization of a site. This places a heavy burden on the United States Environmental Protection Agency (EPA) regions' ability to provide quality assurance oversight for data generated by Contract Laboratory Program (CLP) analysis of these samples, and adds considerable costs and time to the nomination process. If the contaminants of concern have been identified previously, it may be appropriate to characterize the site using field analytical support. In Region 10, the Field Analytical Support Project (FASP) program has been integrated into the Screening Site Inspection (SSI) and Listing Site Inspection (LSI) process to provide cost savings and near real-time analytical information about the site. FASP methods are designed to meet the data quality objectives (DQOs) established for each site. All FASP data used for site characterization are confirmed by analyzing 10 percent of the samples collected for full Target Compound List (TCL) analysis through the CLP. Gas chromatographic methodologies for field analysis of selected PAHs and PCP have been developed for FASP in response to a regional need for site characterization at wood treating facilities. FASP methods are developed for small volumes, rapid extraction and analysis, and minimum labor intensity. Methods developed for FASP will be presented, as well as the results from two LSIs, including a comparison of FASP data to CLP confirmation results at each site.

INTRODUCTION

The United States Environmental Protection Agency (EPA), under the Superfund Amendments and Reauthorization Act of 1986 (SARA), uses the National Hazardous Waste Site Investigation program to identify hazardous waste sites for inclusion on the National Priorities List (NPL). Ecology and Environment, Inc. (E & E) holds the Zone 2 Field Investigation Team (FIT) contract, under which potential hazardous waste sites are investigated, and relative risks and threats to human health and the environment are evaluated. FIT assists the EPA in its goal of identifying sites for the NPL in three stages: 1) Preliminary Assessments (PAs), 2) Screening Site Inspections (SSIs), and 3) Listing Site Inspections (LSIs). A potential hazardous waste site would go through all three phases before it could be listed on the NPL.

In 1988, EPA released the proposed revisions to the Hazard Ranking System (HRS), which is used to score potential hazardous waste sites based on an assessment of rela-

tive risks. Prior to the revised HRS (rHRS), the extent of contamination at a hazardous waste site was determined only after the site actually was placed on the NPL (during the remedial investigation phase of site cleanup). The rHRS includes new guidance for nomination to the NPL, and places greater emphasis on accurate determination of the areal and volumetric extent of contamination during the site assessment phase of work. Coupled with congressional mandates aimed at streamlining the listing process, the new guidance places a heavy burden on the limited analytical resources available in terms of the number of samples required for accurate site characterization, and rapid turnaround of analytical data after sample collection.

The site assessment program obtains most of its required data through the EPA CLP, since the CLP provides cost-effective analyses for a large number of contaminants. Sometimes, however, it may be impractical to utilize the CLP to characterize a site if preliminary data are already available that identify the target analytes of concern. The costs and time involved with a large-scale sampling plan can be minimized by tailoring the type of sample analyses performed to the specific project needs. Also, information obtained from the laboratory during the sampling event may allow the field team to optimize sample locations for proper identification of site boundaries, while minimizing the total number of sample analyses required. These types of laboratory interaction and sample location tailoring are currently difficult to obtain through CLP Routine Analytical Services (RAS).

In addition, RAS contract required quantitation limits may not be adequate to determine the extent of on-site contamination at sites where the NPL listing criteria establishes a need for the lowest obtainable quantitation limits. It also is possible that CLP methodology may be inappropriate under specific matrix conditions present at a site, potentially resulting in further elevation of the quantitation limit above required action levels. Determination of a matrix interference in advance, through real-time analysis, may allow for modification of the CLP method as requested through the Special Analytical Services (SAS) process, to minimize the necessity of resampling.

This paper describes an alternative to the exclusive use of full organics and inorganics CLP RAS analysis of samples collected during the SSI and LSI processes. When compared to CLP RAS, this alternative often results in cost and time savings while providing analytical information that satisfies the data quality objectives (DQOs) for each site.

DQOs

DQOs are statements regarding the level of uncertainty that a data user or decision-maker is willing to accept in results derived from environmental measurements. The DQO process is designed to help the data user match quality needs with the appropriate analytical laboratory and methods so that the right type, quality, and amount of data are collected (1).

When applied to hazardous waste site investigations, the DQO process provides a quantitative basis for designing rigorous, defensible, and cost-effective investigations. The DQO planning process recognizes that decision making is driven by regulatory requirements and by risks to public health and that the uncertainty in decisions will be affected by the type and quality of data collected. DQOs provide a qualitative and quantitative framework around which data collection programs are designed, and can serve as performance criteria for assessing projects (2).

DQOs determine the level of analytical support necessary to provide decision-makers with sufficient confidence upon which to select options with known levels of uncertainty. Choice of specific analytical options may be determined by:

- Health-based concerns,
- Sample analysis cost,
- Analytes of concern or target/indicator analytes,
- Regulatory action levels that dictate method quantitation limits,
- Sample matrices,
- Sample collection, handling, and storage requirements, and
- Statistical uncertainty in the qualitative identification of analytes and errors associated with the quantitation.

All of the above considerations must be weighed to determine the appropriate analytical needs for the project data. Rarely, if ever will a single analytical program provide the best technical information and the most cost effective solution to address all concerns at the site.

The "art" of field analytical support is to match analytical capability to the DQOs required for a specific site in a cost-efficient manner. Once the acceptable level of error in the result is determined, the acceptable level of inherent error in the measurement system can be addressed.

FIELD ANALYTICAL SUPPORT PROJECT (FASP) PROGRAM

Broadly defined, field analytical support is the use of chemists in an analytical laboratory at or near the site of a hazardous waste investigation, removal, or remedial action. Field analytical support is more than a facility or vehicle stocked with instrumentation, glassware, and expendables; it is the interactive management process by which decision-makers and the personnel who provide the analytical results integrate planning, execution, and assessment of analytical data collection into environmental studies. These procedures form the basis of the FASP program.

In the late 1970s and early 1980s, field analytical support for determinations of contaminants at hazardous waste sites was almost exclusively restricted to health and safety monitoring of on-site personnel. Early site screening was limited primarily to air monitoring for volatile organic compounds with hand-held instruments such as the HNu PI101 (photoionization detection) and the Foxboro OVA (flame ionization detection). Within the last decade, more sophisticated analytical instrumentation, such as portable (hand-carried) and transportable (mobile laboratory supported) gas chromatographs and light-weight, compact X-Ray fluorescence and atomic absorption analyzers, have begun to be employed routinely in hazardous waste site investigations. These new instruments, coupled with field-experienced chemists, have provided near real-time organic and inorganic analyses for contaminants in air, soil, water, and other matrices (3).

Under E & E's Zone 2 FIT contract, a FASP program was initiated in 1984. The main purpose of FASP is to support the PA, SSI, and LSI process by utilizing field analytical methods to provide useful information about site contaminants on a real- or near real-time basis. FASP can be a cost- and time-effective alternative or supplement to conventional laboratory sample analysis in many situations. Turnaround time for conventional laboratory analyses, such as CLP RAS is 40 days after receipt of the samples. CLP data for site assessment activities must undergo data validation by a FIT chemist which takes approximately two weeks. By contrast, FASP data are generally provided verbally within 24 hours of sample receipt, and a final deliverable is often available approximately 14 days after the project is completed. FASP data are evaluated during laboratory projects. Additional data validation time is not required.

The EPA recognizes that field analytical methods such as FASP provides, are appropriate for many decisions made in Superfund (American Environmental Laboratory, October 1990). The EPA encourages the use of these field analytical methods for screening, monitoring and other assessments requiring rapid turnaround of data, and for decisions where unconfirmed analyte identity and estimated concentrations are appropriate. FASP methods are currently included in EPA's revised Field Analytical Methods Catalogue. FASP data have been used to:

- Optimize sampling grids,
- Select groundwater well screen depths,
- Guide remedial disposal requirements,
- Provide guidance to cleanup contractors,
- Assist in spill response,
- Select well locations based on soil gas monitoring,
- Provide enhanced site characterization,
- Identify the most appropriate samples for CLP analysis,
- Estimate waste quantities,
- Determine extent of contamination migration, and
- Find "hot-spots".

FASP is not a replacement for or an equivalent of the EPA CLP. FASP does provide real-time data of known (legally admissible) quality, which may be used in situations where data generated by a certified laboratory and standard methodology is not a requirement for decision making. All FASP analytes are, by definition, tenta-

tively identified, and all FASP quantitative data are estimated concentrations because methods and quality control (QC) are a subset or variants of standard CLP QC. Although both qualitative and quantitative accuracy and precision may nearly equal CLP, no attempt is made to alter these limitations. Therfore, to properly identify FASP data as tentatively identified with estimated concentrations, all FASP data in Region 10 are annotated with the qualifier "F". This qualifier also indicates that field methodologies were employed to generate the data.

FASP often is used at sites where previous sampling has been performed and target analytes have been identified. When analytes have been identified previously, unambiguous identification (i.e., mass spectral detection) may not be required. FASP is used most efficiently in the analysis of samples for a limited group of analytes requiring only one or two analytical methodologies. FASP is not used routinely for analysis of samples for unknown contaminants.

FASP STANDARD OPERATING GUIDELINES (SOGs)

The FASP program functions under SOGs that provide guidance on general QC and analyte-matrix-specific methodologies which have been developed within the FASP program. Methodologies are developed on an as-needed basis, to accommodate the FIT program, or any other program in which FASP is utilized. FASP methods are designed to provide near real-time data to field personnel. To accomplish this goal, the methods utilize simplified sample preparation techniques (disposable glassware, smaller scale extractions) based on more exhaustive conventional laboratory methods, such as CLP methods. As field analytical methodologies and the associated QC are generated, they are standardized, reviewed by FASP chemists, and submitted to EPA for review by the Analytical Operations Branch (AOB) Field Methods Workgroup for final approval. By the use of standardized and approved SOGs, consistent data of known quality are generated.

Like EPA or other standard methods, SOGs prepared for field analytical support provide information on the approximate precision and accuracy that the methods may provide for sample analysis. However, FASP methods often are tailored to meet site-specific requirements. This increases the probability of obtaining useful data by overcoming matrix problems, establishing appropriate quantitation limits for the project DQOs, or focusing on specific target analytes.

QC

FASP QC is based on the needs of the FIT program and may vary according to the analytical method and/or specific project needs. There are, however, some general guidelines provided by SOGs which are consistently employed.

Instrument Calibration

Gas chromatographic response to target analytes for the external standard method of quantitation is measured by determining calibration factors (CFs), which are the ratio of the response (peak area or height) to the mass injected. An initial calibration designed to demonstrate the instrument's linear response is generated for each target analyte by analyzing a minimum of three standard concentrations which cover the working range of the instrument. Using the calibration factors calculated from the initial calibration, the percent relative standard deviation (%RSD) is calculated for each analyte at each concentration level. The percent relative standard deviation generally is required to be less than or equal to 25 percent.

The mean initial calibration factor for each analyte is verified by the continuing calibration during each operational period (daily) to ensure detector stability. Mid-range standards are analyzed, and calibration factors are compared to the mean initial calibration factor for each analyte. The relative percent difference generally is required to be less than or equal to 25 percent. If the continuing calibration criteria are not met for each target analyte, a new initial calibration is performed.

Final calibrations are performed at the end of a project, or sampling effort to ensure analytical instrument stability. The calibration factor from the final calibration is compared to the mean initial calibration factor for each analyte. The relative percent difference is required to be less than or equal to 50 percent. If the relative percent difference meets continuing cali-

bration criteria, the final calibration also may be used as a continuing calibration.

Analyte Identification and Quantitation

Qualitative identification of target analytes is based on both detector selectivity and relative retention time as compared to known standards, using the external standard method. Generally, individual peak retention time windows should be less than ±5 percent for packed columns.

The concentration of an analyte in the sample is calculated using the calibration factor for that analyte calculated from the continuing calibration. Reported results are in micrograms per kilogram (µg/kg) without correction for blank results, spike recovery, or percent moisture.

Sample chromatograms may not match identically with those of analytical standards. When positive identification is questionable, the chemist may calculate and report a maximum possible concentration (flagged as < the numerical value) which allows the data user to determine if additional (e.g., CLP RAS or SAS) analysis is required or if the reported concentration is below action levels and project objectives and DQOs have been met.

Similarly, when sample concentration exceeds the linear range, the analyst may report a probable minimum level (flagged as > the numerical value) which allows the data user to determine if additional (e.g., CLP RAS or SAS) analysis is required or if the reported concentration is above action levels and project objectives and DQOs have been met.

Blank Analysis

A method blank is performed with every set of samples extracted; a minimum of one method blank per 20 samples is performed. The method blank must contain less than the project quantitation limit, the minimum reportable value, for each target analyte.

Matrix Spike Analysis

Accuracy is defined as the closeness to which analytical results approach the "true" value. Although it is not possible to measure absolute accuracy for environmental samples, spiked sample analyses provide a measure of extraction efficiency and sensitivity and thus indirectly, the required quantitative analytical accuracy. Matrix spikes are performed by adding a known quantity of target analytes (or a subset of target analytes) to samples specified for QC; a minimum of one matrix spike per 20 samples is performed. The sample chosen should be representative of the matrix type in the sample group. Advisory recovery limits are determined based on site-specific DQOs.

Duplicate Sample Analysis

Precision is defined as the tendency for replicate results to exhibit grouping about a central "point". FASP precision is primarily a function of sample size and homogeneity. The inherent limitations of FASP generally preclude the analyst from obtaining replicate samples with identical matrices, which are required for precision to have true statistical significance for the analysis. Precision in field analysis includes a sampling error component that cannot be avoided. Dry soils with small uniform grain size yield higher precision data because care can be taken to ensure sample homogeneity. Other indeterminate errors may be minimized by using good laboratory practices and standard analytical techniques. The evaluation of analytical precision within a FASP data set is based upon duplicate analyses. Duplicate analyses are performed at a minimum of one duplicate per 20 samples. Advisory relative percent difference (RPD) limits for duplicate analyses are determined based on site-specific DQOs.

Data Confirmation

In order to verify that the tentative identifications and estimated quantitations provided by FASP data are adequate for site-specific DQOs, a percentage of samples collected for FASP analysis are homogenized in the field, split, and sent to the CLP for analysis. Samples may be selected for submission to the CLP after completion of FASP analysis in order to allow for more significant data comparisons. Samples are selected to cover the entire range of sample concentrations for target analytes. Linear regressions may be performed on the data sets; however, field variability of split soil samples may prevent acceptable statistical results. If too few split samples are available, or if field variability is great, relative trends in

analyte concentrations may be used as a comparison of the two data sets.

FASP POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) ANALYTICAL METHODOLOGY

FASP PAH methodology provides identification of a subset of the base/neutral acid (BNA) compounds included on the CLP Target Compound List (TCL). The method provides tentative identification of the PAH compounds listed below, at estimated concentrations:

- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Chrysene
- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene

For the soil matrix, a well homogenized 2 or 3g sample is weighed into a disposable culture tube with a Teflon-lined cap. The sample is extracted with 6 mLs of methylene chloride twice by vortexing for 2 minutes, combining the extracts. The final extract is dried with a small amount of sodium sulfate and then solvent exchanged into isooctane.

Isolation of the target analytes is accomplished by a small-scale silica gel column cleanup. A disposable glass 4 mL giant pipette is filled with a plug of glass wool, silica gel, and sodium sulfate. The column is eluted first with methylene chloride, then petroleum ether (10 mLs of each). The sample, in isooctane, is then introduced onto the column. After the sample is introduced to the column, the column is first eluted with petroleum ether (6 mLs) in order to allow interfering contaminants, such as hydrocarbons, to be removed. The PAHs are then eluted with methylene chloride (10 mLs), and the final volume of the extract is reduced to 1.0 mL under a stream of nitrogen.

The sample is analyzed by gas chromatography, using a J&W 0.53 mm x 15 m DB-5 fused silica megabore column and employing flame ionization detection. A temperature program is utilized to optimize separation of the analytes. The gas chromatographic analysis time is approximately 30 minutes.

Samples are quantitated using the external standard method. Standard mixes are purchased from a commercial manufacturer and diluted to appropriate concentrations for instrument calibration. Calibration factors are calculated for each analyte in the initial and continuing calibrations. The concentration of the analyte(s) in a sample is calculated based on the analyte calibration factors calculated from continuing calibrations.

The quantitation limits for the FASP PAH methodology are 1,000 µg/kg, while CLP RAS required quantitation limits are 330 µg/kg. As the CLP samples do not undergo silica gel cleanup, the final matrix potentially contains a higher degree of interference from petroleum hydrocarbons, which are often present along with the PAHs. When petroleum hydrocarbon interferences are present, the sample often requires dilution before an accurate analysis can occur. This results in an elevation of the actual contractual quantitation limits. Samples analyzed by FASP methodology are relatively free of these interferences, and generally do not require dilution.

The total time for preparation and analysis of 10 soil samples is 490 minutes. In a 10-hour day, the maximum capacity for a field analytical laboratory equipped with one gas chromatographic system is approximately 11 samples during the first day of operation, and 20 samples each day thereafter. This projected capacity does not take into account any dilutions which may be required when high target analyte levels are present.

This method employs only disposable glassware, eliminating time required for cleaning glassware, and minimizing the potential for cross contamination. Solvent volumes are minimal, requiring a total of only 40 mLs per sample, compared to the CLP method for BNAs which requires 300 mLs of solvent per extraction.

FASP PENTACHLOROPHENOL (PCP) ANALYTICAL METHODOLOGY

For soil, a well homogenized 2 or 3g sample is weighed into a disposable culture tube with a Teflon-lined cap. The soil is dried by adding a small amount of sodium sulfate. The sample is then extracted with methanol (10 mLs) by vortexing for 2 minutes. Five mLs of the extract is transferred into a clean culture tube.

The extract is derivitized with a solution of pentafluorobenzyl bromide and hexacyclo-octadecane (18-crown-6 ether) in 2-propanol. One mL of the derivitization solution is added to the sample extract, along with 3 mg of potassium carbonate. The culture tube is then capped, gently shaken, and left in a hot water bath at 80°C for 4 hours. The culture tube is allowed to cool, then the sample is extracted with 5 mLs of hexane by vortexing for 1 minute. Five mLs of carbon-free water are added to the culture tube, and vortexed for an additional minute. The hexane layer, which contains the derivitized PCP, is transferred to a clean culture tube and dried with a small amount of sodium sulfate. The extract is then ready for analysis.

The extract is analyzed by gas chromatography using a 1.0 m. glass column packed with 1.5% SP-2250/1.95% SP-2401 and employing electron capture detection. The isothermal column oven temperature is 275°C, and gas chromatographic analysis time is approximately 20 minutes.

Samples are quantitated using the external standard method. Standards, blanks, and appropriate quality control samples are prepared with each batch of samples derivitized.

The quantitation limit for PCP using this methodology is 50 µg/kg. The quantitation limit for PCP by CLP BNA methodology is significantly higher (1,600 µg/kg). FASP methodology allows for the lower quantitation limit by isolating the PCP present in the sample and removing matrix interferences, and then using a more sensitive instrumental technique (GC/ECD).

The total time for preparation and analysis of 10 soil samples for PCP is 530 minutes. In a 10-hour day, the maximum capacity for a field analytical laboratory equipped with one gas chromatographic system is approximately 10 samples during the first day of operation, and 20 samples each day thereafter. This projected capacity does not take into account any dilutions which may be required due to high target analyte concentration in the sample.

This method, like the PAH method, employs only disposable glassware, and consumes only minimal solvent volumes (21 mLs total) compared to CLP solvent volumes of 300 mLs per sample extracted.

CASE STUDY 1

E & E was tasked to perform an LSI at an active wood treating facility occupying 19 acres in Oregon. The facility operations involve pressure treating wood products using creosote (containing PAH compounds) and PCP in a petroleum oil carrier. The determination of the extent of on-site surface contamination was defined as one of the objectives of the LSI, requiring analysis of 56 on-site grid surface soil samples. Since the target analytes were known, it was determined that site-specific DQOs could be met by using FASP at a substantial cost and time savings compared to a full CLP sample analysis scheme.

Sixty-two surface soil samples were collected at the site for FASP analysis, including six duplicate, or colocated samples. The samples were shipped to the FASP Seattle Base Laboratory for analysis, as the project was not large enough to justify mobilization. The sample analyses were completed within 24 hours of receipt of the last sample shipment.

A cost comparison was calculated for FASP versus CLP RAS analysis of the samples. The total FASP costs included the purchase of required expendables, which totaled approximately $4,546.00 and labor, which totaled approximately $13,300 for 350 hours of effort. If CLP had been utilized for these analyses, the total cost would have been $27,308, which accounts for laboratory charges and data validation. This amounts to a savings of $9,461 by utilization of the FASP program. This comparison indicates that full organics CLP RAS would not be appropriate for these samples. Rather, a focused analysis, such as CLP SAS or FASP would be more appropriate. For near real-time availability of sample data, FASP would be the preferred alternative.

The confirmatory samples were analyzed for

BNA compounds by a CLP laboratory at a frequency of approximately 10 percent (8 samples). Sample quantitation limits were consistently higher for the CLP data set due to the matrix interferences from the oil present in the samples. For most samples, quantitation limits were elevated 2 to 300 times above the contract-required quantitation levels.

Correlation between the FASP and CLP data sets was excellent. FASP identification of PAHs and PCP was confirmed, and relative trends in concentrations generally agreed. A statistical analysis of the data sets was performed using correlation coefficients. FASP and CLP data sets were compared for analytes where four or more pairs of data points were available (i.e., four or more samples sent for confirmatory analysis had results above method quantitation limits for the analyte). The calculated correlation coefficients are summarized in Table 1.

Table 1. CORRELATION COEFFICIENTS FOR FASP AND CLP DATA: CASE STUDY 1

Analyte	Data Pairs Used	Correlation Coefficient (r)
Phenanthrene/ Anthracene	6	0.999
Fluoranthene	6	0.999
Pyrene	6	0.999
Chrysene/ Benzo(a)anthracene	8	0.9997
Benzo(b)fluoranthene/ Benzo(k)fluoranthene	8	0.9775
Benzo(a)pyrene	4	0.9703
Pentachlorophenol	6	0.9696

As a result of the FASP analysis and CLP confirmation, the data generated by FASP were determined to be acceptable for use in determining the on-site hazardous waste quantity. This allowed data users to accurately measure the relative risks resulting from on-site contamination.

CASE STUDY 2

An LSI was performed at an inactive pipe-coating facility, which had generated coal tar, coal tar epoxies, asphalt, and cement mortar wastes over the 51 acres for approximately 30 years. Several target analyte groups had been identified previously, including volatile organic compounds, PAHs, and polychlorinated biphenyls (PCBs). The project objectives required on-site surface soil contamination to be characterized. An on-site grid sampling pattern was used, resulting in collection of 54 samples.

Previous site sampling events had identified the target analytes, allowing for FASP analysis of the on-site surface soil samples while maintaining the project DQOs. The soil samples were analyzed for volatile organic compounds, PAHs, and PCBs at the FASP Seattle Base facility. It was more cost-effective to analyze the samples at the base facility due to the variety of analyses required and the relatively small size of the project.

The cost of FASP analysis of the 54 samples and four field duplicate samples was $20,900 ($1,900 for supplies, $19,000 for labor) compared to CLP analysis costs which would have totaled $57,408. This amounted to a total savings of $36,508 by utilizing FASP. All sample analyses were completed within 7 days of the last sample shipment date.

Six samples (approximately 10 percent of the total number of samples) were split and sent to a CLP laboratory for confirmatory volatile, BNA, and pesticide/PCB analysis. Again, matrix interferences prevented CLP BNA analysis without elevated quantitation limits due to the presence of oil. FASP methodology, involving sample cleanup for specific analyses, removed much of the oil interference.

Correlation between the two data sets was excellent. FASP identification of volatile compounds, PAHs, and PCBs was confirmed by CLP data, and relative trends in analyte concentrations agreed. Calculated correlation coefficients were generated where four or more data pairs were available. One split sample contained extremely high levels of PAHs. CLP results were significantly and consistently higher than the FASP results for all PAHs detected in this sample. It is most likely that this phenomenon was due to the non-homogeneous nature of the soil matrix. Therefore, this data pair was not included in the correlation coefficient calculation. The correlation coefficients are presented in Table 2.

Table 2. CORRELATION COEFFICIENTS FOR FASP AND CLP DATA: CASE STUDY 2

Analyte	Data Pairs Used	Correlation Coefficient (r)
Fluoranthene	4	1.000
Pyrene	4	1.000
Chrysene/ Benzo(a)anthracene	4	1.000
Benzo(b)fluoranthene/ Benzo(k)fluoranthene	4	1.000
Benzo(a)pyrene	4	1.000
Indeno(1,2,3-cd) pyrene/Dibenzo(a,h) anthracene	4	0.999
Benzo(g,h,i)perylene	4	0.999
Aroclor 1254	5	0.945

A statistical analysis of matrix spike recovery data for eight samples collected at both of the sites described above is presented in Table 3.

CONCLUSION

Recently, EPA has placed a greater emphasis on the determination of extent of contamination during site assessments. FASP was initiated under E & E's Zone 2 FIT contract in 1984, and is a viable alternative or supplement available to address the analytical demands for determining relative risks at hazardous waste sites. FASP provides data of known quality, using standard methodologies and QC modified to meet the project DQOs. FASP data can be obtained at a substantial cost and time savings when compared to conventional CLP analysis, and has been used successfully for characterization of sites with known target analytes.

Table 3. AVERAGE MATRIX SPIKE RECOVERIES FOR SOIL SAMPLES AT HAZARDOUS WASTE SITES

Analyte	Average Percent Recovery	Standard Deviation
Naphthalene	70.0	36.8
Acenaphthylene	103	47.3
Acenaphthene	94.3	36.6
Fluorene	90.3	24.9
Phenanthrene/ Anthracene	93.4	38.9
Fluoranthene	118	53.5
Pyrene	123	53.8
Chrysene/Benzo(a) anthracene	121	34.5
Benzo(b) fluoranthene/ Benzo(k) fluoranthene	107	26.6
Benzo(a)pyrene	112	24.0
Indeno(1,2,3-cd) pyrene/ Dibenzo(a,h,) anthracene	98.7	25.8
Benzo(g,h,i) perylene	88.0	28.8
Pentachlorophenol	122	51.4

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DISCUSSION

DOUG PEERY: You were talking about doing 20 samples in a ten-hour day with 30-minute run time. Does that include your QA/QC or did you have another four hours of work time to cover that?

LILA ACCRA-TRANSUE: We did ten samples or 20 sample analyses. So that includes the QC samples that we need to run.

DOUG PEERY: So you're talking about your standards and your QC's within that 20 number.

LILA ACCRA-TRANSUE: Right.

VICKI TAYLOR: How many split sample pairs did you take?

LILA ACCRA-TRANSUE: We take approximately 10%. For the first project we'd taken eight and for the second project, six.

VICKI TAYLOR: So you were basically presenting a correlation coefficient for all the split samples that you took?

LILA ACCRA-TRANSUE: Right. All of the comparable data pairs are reported where they were hits in both samples.

Thermal Desorption Gas Chromatography-Mass Spectrometry Field Methods for the Detection of Organic Compounds

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INTRODUCTION

The overwhelming amount of information required to characterize purported hazardous waste sites, *as well as* to support Superfund site cleanup and closure activities, have catalyzed the development of field instrumentation capable of providing site managers with immediate access to chemical and physical data. The demand for field "practical" methods and instrumentation has been recognized by the U.S. Environmental Protection Agency (1, 2).

Faster data turnaround times and ease of operation have been the primary motivation for selecting *field* gas chromatographic (GC) methods of analysis. Despite recent advancements in field GC instrumentation, typical applications focus on the detection of EPA listed volatile organic compounds (VOCs) in water, air, or soil gas. The primary limitation of commonly employed field GC's is the non-definitive signal response of the detectors (including photoionization, flame ionization, thermal conductivity, and electron capture) which are incapable of providing unambiguous identification of the wide variety of organic compounds that may be present in a highly contaminated sample. Generally, ten to twenty percent of the samples analyzed on-site are "split" for confirmation by GC with mass spectrometric (MS) detection. Since most commercially available mass spectrometers have traditionally been housed and operated in a clean air, temperature controlled room and the notion that economies of scale require highly trained MS operators to be based in multi-MS laboratories, misapprehensions have arisen as to whether MS's can be operated successfully (and profitably) in the field.

The limited availability of field GC-MS's is not a function of MS operating requirements, but more, the perception that significant sample cleanup and QA/QC procedures will be required to obtain useful data as well as the apparent reluctance of instrument manufacturers to enter the field marketplace. Until recently, these misconceptions have perpetuated the myth that GC-MS's belong solely in the laboratory.

Over the last several years, we have discussed field GC-MS applications utilizing Bruker Instruments' mobile mass spectrometer (2-6). The MS, initially designed for NATO as a chemical warfare detector, was manufactured from the outset as a field instrument. In our studies, the MS was transported from site-to-site in a mid-sized truck and was battery operated for ~ 8 to 10-hr at ambient conditions. For example, samples have been analyzed with outdoor conditions, where; temperatures have been between 10 °F and 90 °F, rain, snow, and high humidity. Gas cylinders were not necessary for GC operation since charcoal filtered ambient air served as the carrier gas.

Simple field methods have been developed based on analyte introduction by thermal desorption (TD) followed by *fast* GC separation and MS detection. Screening level and more quantitative TDGC-MS methods have been submitted to EPA's EMSL-Las Vegas for VOCs in water, soil/sediment, soil gas, air *and* polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in soil/sediment for inclusion into the compendium of field methods that will be published by EPA's Analytical Operations Branch. The methods include a menu of QA/QC procedures whose implementation depends upon a given study's objectives. The goal is to provide a practical GC-MS tool that can deliver the quality of data required for the study with minimal sample cleanup. Presented in this paper are typical examples of data quality *and* a comparison of field and laboratory results one can expect from both the screening and more quantitative field TDGC-MS methods for PCBs, PAHs, and pesticides.

EXPERIMENTAL SECTION

A mobile mass spectrometer (Bruker Instruments, Billerica, MA) was used in these studies. The TDGC-MS was powered by battery or electrical supply from the site. The MS was transported to Superfund sites in Westborough (Hocomonco Pond; PAHs) and

North Dartmouth, MA (Resolve; PCBs) in a Chevrolet Blazer. In addition to the instrument's internal data collection and monitoring system, the MS was equipped with an external data system and thermal desorption sampling probe. Sample introduction was made by thermally desorbing (TD) the analyte directly from soil/sediment *or* from an organic extract through the TD sampling probe's (SP) short 3.5 m fused silica capillary column. For direct TD soil/sediment experiments, 0.5 g of soil was placed on an aluminum foil covered petri dish. An internal standard was injected into the soil before the measurement was made. In contrast, the more quantitative measurements required several additional steps: 1) 0.5 g of soil was weighed and extracted with 2 ml of solvent; 2) prior to extraction, a known quantity of surrogate (or target) compound(s) was added to the soil (or field blank) to determine extraction efficiencies (note: this step was required since a single 2 ml extraction yielded analyte recoveries of less than 100%; 3) co-inject known aliquots of extract and internal standard onto aluminum foil covered petri dish; 4) thermally desorb analyte. Shown below are the TDGC-MS operating *and* PCB, PAH, and pesticide experimental conditions:

Operating Conditions

Mass Spectrometer	Bruker Instruments (Billerica, MA)
electron energy	70 volts (nominal)
mass range	45 to 400 amu
scan time	2 sec
MS tune	autocalibrate ($H_2O_{(g)}$; FC-77); 18, 69, 119, 169, 331 amu
mass resolution	set to unity; ca. 10% valley definition
ion detection	17 stage Cu-Be dynode electron multiplier with self-scaling integration amplifier (10^8 linearity)
Sampling Probe Head	260 °C
GC Column	DB5 (J & W Scientific, Folsom, CA)
dimensions	3.5m x 0.32mm i.d.; 0.25μ film thickness
carrier gas	ambient air purified through carbon filters
flow rate	3 to 4 ml/min

	PCBs	PAHs	Pesticides
initial temp	140°C, 30 sec	70°C, 40 sec	120 °C
temp prog	120°C/min	35°C/min	17°C/min
final temp	200°C, 90 sec	233°C, 80 sec	233°C
Internal Standards	d_{10}-pyrene	d_8-naphthalene or d_{10}-pyrene	d_{10}-phenanthrene
solvent extraction	C_6H_{14}	CH_2Cl_2	C_6H_{14}

Data were acquired by using the internal monitor's selected ion monitoring program. The data system reported the total ion current as a logarithmic value. The antilog value is used in conjunction with MS response factors and analyte recoveries to calculate concentrations in the sample. Standards were purchased commercially from the following companies: PCBs (Ultra Scientific, Hope, RI); PAHs (Supelco, Inc., Bellefonte, PA); Pesticides (Chem Service, West Chester, PA); internal standards (Cambridge Isotope Laboratories, Woburn, MA). All standards and soil recovery experiments were prepared with high purity solvents (> 96 %) as received.

RESULTS and DISCUSSION

The objective of this study was to develop *fast* TDGC-MS methods (< 20 min/sample including sample cleanup). Two methods were developed. Analyte introduction for quantitative measurements were made by co-injecting organic extracts (or standard solutions) of PCBs, PAHs, or pesticides and internal standard(s) onto an aluminum covered petri dish followed by TDGC-MS and for screening measurements by direct thermal desorption from soil/sediment.

The surface monitor program mode was employed in this study. Target compounds (maximum number twelve) were detected by selected ion monitoring (SIM) MS. The (logarithm) ion current was recorded and displayed visually on the system's monitor. Found in Figure 1 are typical PCB and pesticide outputs. Three fragment ions representative of each compound(s) and an impossible ion (see below for rationale) were selected for detection. For example, in cell A the target ions and their relative intensities for the three monochlorinated PCBs were 188 (100%), 190 (33.5%), 152 (31.1%), and 189 (0%). Similarly, cells B-H in Figure 1a illustrate the SIM four ion current responses for chlorination levels 2 - 8, respectively; cell I, d_{10}-pyrene (internal standard); cells J - K, PAH surrogates; and cell L, hydrocarbon signals indicative of matrix complexity. Detection was made, and printed on screen, when the signals from the four ions relative to each other agreed to within preset criteria over a predetermined retention time window. In this mode, SIM response may be considered analogous to selective GC detection. Note above, that the last fragment ion for the monochlorinated PCBs had a relative intensity of 0%. Inclusion of an impossible ion served to provide selective detection. For example, an increase in fragment 1 ion current relative to fragments 2-4 within the target compound's retention window precluded compound identification. Thus, the mathematical algorithm assisted in screening out interferants present in the sample.

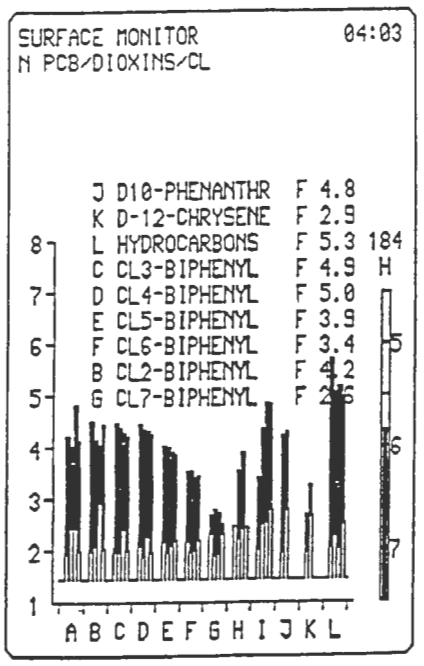

Figure 1a

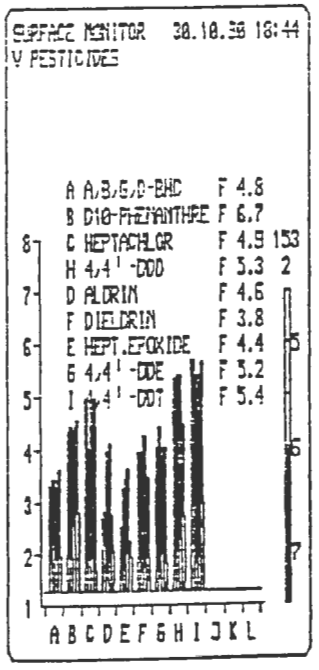

Figure 1b

Figure 1. Typical Field TDGC-MS SIM response of a standard solution containing PCBs (1a) *and* chlorinated pesticides (1b).

The *fast* GC linear temperature programs and MS detection provided sufficient separation to identify compound(s) as shown in Table 1. Figure 2 is a typical instrument print out for the amount (4-ion total current count, in log values, left vertical axis) vs. time response curves (horizontal axis) for four of the chlorinated pesticides shown in Figure 1b. In addition to the compound and amount detected, other information visible on the display included "real-time" monitoring of: logarithm of ion current, left vertical axis; MS vacuum pressure, right vertical axis; and column temperature, above right vertical axis.

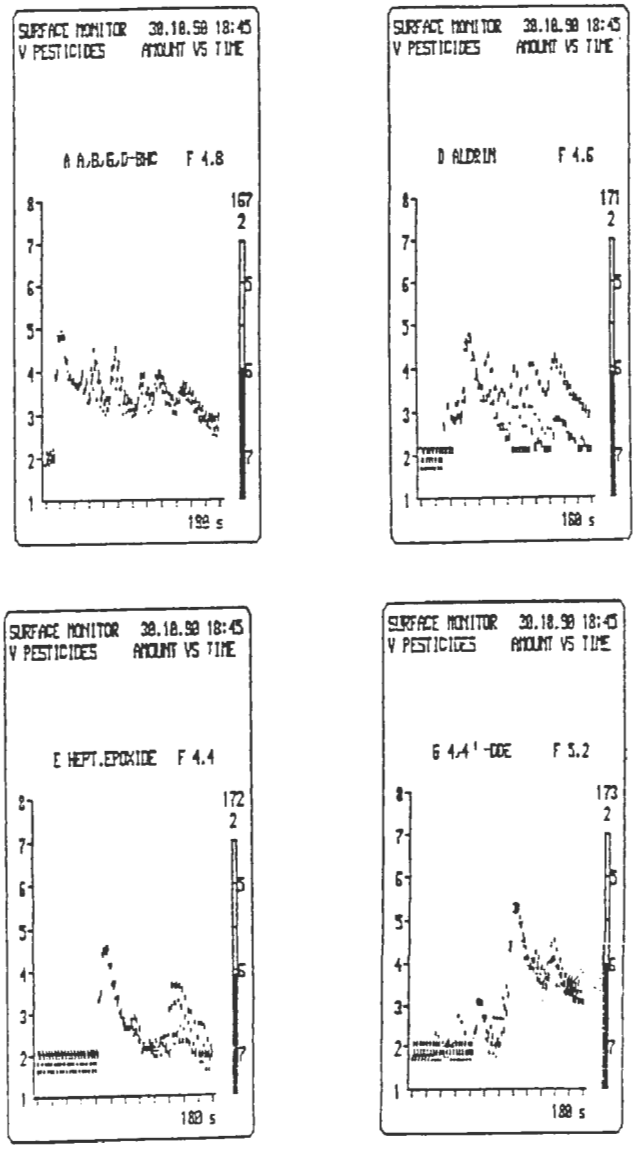

Figure 2. Amount versus time curve for several chlorinated pesticides shown in Figure 1.

TDGC-MS experiments were performed between the concentration range of 40 and 4000 ng/compound. Repetitive measurements at each concentration yielded differences in the log value of $\pm$ 0.1, producing ion current differences of less than 30%. Table 1 lists typical response factors (RF) and percent relative standard deviations (%RSD) calculated for PCBs, PAHs, and pesticides thermally desorbed from an organic extract. Plots of signal versus concentration were linear (r= 0.999) with the %RSD for the average RF less than 30%, meeting initial and continuing calibration criteria in the Contract Laboratory Program. Table 2 lists representative RF and RSDs for PCBs and PAHs thermally desorbed directly from soil. Despite somewhat larger percent RSDs for some PAHs, measurement precision at this level will only be critical at site cleanup "action" levels. It should be pointed out that thermal desorption extraction efficiencies differ greatly for some PAHs (see Table 3 for minimum detectable quantity. Note: RF in Table 2 calculated over linear range as shown in Table 3). Minimum detection levels for most compounds were ~ 1 ppm for soil/solvent extraction and slightly higher for direct soil thermal desorption. Because TDGC-MS experiments can be performed in 5 to 20 min depending on the method employed (with known data quality), many more analyses can be performed than currently practiced for site characterization, stockpiling, and worker/community protection activities. The frequency for performing continuing calibration checks may be determined (on-site) by following surrogate compound RF values (see below).

Research has shown that compound recoveries vary with soil-type. For example, PCB/hexane (0.5 g/2 ml hexane, 2 min) extraction recoveries were 69 $\pm$ 5% for 50 ppm backyard (organic) soil, 80 $\pm$ 2 %, for 25 ppm sandy material from the Resolve Superfund site in North Dartmouth, MA, and 73 $\pm$ 5 % for an ERA, 35 ppm, soil. Therefore, appropriate surrogate compound(s) and/or target standards must be added to samples as the soil-type varies. Such experiments can be used to determine instrument performance as well.

Tables 4 - 7 illustrate typical examples of data quality one can expect from the field TDGC-MS methods. Split samples were collected by EPA's Region 1 oversight contractor *and* analyzed in the field (Tufts) and lab (Lockheed ESC, Las Vegas, NV). Table 4 compares field and lab GC-MS measurements for total PCB present in several samples obtained from the Resolve site while Table 5 delineates chlorination level comparisons for two of the samples. The field and lab results are in excellent agreement.

Shown in Tables 6 and 7 are field and lab comparisons for four PAH samples from the Hocomonco Pond (Creosote contaminated Superfund) site. Note that the samples in Table 6 and the sample labeled HP-SB5 in Table 7 were performed by SIM using the system's internal monitor as described above. In contrast, the sample labeled pond (Table 7) was analyzed by total ion current, selected ion monitoring extraction. The advantage of this detection method was that full mass spectral fragmentation data and compound library matching was applied. On the other hand, the disadvantage was that ion current from matrix components may add to the SIM signal resulting in higher concentrations than what might actually be present. This, however, is no different than what can occur using traditional CLP, MS methods. Field and lab comparisons for PAH samples also appear to be in good agreement.

Additional data will be presented describing further application of the field TDGC-MS methods. Illustrations will be given documenting cost effectiveness. Results will show that GC-MSs can be operated in the field, provide rapid access of data, and allow project managers to make decisions on-site.

ACKNOWLEDGEMENTS

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Table 1. Thermal Desorption Field GC-MS Response Factors and Percent Relative Standard Deviations - from Extract (Quantitative Method)

Polychlorinated Biphenyls

Chlorination Level	Ave RF(n=5)	% RSD
Cl-1	0.47	20
Cl-2	0.26	17
Cl-3	0.27	17
Cl-4	0.16	15
Cl-5	0.15	12
Cl-6	0.10	15
Cl-7	0.06	17
Cl-8	0.03	10

Polycyclic Aromatic Hydrocarbons

naphthalene	1.37	123
acenaphthylene	8.63	123
acenaphthene	0.82	248
fluorene	0.58	123
phenanthrene/anthracene	4.59	123
fluoranthene/pyrene	9.52	95
chrysene/benz(a)anthracene	0.90	133

Chlorinated Pesticides

BHCs	0.10	96
Heptachlor	0.02	235
Aldrin	0.07	163
Heptachlorepoxide	0.03	109
Dieldrin	0.02	254
4,4'-DDE	0.32	163
4,4'-DDD	0.16	186
4,4'-DDT	0.12	197

Table 2. Thermal Desorption Field GC-MS Response Factors and Percent Relative Standard Deviations - Direct from Soil

Polychlorinated Biphenyls

Chlorination Level	Ave RF(n=5)	% RSD
Cl-1	13.44	19
Cl-2	3.75	25
Cl-3	3.91	23
Cl-4	2.55	16
Cl-5	2.02	16
Cl-6	1.61	16
Cl-7	1.04	23
Cl-8	0.36	19

Polycyclic Aromatic Hydrocarbons

naphthalene	2.39	75
acenaphthylene	1.21	356
acenaphthene	0.33	52.1
fluorene	0.16	165
phenanthrene/anthracene	0.25	213
fluoranthene/pyrene	0.06	310
chrysene/benz(a)anthracene	0.003	229

Table 3. PAH Dynamic Range Directly Desorbed from (0.5 g) Soil Matrix.

Compound(s)	Concentration (ng)	Signal (n=5)	Linearity (r)
Naphthalene	4000	510084 ± 22.9%	0.999
	2000	255648 ± 22.9%	
	1600	210541 ± 31.2%	
	800	110357 ± 12.9%	
	120	28371 ± 13.2%	
	80	5312 ± 23.4%	
	40	1995[a] ± 22.4%	
Acenaphthylene	4000	255648 ± 22.9%	0.999
	2000	129245 ± 26.1%	
	1600	94858 ± 10.8%	
	800	51454 ± 26.1%	
	80	3575 ± 13.2%	
	40	794[a] ± 17.2%	
Acenaphthene	4000	94858 ± 10.8%[a]	0.999
	2000	23397 ± 12.7%	
	1600	20307 ± 22.9%	
	800	9936 ± 34.5%	
	80	740 ± 12.7%	
	40	251[a] ± 16.8%	
Fluorene	4000	52714 ± 11.0%	0.999
	2000	24197 ± 32.8%	
	1600	18585 ± 12.7%	
	800	8971 ± 13.2%	
	120	371 ± 12.8%	
	80	794[a] ± 13.4%	
	40	251[a] ± 15.4%	
Phenanthrene & Anthracene	8000	42578 ± 35.4%	0.999
	4000	21245 ± 12.2%	
	3200	16271 ± 26.1%	
	1600	8084 ± 22.9%	
	240	877 ± 24.3%	
	160	3981[a] ± 18.6%	
	80	316[a] ± 20.2%	
Fluoranthene & Pyrene	8000	17498 ± 24.3%	0.999
	4000	8629 ± 13.8%	
	3200	6854 ± 13.8%	
	1600	3221 ± 40.1%	
	240	371 ± 12.8%	
	160	195[a] ± 15.3%	

[a]These values were not included in the dynamic range.

Table 4. Comparison of Field and Lab GC-MS Results for Total PCBs in Samples from the Resolve Superfund Site, North Dartmouth, MA

EPA ID#	Quantitative TDGC-MS (ppm)	Screening Level TDGC-MS (ppm)	Lab GC-MS (ppm)
TUF-RS-SO-A26-2-4	368.3	309.4	298.6
TUF-RS-SO-AI-5-2	274.6	213.6	260.0
TUF-RS-SO-A42-6-8	23.1	7.2	15.9
TUF-RS-SO-A37-0-2	9.1	3.2	1.3
TUF-RS-SO-AI4-0-2	7.6	1.6	5.0
TUF-RS-SO-A5A-2-4	1.7	1.7	0.4
TUF-RS-SO-NH24-2-4	1.7	-	-
TUF-RS-SO-A14-6-8	1.3	-	3.0
TUF-RS-SO-A7-4-6	ND	ND	ND

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University
Sample collected by EPA's Region 1 oversight contractor
-, Samples were not analyzed

Table 5. Comparison of Field and Lab GC-MS by Chlorination Level (ppm), Resolve Superfund site, North Dartmouth, MA.

ID Sample #	TUF-RS-SO-A15-2		TUF-RS-SO-A42-6-8	
Cl-level	Field TDGC-MS	Lab GC-MS	Field TDGC-MS	Lab GC-MS
Cl-1	12.5	ND	0.5	ND
Cl-2	7.6	10.8	1.5	1.0
Cl-3	60.3	56.5	4.5	4.1
Cl-4	121.4	122.8	5.1	5.3
Cl-5	59.5	53.6	6.3	4.3
Cl-6	20.9	15.9	3.0	1.2
Cl-7	1.7	0.4	0.3	ND
Cl-8	0.7	ND	1.9	ND
total PCB	274.6	260.0	23.1	15.9

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS (Quantitative Method) performed by Tufts University
Sample collected by EPA's Region 1 oversight contractor

Table 6. Comparison of Field and Lab GC-MS Results for PAH's From the Hocomonco Pond Superfund Site in Westborough, MA, in ppm.

	DSTB22(0'-2')		DSTB22(2'-4')	
	Lab	Field[1]	Lab	Field[1]
Naphthalene	0.1	ND	2.2	ND
Acenaphthylene	0.1	0.1	ND	0.7
Acenaphthene	1.4	0.1	6.0	0.2
Fluorene	2.9	1.5	16.3	3.0
Anthracene & Phenanthrene	8.3	40.3	81.8	72.7
Pyrene & Fluoranthene	11.8	10.6	112.2	60.5
Chrysene & Benz(a)anthracene	6.0	6.2	37.2	37.2
Benz(b)fluoranthene, Benz(k)fluoranthene, & Benz(a)pyrene	3.2	23.8	17.7	22.3

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University (Thermal Desorption of Methylene Chloride Extract)
[1]Data collected by Selected Ion Monitoring (Internal Data System)

Table 7. Comparison of Field and Lab GC-MS Results for PAH's From the Hocomonco Pond Superfund Site in Westborough, MA, in ppm.

	POND		HP-SB5	
	Lab	Field[2]	Lab	Field[1]
Naphthalene	1.3	1.9	54.8	32.0
Acenaphthylene	1.4	ND	ND	ND
Acenaphthene	0.7	ND	ND	1.2
Fluorene	2.5	ND	ND	0.8
Anthracene & Phenanthrene	16.7	10.4	ND	ND
Pyrene & Fluoranthene	30.7	43.6	ND	ND
Chrysene & Benz(a)anthracene	37.2	55.2	ND	ND

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University (Thermal Desorption of Methylene Chloride Extract)
[1]Data collected by Selected Ion Monitoring (Internal Data System)
[2]Data collected as Total Ion Current Chromatogram and quantified by Selected Ion Monitoring Extraction (External Data System)

DISCUSSION

ALAN CROCKETT: I found your presentation and the results extremely informative and the accuracy or the precision you were getting was fantastic. Did you say that you were using two tenths of a gram sample or a two-milligram sample?

AL ROBBAT: A half a gram.

ALAN CROCKETT: That's impressive just being able to sub-sample a jar of soil as repetitively as you've been able to. What's your preparation procedure for homogenization of soil that comes into your facility?

AL ROBBAT: These samples were all homogenized by EPA Region I. We didn't do anything more after we got them, except stir them up a little bit.

ALAN CROCKETT: How did they homogenize when you get them so homogeneous?

AL ROBBAT: Basically they screen them and then they collected them in a large jar and simply just rotated them. We did not do any of the real homogenization of the sample.

ALAN CROCKETT: What's the cost of the instrumentation by the way?

AL ROBBAT: I think it's about $180,000 but your best bet is to ask Bruckner Instruments.

JON GABRY: What are your power requirements for the unit?

AL ROBBAT: We use six 24-volt batteries. Six 24 volt batteries out in the site. We also can power-up at the site if there's electrical supply. So again, if you're interested in those types of details, I would suggest you visit the Bruckner Instruments booth.

RAPID DETERMINATION OF SEMIVOLATILE POLLUTANTS BY THERMAL EXTRACTION/GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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Abstract

There is considerable interest in rapid, field deployable analytical systems. Conventional gas chromatography/mass spectrometry analytical techniques provide sensitivity and specificity but require cumbersome solvent extractions. Thermal extraction offers a fast and safe alternative to classical extraction procedures for a wide range of semivolatile pollutants. In this technique samples are loaded into porous quartz crucibles with no preparation other than weighing required prior to analysis. Analytes are volatized into the helium carrier gas flow at controlled preprogrammable temperature profiles and subsequently cyrocondensed onto a conventional gas chromatographic column. The method was demonstrated by analyzing for a representative group of organic pollutants covering a wide range of polarity/volatility contained in natural soil matrices at concentrations as low as 0.5 ppm using a Pyran Thermal Chromatograph. Analyses were independently performed by three different laboratories (Institute for Environmental Studies, Louisiana State University; Engineering Toxicology, Texas A & M University, Ruska Laboratories, Inc.) using an on-line Finnigan Ion Trap Detector for identification and quantification.

Average correlation coefficients for calibration curves ranged from 0.938 to 0.997 for compounds less volatile than naphthalene. Naphthalene and more volatile compounds experienced variable losses during open-air sample loading. Dialkylphthalates underwent partial decomposition during the thermal extraction process. Recoveries varied depending on soil types as well as on the physical and chemical nature of analytes, with generally the highest thermal extraction yields for river silt and the lowest yields for clay. Typical recoveries were 10 to 30% for polynuclear aromatic hydrocarbons, 60 to 70% for hexachlorobenzene, and nearly 100% for chloronaphthalenes. However, the pesticide aldrin showed recoveries of at most 19%. A majority of the analytical results are within an accepted range for quantitative analysis. The Pyran system can be adapted to be

deployable. With sample turn-around times of typically 30-60 minutes this instrument should greatly facilitate remediation and hazardous waste cleanup efforts.

Introduction

Transportation, field deployable analytical systems that provide unambiguous data on the amount of semivolatile organic pollutants can aid in the rapid assessment and cleanup of hazardous waste sites. By complementing the Environmental Protection Agency's Control Laboratory Program through interactive field management, the efficient remediation of hazardous wastes sites can be accomplished (R. J. Bath, personal communication).

Mass spectometry provides the specificity and sensitivity necessary for the identification and quantification of most environmental pollutants. However, to introduce analytes into the mass spectrometer, the pollutants must first be extracted from the soils. Normally, organic solvents are used for this purpose, a cumbersome and labor intensive approach. Thermal extraction, in contrast, desorbs analytes from their matrices (soils) by controlled heating under conditions which avoids analyte decomposition (as opposed to pyrolysis). In this report, we describe results from a study aimed at verifying the suitability of thermal extraction as alternative to conventional extraction for a representative cross section of semivolatile organic pollutants. We establish the factors controlling analyte recoveries from different types of matrices. Three laboratories participated in this study, using identical instrumentation (Institute for Environmental Studies, Louisiana State University, Texas A & M University, College Station, and Ruska Laboratories, Inc., Houston).

Instrumentation

A Level 2 Thermal Chromatograph (Ruska Laboratories, Houston, Texas) was interfaced with a Finnigan Ion Trap Detector. Samples were heated in a quartz chamber using a linear temperature program and semivolatile analytes purged with helium gas. These analytes were cyrocondensed onto a fused silica chromatographic column (Hewlett Packard HP-5, 12 m x 0.2 mm) cooled with liquid carbon dioxide, separated, and identified by mass spectroscopy. Thermal extraction efficiencies for specific toxicants were also monitored by thermal extraction under identical conditions in an identical quartz chamber coupled to a flame ionization detector (Level 1 Thermal Extractor). Schematic diagrams of these instruments are shown in Fig. 1.

Other experimental parameters were chosen as follows: 30 ml/min He carrier flow during thermal extraction phase, 30:1 split ration between thermal extraction chamber and GC column, 1 ml/min carrier flow through GC column.

Standards Preparation

Test soils were prepared by adding stock solutions of 20 semivolatile organic pollutants covering a wide range of polarity/volatility to three different organic-lean natural soil matrices: kaolin clay, sandy river silt, and subsurface terrestrial soil from Livingston Parish, Louisiana containing 30% clay, 66% silt, and 4% sand with a total organic content of 0.11%. stock solutions of the 20 standards (see Table 1) were prepared by weighing pure

compound standards (primarily from Aldrich Chemical Co.) and diluting 4000 µg/ml stock standard (PP-HC8, Chem Service, Inc.; lot #25-121B) with dichloromethane to 20 ng/µl per component.

The three soils were crushed using a mortar and pestle and sieved through a 850 µm sieve. The sieved soils were slurried for 1 hour with the appropriate amount of stock standards (pure dichloromethane for controls), the solvent then removed at room temperature by evaporation under a fume hood to produce two sets of test soils with concentrations of 50 ppm and 0.5 ppm, respectively, per analyte. The soil standards were then sent to the three participating laboratories for independent analyses in well-filled teflon lined screw cap vials and stored at 6° to avoid analyte losses.

Methods

Soil samples were weighed into the porous fused silica crucibles, while standard stock solutions (20 ng/µl) were injected onto the porous fused silica lids of the sample crucibles using a 10 µl syringe just prior to loading into the thermal extraction chamber. All samples were heated from 30° to 260° at 30°/min and held isothermally at 260° for 10 min before cooling to 30°. The "trap" and "splitter" regions (see Fig. 1) were held isothermally at 300° and 310°, respectively; interface and transfer line temperatures to the MS were held between 280° and 290°. The column was held at 5° until the thermal extraction process was complete, the temperature programmed to 285° at 10°/min and kept isothermal for 5 min. Total cycle time was 59 min. The ion trap detector was scanned from 47 to 440 amu at 1 scan/sec, peak threshold was set at 2, and a mass defect of 100 mmu/100 amu was used. Full scan mass spectra of eluting compounds standards were verified using the NBS mass spectra library. Areas and retention times of characteristic ion masses were recorded after each run for each of the 20 compounds and internal standards. Calibration curves for each of the 20 compounds in the stock solution (20 ng/µl) were obtained by injecting 2, 5, 10, 15 and 20 µl onto the crucible lids (corresponding to 40, 100, 200, 300, and 400 ng/component, respectively). Ten µl (200 ng/component) of the deuterated internal standards (Table 2) were also added to the lid prior to each of the above five runs. This experiment was done in triplicate at Ruska Laboratories, using a Finnigan Ion Trap Detector for two runs as described above and a Hewlett Packard Mass Selective Detector (MSD) once for comparison. Just prior to each run of the standard soils (10.0 to 13.8 mg for the 50 ppm standards and approx. 100 mg for the 0.5 ppm standards), 10 ul (200 ng/component) of the deuterated internal standards were injected into the soil/sediment. Response factors (RF) and percent relative standard deviations (%RSD) were calculated for each compound based on EPA's "Test Methods for Evaluating Solid Waste, Physical, Chemical Methods", SW-846, Third Edition, Method 8270 (GC-MS for semivolatile organics, capillary column technique). RF values are based upon the results of the on-lid injections of the stock solutions.

Soil/sediment samples were also analyzed using the Level 1- FID instrument (see Fig. 1) to further

eludicate the thermal extraction process in an independent study at Louisiana State University. This set of experiments seeks to identify factors influencing analyte recoveries by systematically varying operator-controllable variables including gas flow rates, additives to facilitate extraction, extraction temperature and duration; as well as to define limiting factors for target analytes and matrices. Three analyte solutions were prepared: n-triacontane ("C-30"), pyrene, and hexachlorobenzene ("HCB"). These compounds were chosen for their thermal stabilities and chemical inertness. Two are structurally similar, all three are neutral and devoid of reactive functionalites. Ten µl of stock solutions in dichloromethane (10 mg/ml for pyrene, HCB; 2 mg/ml for C-30) were spiked onto the soils immediately prior to analysis. The resulting FID signals were integrated to calculate analyte recoveries (Table 3), with the FID signal of the pure analytes (no matrix) as reference.

Conclusions

Level 1 Thermal Extraction/FID

Thermal extraction efficiencies vary considerably with the nature of analytes as well as matrices (Table 3). While conventional solvent extraction procedures would be expected to produce similarly high recoveries for n-triacontane, pyrene, and hexachlorobenzene, thermal extraction produced markedly different results for clay as matrix (Fig. 2a). HCB recoveries were quantitative, while C-30 and pyrene recoveries ranged at approx. 30%. Variation of the matrix had a less pronounced effect on the recovery of pyrene. These results cannot be explained solely in terms of polarity or volatility. Not surprisingly, percent deviations of recovery decrease dramatically in the presence of a soil matrix (Fig. 2b). The increase of helium flow during the thermal extraction process from 40 to 100 ml/min did not increase the extraction yields of C-30 significantly (see Table 3); however, addition of polar additives to the soil samples immediately before thermal extraction, such as water or phosphoric acid, improved the recovery of pyrene from clay markedly (Fig. 3c). Figure 2d illustrates blockage of reactive sites of the soil matrices by repeated spiking of the same river silt sample. Thermal extraction efficiences increased from 25 to 65%. Simple physical obstruction of the carrer gas flow is certainly one of the factors contributing to reduced recoveries. The soil samples "cake" and block the desorption of analytes into the carrer gas flow. Thus, recoveries sank to 69% for pyrene and to 82% for C-30 when standards were spiked onto the lids of crucibles filled with 100 mg clay without direct contact between analyte and matrix (Table 2). Repeated thermal extraction, the increase of extraction temperatures above 450°, or an extension of extraction times were not promising, as illustrated by Fig. 4a-c. These figures compare the thermal desorption of identical amounts of pyrene (100 ng) from a porous quartz crucible (Fig. 4a) and spiked into a kaolinite clay sample (Fig. Figure 4b) using the temperature profile shown in Fig. 4c under otherwise identical conditions. Not only is the thermal desorption of the standard from the spiked clay considerable below 100%, but it is also shifted to higher temperatures. At 450°, no further analyte was released upon prolonged heating. The fate of the unextracted

analytes is currently unknown and subject to future investigations.

Level 2 Thermal Extraction/GC/MS

The results of analyses from all three laboratories are summarized in Table 1. The 20 organic compounds and corresponding characteristic ion masses are listed along with linear correlation coefficients (r) derived from the five point calibration curves of the on-lid stock solution injections. Fig. 3 shows examples of four calibration curves from one laboratory; the more volatile components (e.g. naphthalene) experience variable rates of evaporation after injection of the standard stock solution onto the porous quartz crucible lids prior to sample insertion into the pyrocell (approx. 2 min from injection onto the lid until sample loading). Dioctyl phthalate signals were relatively low except at high concentration levels (300-400 ng); after it appears that much of this compound degraded to phthalic anhydride (which was always detected) during the on-lid calibration runs. Diethyl phthalate, in comparison, showed good linearity and less degradation. Pentachlorophenol linearity was not as good as that of other compounds in the same volatility range. All other compounds showed good linearity.

Also listed in Table 1 are the percent relative standard deviations (%RSD) of calculated response factors based on the on-lid injections of 20 ng/µl mix of 20 compounds plus the deuterated internal standards listed in Table 2. Since %RSD values are also a measure of the precision for each compound, it is not surprising that most volatile compounds also show the highest deviations. Although there is some variation between the participating laboratories, specific compounds tend to yield high %RSD values while others showed consistently good precision. The same holds for deuterated standards. Again, the more volatile naphthalene-d8 and dichlorobenzene-d4 showed the most variation, phenanthrene-d10 and chrysene-d12 the least.

From the obtained data set, recoveries could be calculated either by the external standard method using the least square fits of the five point calibration curves for all compounds or, alternatively, by internal standard quantitation based on the response factors calculated for each compounds. Table 1 lists results for both methods, which do not reflect the expected improved accuracy for the internal standard method. Due to the considerably different chemical and physical environments the standards experience while being partially adsorbed by the soil samples and partially by the porous crucibles, no high degree of accuracy can be expected by the internal standard method. The implicit assumption made in conventional chromatography, namely that standards and analytes are subjected to identical environments, cannot easily be realized in thermal extraction.

Percent recovery appears to be dependent on a number of factors including polarity, molecular weight, and interactions with constituents of the soil matrix, both organic and inorganic. Not surprisingly, recovery was significantly greater for many compounds from the river silt than from the clay or subsurface soils (e.g., phenanthrene: 11% from clay and 31% from silt) while chloronaphthalene was close to 100% for both clay and silt. The

recovery of diphenylamine was equally low (approx. 5%) for clay and silt. Since the subsurface soil contains about 30% clay, percent recovery is generally in between those for clay and silt. It is interesting to compare recoveries for the structurally similar tricyclic compounds dibenzothiophene, fluorene, and carbazole. In all three soil types the order of recovery efficiency was dibenzothiophene>fluorene>carbazole, which likely reflects increasing binding to the soil matrix. At the 0.5 ppm concentration levels, naphthalene, chloronaphthalene, fluorene, hexachlorobenzene, dibenzothiophene, phenanthrene, aldrin, and pyrene were all detected in the soil standards in at least two of the three laboratories.

It is apparent from these results that small aliquots of soils can be analyzed by thermal extraction/GC/MS without any prior sample preparation. While the method is generally suited for situations requiring high precision or low detection limits, it performs well a analyte concentrations>50 ppm, is amenable to full automation and will serve for rapid screening of soils contaminated with thermally stable organic semivolatiles, a class of compounds that includes PNA's PCB's, most petroleum products and pesticides and is commonly encountered in hazardous waste cleanup efforts.

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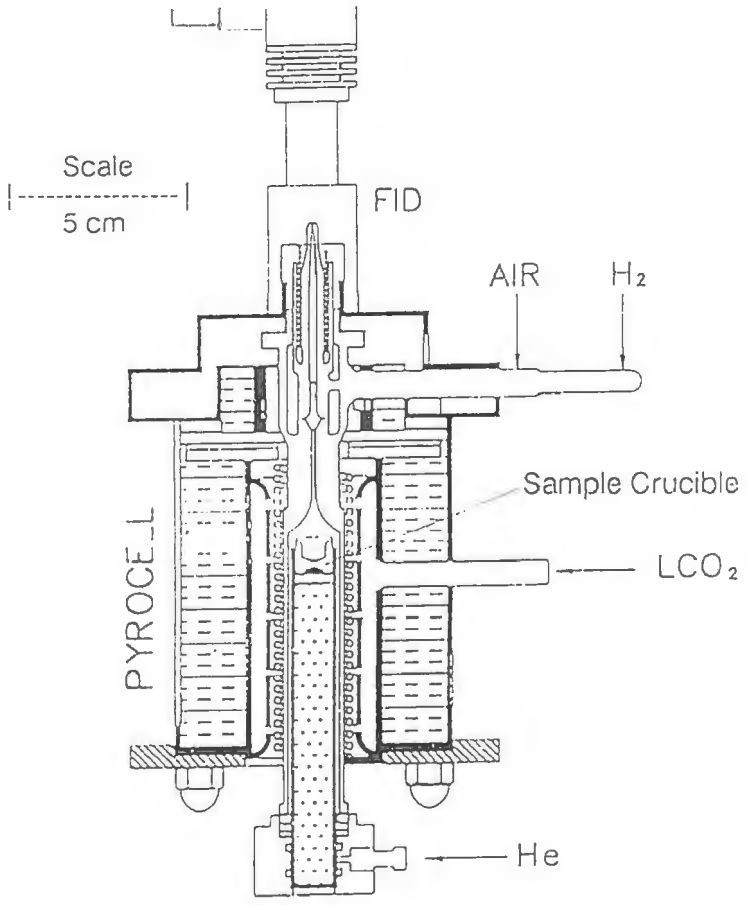
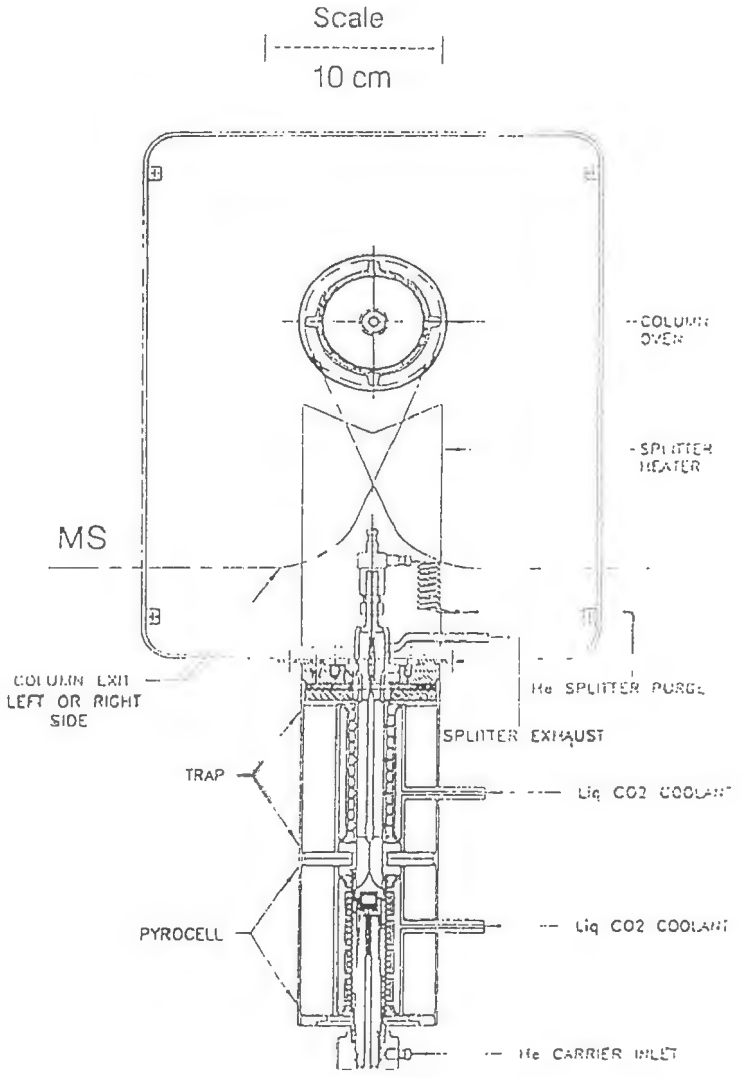
Acknowledgements

We thank Drs. R.J. Bath and D. Flory for helpful comments and suggestions.



LEVEL I-FID ANALYZER



TC ANALYZER

Figure 1

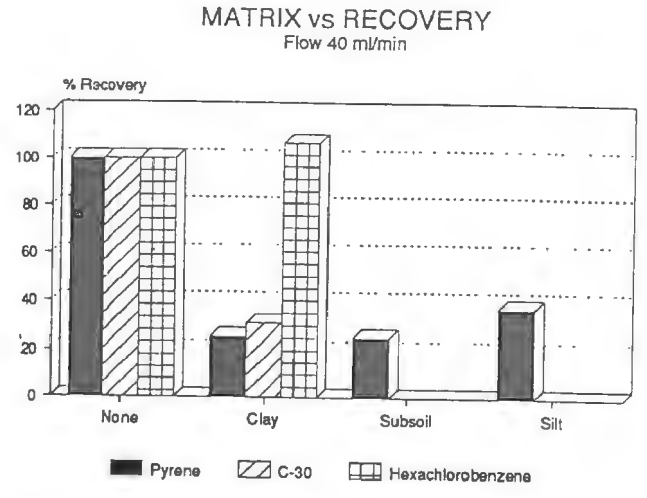


Fig 2a

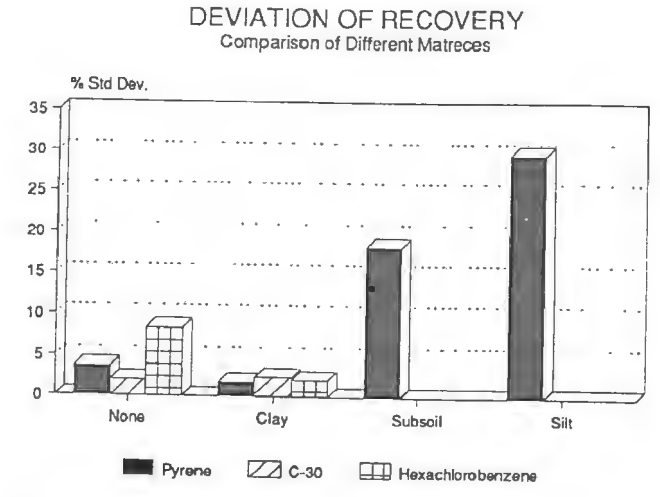


Fig. 2b

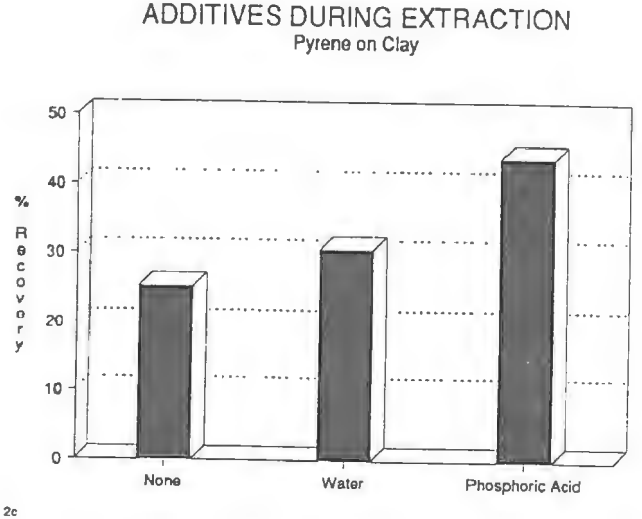


Fig 2c

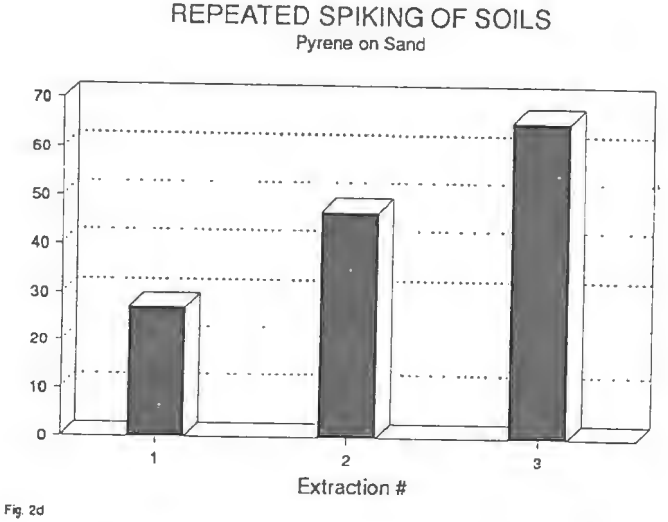


Fig. 2d

NAPHTHALENE

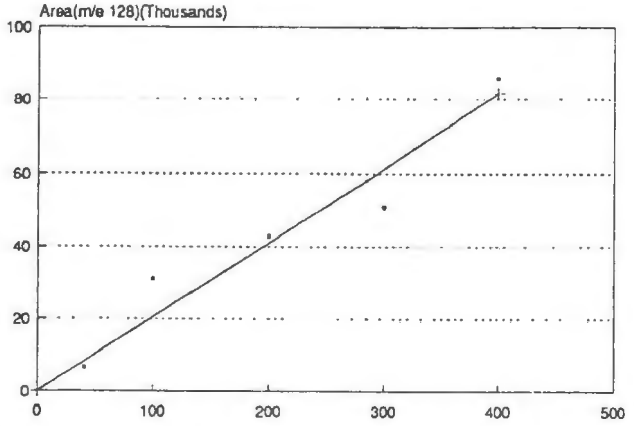


Fig. 3a

HEXACHLOROBENZENE

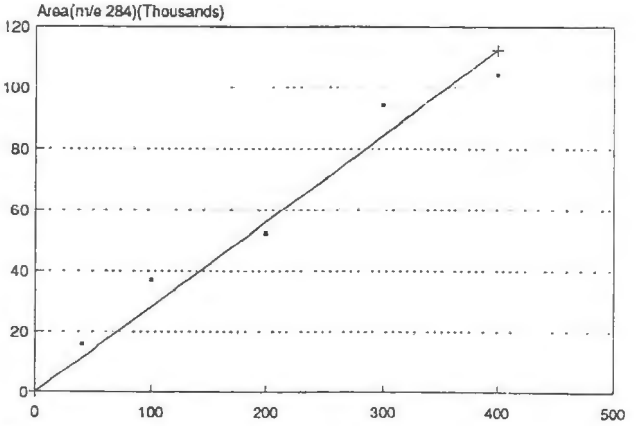


Fig. 3b

PHENANTHRENE

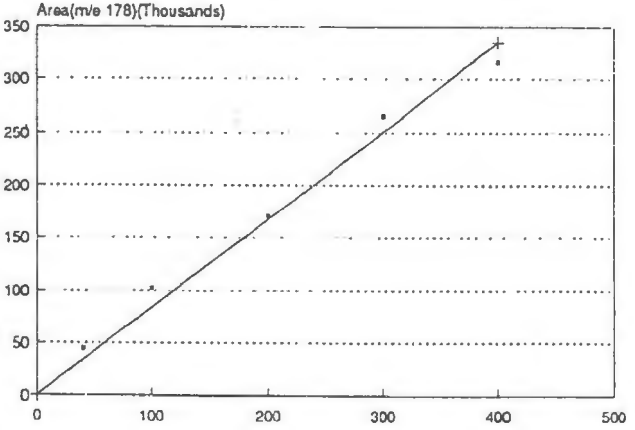


Fig. 3c

BENZO(A)PYRENE

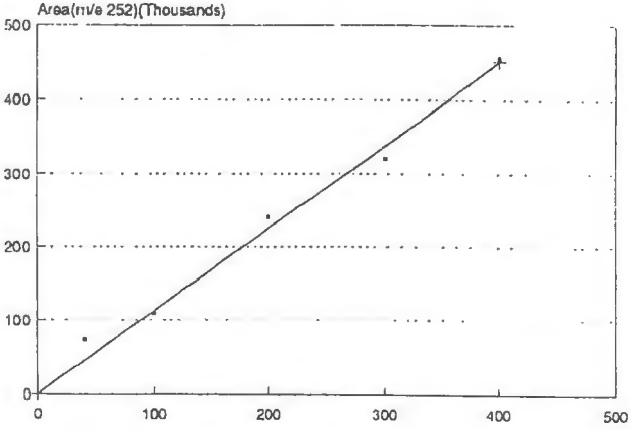


Fig. 3d

TABLE 1. Precision of semi -volatile standard calibration curves and percent recovery

									% RECOVERY 2 50 PPM STANDARDS												% RECOVERY 4		
	QUAN	MEAN	MEAN 1	%RSD OF RF 2					CLAY				SILT				SUBSOIL						
COMPOUND	MASS (m/z)	r 5	%RSD	RL			TAM	LSU	RL	TAM	LSU	AVE	RL	TAM	LSU	AVE	RL	TAM	LSU	AVE	CLAY	SILT	SOIL
2-chlorophenol	128	0.9152	110	147	73	-	34	-	15	46	-	30	19	25	-	22	2	-	-	2			
4-methylphenol	107	0.9481	85	96	76	-	84	-	8	10	11	10	8	6	6	77	9	8	4	7			
2,4-dichlorophenol	162	0.8962	67	78	50	78	68	64	9	26	33	23	23	23	15	20	25	44	9	26			
naphthalene	128	0.7484	66	88	35	59	43	103	60	100	72	77'	93	128	138	120'	27	41	121	63'	33	93	67
4-chloro-3-methylphenol	107	0.9708	29	27	26	27	19	46	7	11	9	9	14	12	9	12	9	15	4	9			
1-chloronaphthalene	162	0.9385	23	29	6	22	22	35	69	77	141	96'	83	118	109	103'	61	78	-	70'			
2,4-dinitrotoluene	165	0.9848	26	18	41	16	24	31	10	6	4	7	11	12	7	10	10	16	4	10			
fluorene	166	0.9887	14	10	9	24	8	22	4	15	9	9'	28	31	17	25'	12	27	18	19'	34	55	45
diethylphthalate	149	0.9717	34	14	66	14	10	60	-	-	-	-	-	-	-	-	-	-	-	-			
diphenylamine	169	0.9801	20	21	32	14	8	25	8	3	5	5	8	4	5	6	8	7	4	6			
hexachlorobenzene	284	0.9901	10	6	7	4	22	9	71	76	57	68'	71	67	54	64'	58	78	103	80'			
dibenzothiophene	184	0.9946	7	7	3	4	15	5	12	28	19	20'	40	39	26	35'	32	53	66	50'			
pentachlorophenol	266	0.9537	44	51	56	28	28	56	-	-	-	-	-	-	-	-	-	-	-	-			
phenanthrene	178	0.9943	8	8	3	5	19	7	8	13	12	11'	36	33	23	31'	28	47	46	40'	50	78	85
carbazole	167	0.9932	10	11	11	5	13	11	4	3	4	4	10	7	6	8	8	12	7	9			
aldrin	66	0.9924	11	8	4	5	29	8	2	3	4	3	23	20	15	19'	11	21	13	15			
pyrene	202	0.9971	7	7	3	8	14	5	4	12	5	7	20	24	13	19'	11	32	17	20	35	66	52
bis(2-ethylhexyl)phthalate	149		-	-	-	-	53	-	-	-	-	-	-	-	-	-	-	-	-	-			
benzo(k)fluoranthene	252	0.9922	38	26	19	39	38	70	10	1	1	4	14	7	7	9	10	18	4	11	3	15	10
benzo(a)pyrene	252	0.9931	37	38	10	36	38	64	9	1	1	4	14	5	6	8	10	20	2	11	2	14	9

1 Based on 25 on-lid injections; 4 different instruments; 3 different laboratories. 40 to 400 ng per component per injection.

2 Response factors (RF) and percent relative standard deviation (%RSD) were calculated based on EPA method 8270 of SW-846; i.e.: RF: (area quan mass compound) (ng deut. internal standard)/ (area quan mass of deut. std.) (ng compound) %RSD = 100 (SD/RF)

3 Percent theoretical recovery based upon linearity of lid injections (slope and y-intercept) and not on deuterated internal standards spiked into soil. Average of 9 replicates (about 10mg soil 50 ppm per component); 3 different instruments at 3 different laboratories

4 Based on deuterated internal standards spiked directly on soil and corresponding RF values; only PNAs are compared due to the chemical similarities with the standards.

5 Average linear correlation coefficient for the on-lid five point calibration from three different laboratories.

These compounds were also detected from the 0.5 ppm standards in at least 2 of the 3 laboratories.

TABLE 2

Variations of Internal Standard Areas

Deuterated Internal Standards	Quan. Mass	Mean %S	Ruska	Ruska	Ruska	TAMU	LSU
.1,4-dichlorobenzene-d4	152	106	75	155	139	73	89
naphthalene-d8	136	57	41	74	70	43	57
acenaphthene-d10	164	17	7	22	13	10	32
phenanthrene-d10	188	8	6	9	11	6	8
chrysene-d12	240	7	6	11	11	3	4
perylene-d12	264	34	43	38	26	19	45

* Values are based on 25 on-lid injections recorded at 3 different laboratories; 200 ng/component, injection.

TABLE 3

Evaluation of Thermal Extraction on Pyran Level1

Exp#	Analyte	Amt(ug)	Matrix	He ml/min	No.of Obs.	Avg	%Dev	%Rec
1	pyrene	100	none	40	3	2837.3	3.7	100.0
2	pyrene	100	clay	40	3	717.0	1.8	25.3
3	pyrene	100	subsoil	40	3	716.3	18.3	25.2
4	pyrene	100	r.silt	40	3	1063.0	29.7	37.5
5	C-30	20	none	40	3	1101.0	1.4	100.0
6	C-30	20	clay	40	3	341.0	18.5	31.0
7	C-30	20	none	100	3	1241.3	2.0	100.0
8	C-30	20	clay	100	3	396.7	2.4	32.0
9	HCB	100	none	40	3	613.7	8.4	100.0
10	HCB	100	clay	40	3	667.7	2.1	108.8
Addition of phosphoric acid, 85%, 0.1 ml								
11	pyrene	100	r.silt	40	2	1246.5	18.1	43.9
Addition of water, 0.2 ml								
12	pyrene	100	clay	40	1	868.0		30.6
Standards on lid of crucible filled with soil								
13	pyrene	100	clay	40	1	1984.0		69.9
14	C-30	20	clay	100	3	1018.7	4.7	82.1
Repeated spiking of previously extracted soil								
					Extr.#			
15	pyrene	100	r.silt	40	1	768.0		27.1
16	pyrene	100	r.silt	40	1	1330.0		46.9
17	pyrene	100	r.silt	40	1	1860.0		65.6

C-30: n-triacontane
HCB: hexachlorobenzene

DISCUSSION

AL ROBBAT: Have you tried looking at organic extracts? Can you place an organic extract in the soil and look at the thermal desorption properties? In other words, take the soil, extract it with methylene chloride, taken out of part of the extraction, and run your experiment?

THOMAS JUNK: In other words, you introduce an organic extract that has been extracted in a conventional procedure to see how that behaves in the instrument itself? I'm not quite sure that I understand your question.

AL ROBBAT: We found the same thing. For example, for PAHs, if you take the thermal desorption sample probe and place it directly over the soil, you get between 7% and 15% extraction recoveries. What I'm suggesting is that if you use the simple 2 mL extraction procedure that I described, take a half a gram of soil, add 2 mLs of methylene chloride, extract it, add that extract to your cell, can you perform that experiment? Can you use say, 10 µls or 20 µls of extract in your cell. Have you tried that experiment?

THOMAS JUNK: Yes, you can. You can use a conventional extract and absorb it onto the porous quartz crucible. In order words you could go through the addition of a small amount of solvent into the soils that would then by and large produce a similar effect as the one you just mentioned.

AL ROBBAT: Right.

THOMAS JUNK: Yes, we've tried that. And in some cases it produces satisfactory results. However we have not consistently found an improvement over classic extraction procedures. I think I can cover that together with the addition of various cold solvents that I just mentioned, such as with phosphoric acid or water. And yes, we do see an increase, bu the increase for phosphoric acid for example, was much more significant than that for other cold solvents.

STEPHEN BILLETS: I want to say from the standpoint of testing this technology that Ruska Thermal Extraction System is in the EMSL-Las Vegas Laboratory currently undergoing evaluation for possible use in a field demonstration study. So we are conducting, in our laboratory, a complementary effort to what Thomas described.

THE APPLICATION OF A MOBILE ION TRAP MASS SPECTROMETER SYSTEM TO ENVIRONMENTAL SCREENING AND MONITORING

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ABSTRACT

This paper presents examples of the use of a mobile Ion Trap Mass Spectrometer (ITMS, Finnigan MAT) for on-site environmental screening and monitoring of vapors by gas chromatography/mass spectrometry (GC/MS). The instrument is built around a miniaturized ITMS system, with a novel direct vapor sampling inlet and coupled to a high speed transfer line GC column (short capillary column with fixed pressure drop). The column is temperature controlled inside the standard ion trap transfer line housing. This provides for high speed analyses at 10-60 s intervals using an automated sampling system constructed with only inert materials in the sample path.

Specific laboratory and field applications exemplify key characteristics of the system including sensitivity, specificity for a broad range of compounds, ruggedness for field testing in harsh environments, and general speed and versatility of the analytical technique. The system has been calibrated for alkylbenzenes at concentrations as low as 4 ppb in air and used to monitor these compounds in an office space. Both the MINITMASS and a simpler Ion Trap Detector (ITD) based system have been used to monitor organic vapors from acetone through 5 ring polycyclic aromatic hydrocarbons produced in laboratory scale reactors for studying the thermal desorption and incineration of hazardous wastes. The ruggedness of the MINITMASS system has been demonstrated by vapor sampling in the Utah summer desert and at a 600 MW coal fired power plant. Finally, the analysis speed and versatility are described for vapor monitoring of volatile organic compounds at an EPA national priority list waste site.

INTRODUCTION

Preliminary data obtained with a miniaturized Ion Trap Mass Spectrometer (MINITMASS) system developed in close collaboration with the manufacturer (Finnigan MAT Corp.) were presented at the first International Symposium on Field Screening Methods for Hazardous Waste Site Investigations (1). The MINITMASS system was shown to be capable of performing tandem MS (MS^n) analyses in electron ionization (EI) as well as chemical ionization (CI) mode and featured a special air sampling inlet in combination with so-called "transfer line gas chromatography" capability (2,3). Due to its relatively low weight (approx. 280 lbs.), the MINITMASS system was readily transported inside a small mobile laboratory mounted on a regular 3/4 ton pick-up truck (1). Some of the main shortcomings of the MINITMASS system included: insufficient sensitivity (high ppb/low ppm range), limited mobility for many field screening applications (due to a shock sensitive turbomolecular pump), untested performance with low volatile (e.g., PAH type) compounds and lack of field test data at actual hazardous waste sites.

Since October 1988 the MINITMASS system has been tested under a variety of conditions at several outdoor as well as indoor locations. Moreover, several hardware and software improvements have markedly increased its sensitivity (currently ~1 ppb for alkylbenzenes (3)) and applicability to low volatile compounds (e.g., 3-5 ring PAH's (4)) while enabling true mobility through the installation of a more rugged vacuum pump. In addition, a simplified mobile ITD (Ion Trap Detector) system was constructed and tested for dedicated hazardous waste combustion applications which do not require MS^n

capabilities (5,6). Hazardous waste related monitoring applications of both systems will be described in the following paragraphs. Some of these results have been presented elsewhere (2-6) but are included with various new data for completeness in this overview of the instrument's current performance.

EXPERIMENTAL

General Parameters

The direct atmospheric vapor sampling inlet described in detail elsewhere (2,5,6), consists of three concentric tubes with appropriate flow control plumbing and electronics. The inlet system is made from deactivated fused silica, quartz and glass, or glass-lined metal tubing. The sample path contains no moving parts. When sampling, the gas is exposed to the column inlet for a controlled period of time (0.3 to 2 s) while 30 to 200 μL of sample is admitted to the column. Helium carrier gas flow is then restored for the rest of the sampling cycle and GC separation of the sample takes place.

This inlet is coupled to a 1 m long fused silica capillary column which enables nominal GC separation of components and provides a pressure drop between the near-ambient sampling environment and the high vacuum of the mass spectrometer ion source. With the fixed pressure drop, the chromatographic conditions are controlled primarily by column length, radius and temperature (2). The fused silica capillary column used in this work was either a 0.15 mm ID x 1.2 μm methyl silicone film (CP-Sil-5 CB, Chrompak) with 1.5-2 ml/min He flow or a 0.18 mm ID x 0.4 μm film DB-5 (J&W Scientific) with ca. 4 ml/min He flow.

This transfer line GC inlet system was used with both a regular Finnigan MAT ITD and the MINITMASS system with axial modulation and tandem MS capabilities (1), although this paper describes results from use in only the single MS mode. In addition to these special capabilities, the MINITMASS system permitted higher flow rates by virtue of the axial modulation feature and was thus the only system which could use the 0.18 mm ID column. The combination of increased MS resolution and increased flow rates resulted in higher sensitivity.

Field Testing

In field tests sponsored by the EPA, vapor standards were diluted into a 5 m long x 2.5 cm ID glass and Teflon® manifold with a 2.2 l s^{-1} total flow. These standards included both 50 ppm compressed gas mixtures and equilibrium headspace vapors of pure compounds injected into the manifold with a motor driven syringe pump. The 50 ppm gas standards were diluted to calibration mixtures of 20 to 350 parts per billion (ppb) in air, while the syringe pump produced mixtures ranging from 16 ppb to over 10 ppm, depending on the compound vapor pressure, syringe diameter and motor speed.

Vapor standard calibration data were obtained scanning from m/z 45 or 50 to 200 at 4 scans s^{-1}. The inlet and transfer line were maintained at 25°C, while the ion trap was maintained at 85°C. The temperature of the mixing chamber was ambient and not controlled. The vapor inlet drew up to 120 ml min^{-1} from the EPA vapor manifold. A .5 s vapor sample pulse was frequently used, although the EPA experiments involved varying the sample time from 330 ms to 2.5 s with a routine pulse width of 715 ms.

Combustion Monitoring

Exhaust from a rotary kiln simulator was monitored for gas phase hydrocarbons during the combustion of polymeric medical supplies (6). The 11 g batch samples were loaded into the kiln and incinerated at 600°C. Rapid on-line analyses were obtained using the unmodified ITD system. A sample flow of 25 to 50 ml min^{-1} was drawn from the kiln exhaust gases in a transition area preceding the afterburner. Vapor samples were taken at 10 s intervals to monitor concentration transients during sample combustion. The .15 mm ID column was used in this system at a constant temperature of 30°C or 82°C with the vapor inlet at 60 or 100°C, and the mass spectrometer was scanned from m/z 35 to 120 or 50 to 148 at 4 scans s^{-1}. Exhaust from a thermal bed reactor for hazardous waste studies (7) was monitored using the MINITMASS during thermal desorption of polycyclic aromatic hydrocarbons (PAHs) from contaminated soils obtained at former coal gas plant sites (4). The soils were heated to 400°C under a radiant heater with a preheated nitrogen flow of .5 l min^{-1} above the bed of soil. The exhaust gas was sampled at 60 s intervals with 2 s vapor sampling pulses. The inlet was operated between 150 and 175°C and the transfer line was maintained at 125°C. The separation was performed in the .18 mm ID column specified above. The ion trap manifold was 200°C and the MS was scanned from m/z 100-300 at 4 scans s^{-1}.

RESULTS AND DISCUSSION

Sensitivity and Dynamic Range

The basic objective of vapor sampling short column gas chromatography is to provide sufficient separation of the

organic compounds of interest from the major atmospheric constituents to allow optimum use of the sensitivity, specificity and speed of the detector. The sensitivity of the MINITMASS system utilizing this principle is demonstrated by the analysis of toluene vapor in air in Figure 1. This figure shows ion chromatograms for six repetitive samples of toluene in air at a concentration of 16 parts per billion (ppb, volume or molar ratio). The sampling points are indicated in the total ion chromatogram (TIC) of Figure 1a by the baseline depressions at 25 second intervals. The short pulses of air, ca. 70 µl in 0.7 s, suppress the baseline by overloading the ion trap with air ions so that even background ions in the MS are not detected. However, the well resolved toluene peaks elute from the short column 20 s later with excellent sensitivity and signal to noise (s/n) as indicated by the selected ion chromatogram of summed ion peaks at m/z 91 and 92 shown in Figure 1b.

In addition to this 16 ppb data, Table 1 presents a set of calibration points for toluene showing the degree of sample repeatability expressed as relative standard deviation. For statistical reasons, a minimum of 5 consecutive vapor samples were taken at each concentration. These concentrations were prepared via the syringe pump method described above, and response was measured via the peak area of the m/z 91 trace from a .715 s vapor sample. A linear fit to the full set of data points was obtained with the correlation coefficient R = .998, indicating a linear dynamic range of 3 or more orders of magnitude.

A practical application of alkylbenzene analysis is shown in Figure 2 using the thin film column (0.4 µm rather than 1.2 µm used in Figure 1). Figure 2 presents two ion chromatogram traces from indoor atmospheric sampling in one of our office work areas. The m/z 91 trace clearly shows peaks for toluene, ethylbenzene, m- and p-xylene and o-xylene. The estimated toluene concentration is 70 ppb, presumably derived from the glue used on the recently installed ceiling tiles. The MINITMASS system, with its axial modulation capability and the higher flow of the .18 mm ID column has shown alkylbenzene detection limits near 1 ppb with a s/n greater than 2. The normal ITD-based system, limited to the 1.5 ml/min of the .15 mm ID column, has shown detection limits of approximately 20 ppb.

Speed and Selectivity

An example of the GC/MS vapor analysis of a 7 component standard gas mixture is shown in the partial chromatograms of Figure 3. Figure 3a shows the total ion chromatogram (TIC) while the concurrent selected ion chromatogram profiles show the major ions from four of the test compounds. Arrows in the TIC profile indicate the beginning points for 3 subsequent 715 ms samples with a 30 second sampling interval. Although the 1,1,1-trichloroethane (111TCA) and benzene peaks are not completely resolved in the TIC, they are readily quantitated based on the selected ions from their unique mass spectra. Note that the small vinyl chloride peaks at scan numbers 5, 125 and 245 are partially cut off by the large air pulse baseline disturbances from which they are incompletely separated. However, even this early eluting compound had a reproducible, linear response curve over the range of 20 to 350 ppb which we tested. In other words, the limited resolution of the short GC column is sufficient to greatly enhance the specificity and selectivity of the mass spectrometer.

A major asset of the speed of short column GC/MS is the ability to do on-line monitoring in a nearly real-time mode. Figure 4 shows a set of chromatograms monitoring the evolution of volatile organics from the combustion of polypropylene materials in a rotary kiln simulator (6). For these experiments the ITD system with the .15 mm ID, thick film (1.2 µm) column sampled gases just prior to the afterburner. A 0.5 s sampling every 10 s with the column at 82 C was sufficient to follow the transient concentrations of aromatics during the 2 min experiment. Selected ion traces at m/z 78 and 91 show the specific benzene and toluene peaks in the repetitive analyses. Figure 4b explicitly plots the quantitated evolution curves obtained from peak areas of selected ions for benzene, toluene, phenol and styrene. With the column at 30°C, compounds as small as acetone were separated from air with benzene eluting at 7s. The peak concentrations of these hydrocarbons occurred before and after the point at which the melting plastic was totally engulfed in flame in the 600 C rotary kiln simulator.

Figure 5 illustrates the high boiling range of compounds which can benefit from the speed and selectivity of short column GC/MS in an analysis of polycyclic aromatic hydrocarbon (PAH) vapors during thermal treatment of a contaminated soil (4). By elevating the temperature of the thin film column to 125 C, compounds with boiling points ranging from 218 to 340 C were readily analyzed with a 60 s sampling internal. The numbered peaks in the TIC represent 1) naphthalene, 2) methylnaphthalenes, 3) C_2 naphthalenes, 4) fluorene, 5) phenanthrene and 6) anthracene. Although the GC resolution was insufficient to separate some of these isomers, the selected ion chromatograms show the obvious benefits. In Figure 4b the m/z 154 trace shows a prominent peak for biphenyl with additional unresolved humps for fragments from

larger compounds. The m/z 168 trace indicates that the short column is able to resolve the methylbiphenyls (at 12 s) from the dominant dibenzofuran peak (at 14 s). The m/z 184 trace shows separate peaks for the C_4 naphthalenes at 22 s, dibenzothiophene at 37 s, and ions associated with the intense phenanthrene (m/z 178) peak.

Instrument Ruggedness

Although the commercial versions of both the ITD and ITMS instruments were designed principally for stationary laboratory operation, the modified ITMS, which was built around a normal ITD chassis, has held up well under the rigors of harsh transportation and environmental operating conditions. Two examples of applications in particularly harsh environments include the Utah summer desert and flue gas sampling from a coal fired 600 MW power plant.

The desert testing was the maiden use of the system to discover potential field problems. It involved operation of the instrument in the mobile lab on the back of a 3/4 ton pickup truck to sample various chemical vapors released from a permanent dissemination line (1). The instrument was severely bumped and jostled as we maneuvered the truck to sample in the shifting winds on the brush covered terrain. Operation was complicated at the time by the necessity of venting and then restarting the instrument before and after each move to avoid a turbomolecular pump crash. Typical down time was approximately one hour between data acquisitions, including cool down and warm up. Despite the rigorous handling, the instrument's only failure during the 2 weeks of testing was an overrated power transistor which had previously failed in normal lab operation on a different ITMS. The turbomolecular pump has recently been replaced with a more rugged model to allow true "mobile" use in addition to "transportable" operation but has not yet been rigorously tested in the "mobile" mode.

The flue gas sampling involved rolling the MINITMASS instrument to a seventh floor site at a Utah Power and Light Company 600 MW coal fired power plant. The objective was to do on-line analysis for aromatic hydrocarbons in the 350 C flue gas as it exited the main boiler sections. No organics were observed in the 1.5% excess oxygen combustion products although our on-site detection limits were 4 and 10 ppb for alkyl benzenes and alkylnaphthalenes respectively. However, simply operating the instrument was a major accomplishment in this harsh environment. Fly ash was continuously raining in the ambient atmosphere from the overhead structures; the whole work site was constantly rocking and rumbling; and the ambient temperature ranged from ca. 4 to 35 C (40 to 95 F). A makeshift plastic tent with a crude window fan and filter was assembled over the instrument to supply some measure of environmental control (in addition to the chassis mounted fans and filters).

A recent example of the instrument's more "routine" transportability was demonstrated in EPA testing in New Jersey. The MINITMASS system was successfully driven across the country in its mobile lab and brought into operation with verified performance capability within 6 hours after arrival at the national priority list (NPL) landfill site. This start up time included transferring the instrument from the mobile lab to the EPA site trailer and diagnosis and repair of a broken thermocouple. Operation in the mobile lab itself had previously been verified in less than 1 hour.

Versatility of Inlet Sampling

One of the unique features of our vapor sampling inlet is the ability to readily vary the sample volume injected onto the column by a simple change in the sample pulse width. Figure 6 shows calibration data for toluene from a gas standard sampled with a 495 ms pulse compared to the typical 715 ms sampling. The linear regression lines along with 95% confidence intervals are shown for each of the two data sets. The shorter sampling pulse has very similar repeatability with the smaller response slope corresponding directly to the smaller sample and reduction in pulse time within 4%. Figure 7 also demonstrates the linearity of mean peak area response versus sample pulse width for two different series of gas mixtures. The lower concentration data are from the analysis of an "unknown" gas mixture (ca. 30 ppb of the gas standard shown in Figure 3) which was run with 2.5 s sampling to maximize sensitivity for the later eluting compounds. The high concentration data was a test of increasing GC resolution for the overlapping peaks dichloromethane (DCM), 1,2-dichloroethane (12DCE) and 1,1-dichloroethane (11DCA) in a gas mixture standard by decreasing the pulse width to 330 ms. The combined data sets demonstrate excellent linearity over an eightfold change in sample size.

Figure 8 illustrates the effect of sampling duration on resolution and sensitivity. The same mixture of DCM, 12DCE, 11DCA and tetrachloromethane at 350 ppb each is used in 8a with a sampling time of 330 ms and in 8b with a time of 715 ms. Clearly the 330 ms time improves the resolution of the early eluting compounds, but comparison of the m/z 82 selected ion trace indicates that the tetrachloromethane which elutes at 7 s has only 70% of the peak height obtained at 715 ms. For detection of compounds at the lowest levels, peak height

becomes the limiting factor as the ion counts must exceed the noise threshold.

Another aspect of the vapor sampling performance of our inlet is the ability to readily sample from atmospheres at different ambient pressure and limited small total volume. Most of the EPA testing involved sampling standard gas mixtures from a high flow manifold operating at reduced pressure conditions similar to those which might exist in a system drawing samples from many separate remote points on a fence line. However, at the end of this series of experiments, several Tedlar bag samples were also analyzed. In order to maximize the number of separate samples from a single 1 liter Tedlar bag, the total sample drawn into our inlet was reduced from 120 ml/min to 25 ml/min. One of the gas mixture standards was then diluted to 2.5 ppm in a Tedlar bag and our duplicate analysis of it showed responses within 4% of perfect linearity for the manifold calibration lines.

Figure 9 shows the total ion chromatograms for the analysis of landfill wellhead vapors from the NPL site which were sampled into Tedlar bags and diluted by 1/5 with clean air. The identified compounds from these two analyses are listed in Table 2 with detected concentrations for those previously calibrated.

CONCLUSIONS

The results presented here have demonstrated MINITMASS performance in several key areas of capability which might be expected from an on-site, vapor sampling, short column GC/MS system based on an ion trap mass spectrometer. These include specifically: detection limits of less than 10 ppb for a variety of volatile organic compounds; selective analysis of 21 compounds or more in a single one minute chromatogram with boiling point windows depending on column type and temperature; repetitive sampling as frequent as each 10 s for monitoring transient vapor concentrations; and direct variation of sample size with sample pulse time to readily optimize GC resolution versus ultimate sensitivity. The examples of operation in harsh environments and at remote sites further suggest that the instrument is rugged enough for most field screening and hazardous waste site investigations. These specific capabilities also apply to a similarly equipped standard ITD system except for the order of magnitude sensitivity difference with the ITMS enhancement. Although the MINITMASS has the additional advantages of capabilities for MS^n and truly mobile operation as compared to the ITD described here, many applications do not require tandem MS and the more rugged turbo could be user installed. However, the main advantage of the standard ITD for vapor sampling GC/MS is its high sensitivity in a commercially available instrument. Coupling the vapor inlet to bench top MS such as the ITD or a Hewlett Packard MSD is also a much more economical way to get transportable GC/MS into a field screening, stack monitoring or even process control application than the prototype MINITMASS.

This paper also suggests the need for further development in associated areas of field testing instrumentation. Foremost are the advantages in compound range and analysis speed which could be gained by broader temperature range operation and temperature programming for the transfer line column. Second is the capability for rapid on-line enrichment in case of more dilute target compounds or less sensitive detectors. And finally, there is the need for continuing development in all aspects of miniaturization (size, weight, power requirements) and ruggedization of fieldable GC/MS systems.

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Table 1

Concentration (ppb)	Peak Area	RSD %
16	227	14
161	1430	3.4
245	2540	1.0
9450	86530	1.7

Table 2
Tedlar Bag Samples of NPL Site Wellhead Vapors

Scan No.[1]	Compound[2]	Concentration (ppb)	
		I-4 (1/5)	I-6 (1/5)[3]
8	11DCE	85	--
9	DCM	480	42
21	12DCA	94	210
26	Benzene	340	15
36	Trichloroethene		--
46	Cyclooctane		--
48	Chlorocyclopentene		
55	Cyclooctane		t
60	Cyclooctane		--
68	Toluene	30,000	1,500
72	Cyclooctane		t
91	Cyclooctane		t
102	Perchloroethene	430	--
165	Ethylbenzene	1300	82
179	m,p-Xylene	3900	270
210	Styrene		
217	o-Xylene	800	75
396	C_3-benzene		--
430	C_3-benzene		--
460	C_3-benzene		--
490	C_3-benzene		--

[1] Scan number corresponding to chromatograms in Figure 9. This number divided by four equals retention time in seconds.

[2] Positive identification for standard compounds which were used in EPA testing while others are tentative, e.g. cyclooctanes could be octenes.

[3] Compounds in I-4 but not seen in I-6 indicated by dashes while t indicates traces detected.

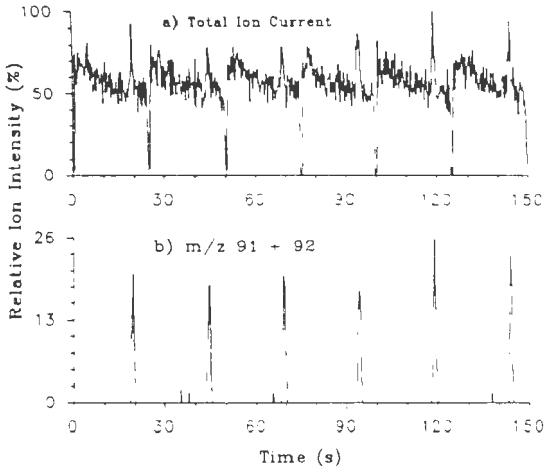

Figure 1. (a) Total ion chromatogram for 6 repetitive samplings of a 16 ppb toluene vapor standard. The points of injection can be identified by the suppression of the baseline. (b) A selected ion trace of m/z 91 and 92 for the same 6 samples. The threshold setting of the MS prohibits exact calculation of the signal to noise ratio, but it appears to be 8 to 1 based on height, and >20 to 1 based on area. Adapted from reference 2.

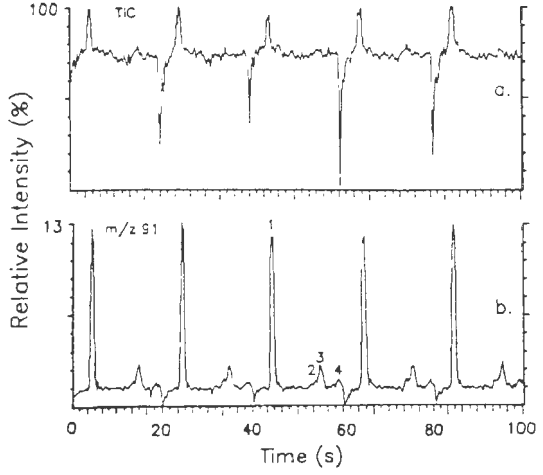

Figure 2. Repetitive sampling of background levels of alkylbenzenes in a room with a recently tiled ceiling. Labelled compounds in (b) the selected ion trace for m/z 91 are: 1) toluene; 2) ethylbenzene, 3) m,p-xylenes and 4) o-xylene.

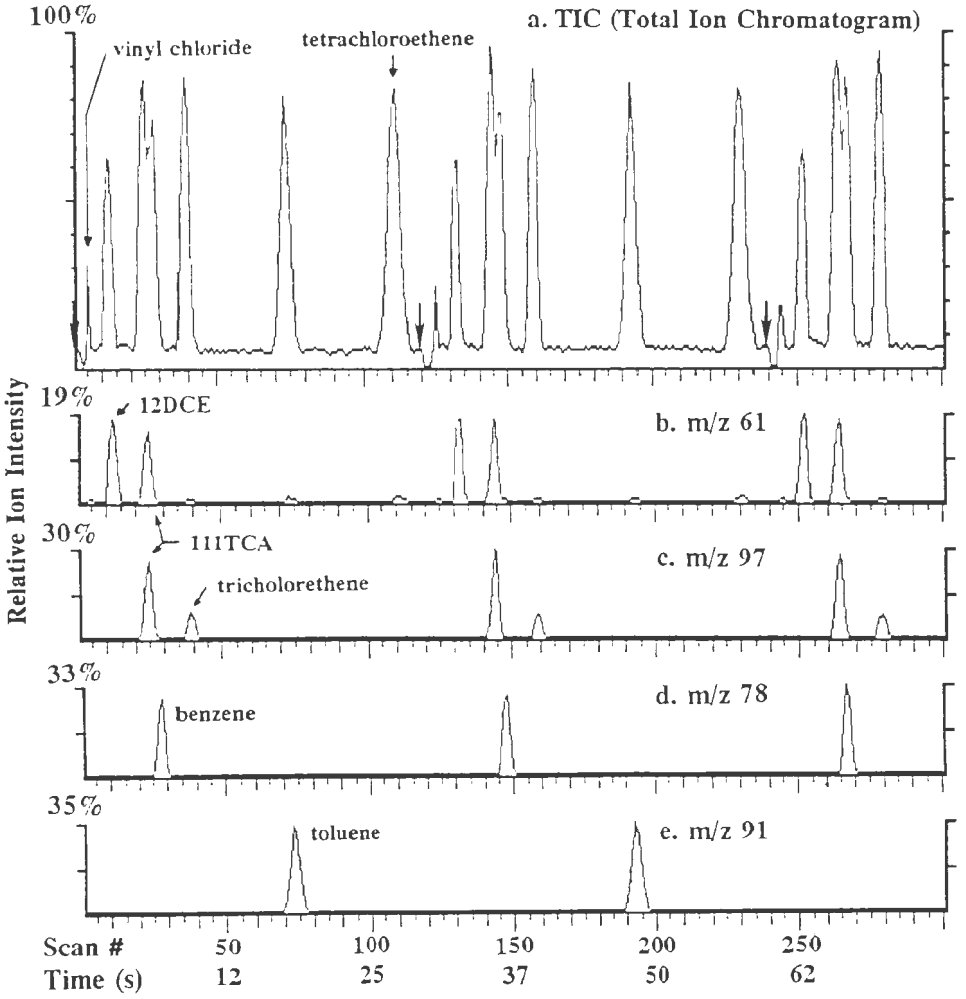

Figure 3. Example analysis of a 7 component gas mixture at 350 ppb showing 3 repetitive samplings at 30 s intervals in a) total ion chromatogram and selected ion chromatograms for quantitation of b) 12DCE, c) 111TCA, d) benzene and e) toluene. Note presence of ions m/z 61 from vinyl chloride, 111TCA, and trichloroethene and m/z 97 from trichloroethene that do not interfere with quantitation because of chromatographic separation.

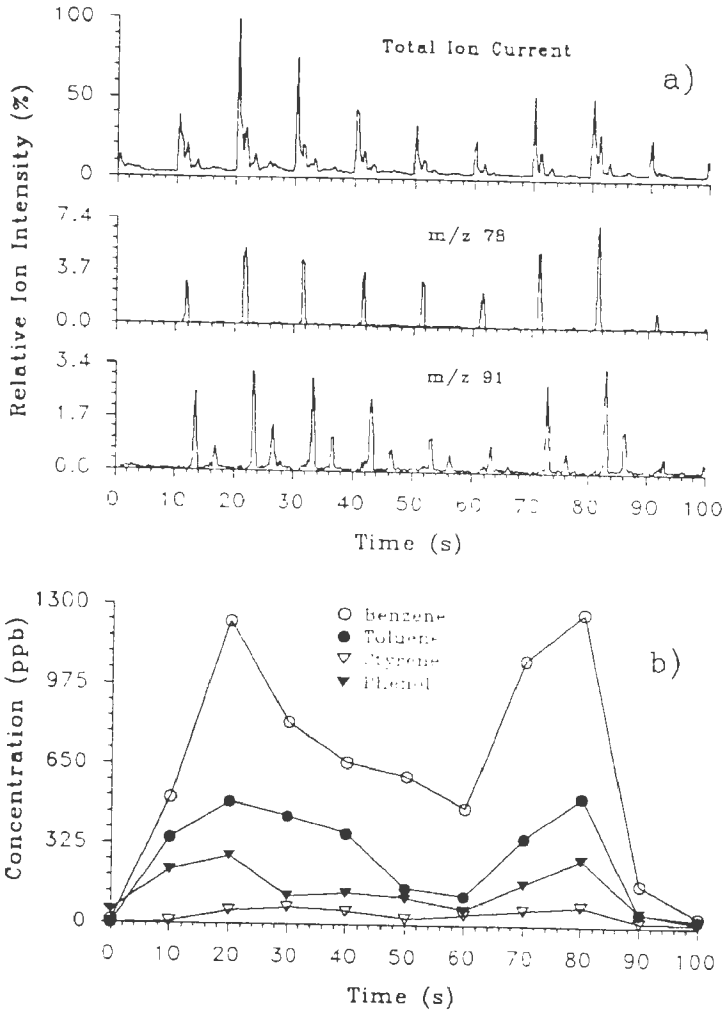

Figure 4. (a) Ion profiles for a sequence of vapor samples taken during the combustion of 11 g of polypropylene materials in a laboratory scale rotary kiln simulator. The ion m/z 78 is due to benzene, while m/z 91 indicates first toluene, and then partially resolved ethyleenzene and xylene isomers as in Fig. 2. (b) Concentration profiles in parts per billion (ppb) for 4 compounds obtained from the integrated peak areas of selected ions 78, 91, 104 and 94 for benzene, toluene, styrene and phenol respectively. Adapted from reference 2.

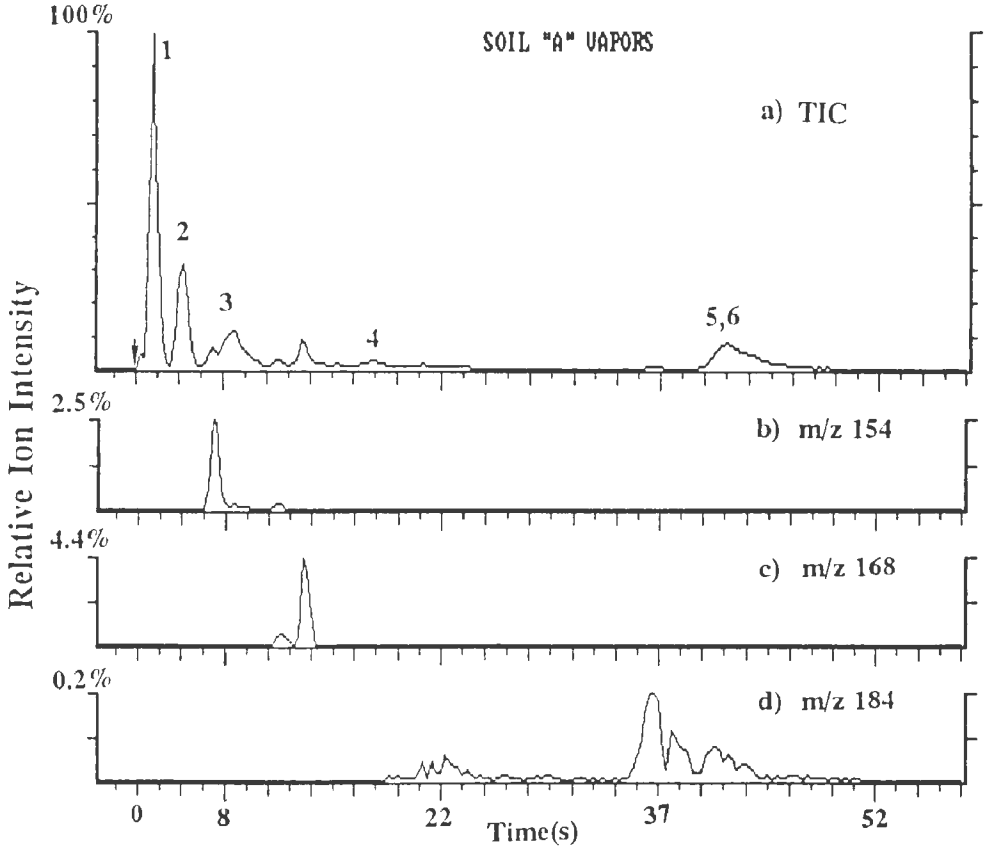

Figure 5. On-line vapor sampling GC/MS analysis during a 400 C thermal desorption of a contaminated soil. Chromatograms of the total and selected ion signals are shown for the vapor sample taken 12 min into run. PAHs labeled in the TIC trace: 1) naphthalene, 2) methylnaphthalenes, 3) C_2 naphthalenes, 4) fluorene, and 5,6) unresolved phenanthrene and anthracene. Additional compounds indicated as prominent peaks in the selected ion traces are: biphenyl, m/z 154; dibenzofuran, m/z 168; and dibenzothiophene, m/z 184. Adapted from ref. 4.

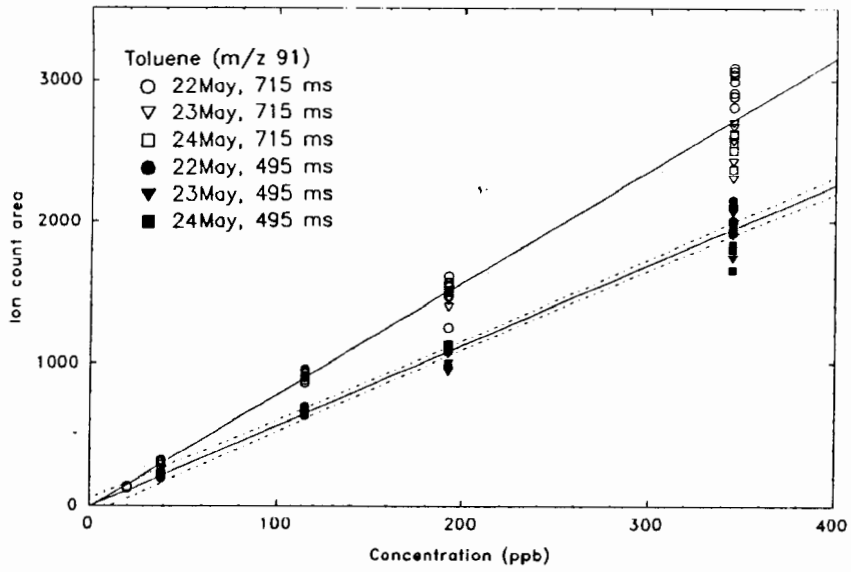

Figure 6. Comparison of toluene calibration data from 715 ms and 495 ms pulse width sampling. These standard concentrations were diluted from a 50 ppm in air compressed gas mixture. Note that the spread of individual data points comprises three separate days of system operation.

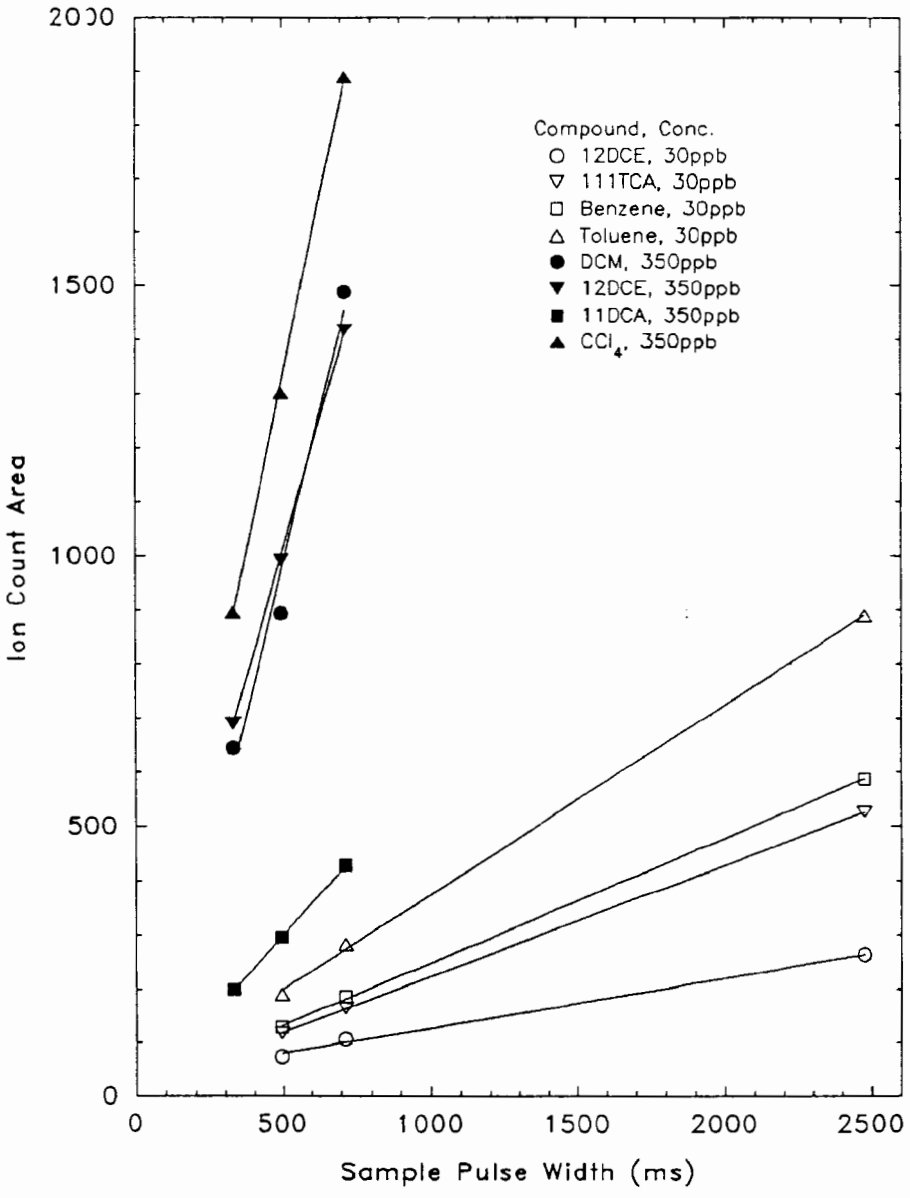

Figure 7. Mean peak area response versus sample pulse width data for one gas mixture at ca. 30 ppb and another at 350 ppb.

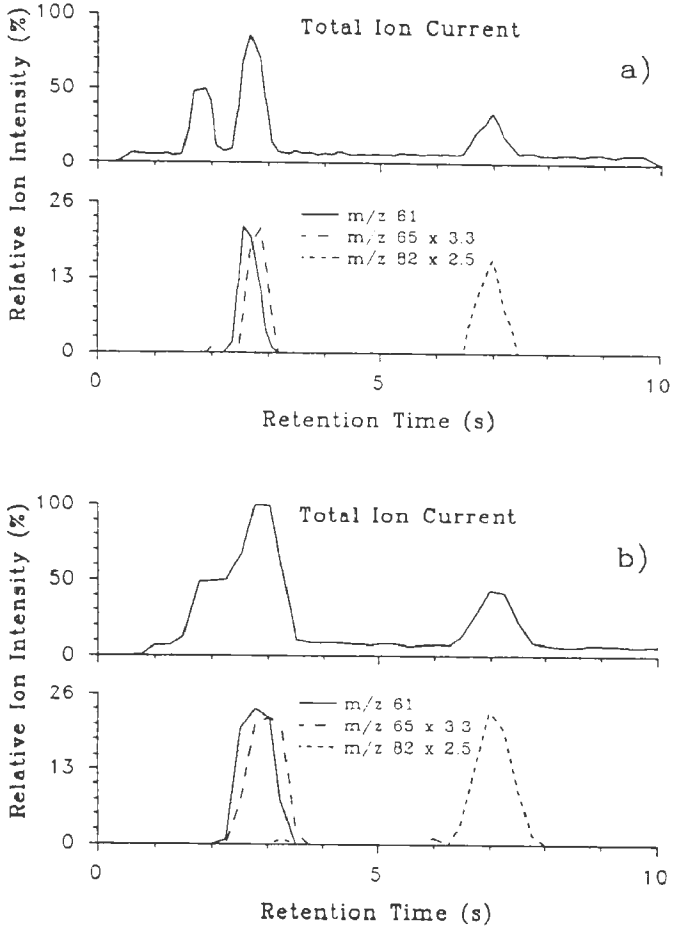

Figure 8. Ion profiles showing the effect of sampling time on chromatographic resolution and sensitivity. (a) was obtained from a 330 ms vapor sample and shows the separation of dichloromethane (the first peak) from the complex of 1,2 dichloroethene (m/z 61) and 1,1 dichloroethane (m/z 65). Separating these latter two compounds may be possible with even shorter sample pulses. The ion profiles in (b) were obtained at 715 ms and illustrate the relationship between sample duration and sensitivity. The m/z 82 (tetrachloromethane) trace has a 50% increase in peak height which correlates to absolute sensitivity of the instrument. Adapted from reference 2.

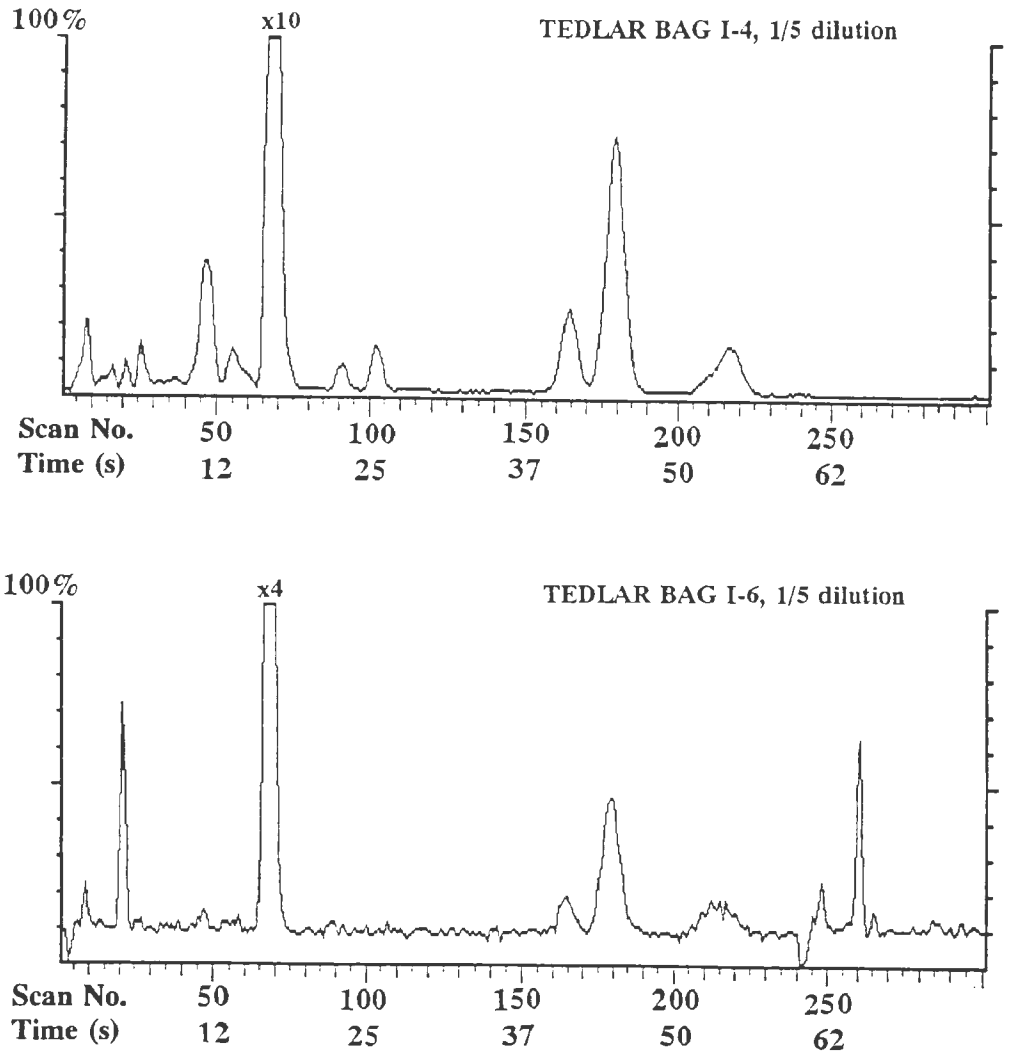

Figure 9. Total ion chromatograms from analysis of 1/5 dilution Tedlar bag samples from NPL landfill site injection wells I-4 and I-6.

DISCUSSION

MAHADEVA SINHA: In all your slides when you talk about sensitivity, I couldn't get a good feeling. How did you find your detection limit of sensitivity of 1 ppb or 10 ppb?

WILLIAM McCLENNEN: Basically it is a matter of looking at peak areas that we're doing quantitation on. Routinely we would compare the peak area of any peak we could find at the retention time we were looking at to any background peak in that vicinity or another area of the chromatogram. So the one picture I put into the paper that will accompany the proceedings of this will show a 16 ppb toluene peak with virtually no baseline. There is, I think, three little blips on the baseline. We estimated that there are signal to noises, at least the factor of 20 or more. So basically it's a matter of looking at any discernable peak, any disruption of the baseline noise in the area of the retention time that we're identifying the compound.

MAHADEVA SINHA: Toluene works very good because you have almost the base peak for the entire mass spectrum there. Other peaks are pretty small. But when you get the mass spectrum itself, do you just identify the peak itself, one parent peak, or the complete mass spectrum of that?

WILLIAM McCLENNEN: The mass spectrum. Typically we take data with a full scan, so we can look at all the ions that we would typically expect. And we can compare them to library spectra or spectra that we know.

MAHADEVA SINHA: What if I change that compound and go to, let's say, carbon tet or a diehloroethylene, what becomes your sensitivity at that point?

WILLIAM McCLENNEN: Again, that's where I've hedged a little bit. For compounds that do not show one nice peak or one nice fragment ion or molecular ion we have a slightly lower detection limit. All of our quantitation for the results I've shown you has been on single ions, not trying to combine several ions. But we still have detection limits for the chlorinated compounds that I showed. We were still looking at standards that were less than 20 ppb and getting good spectra for them.

FIELD MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS BY ION TRAP MASS SPECTROMETRY

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ABSTRACT

We have developed a second generation transportable gas chromatograph/ion trap detector (GC/ITD) for the *in-situ* characterization of chemical waste sites. This instrument is extensively based on commercial instrumentation and can be used for field analysis of volatile organic compounds (VOCs) in soil and water. A purge and trap GC is used for sampling and separation of VOCs from the environmental matrix before their introduction to the ion trap detector for mass spectral analysis. A secondary microprocessor controls the sampling and GC hardware in parallel with the ion trap detector, which in turn is controlled by the host PC. The analysis of water samples is demonstrated by using surrogate samples spiked with the 24 VOCs contained in the Supelco A & B Purgeable Standards, acetone, methyl ethyl ketone, and methyl isobutyl ketone. Our first transportable GC/ITD was demonstrated at a chemical waste site for the analysis of volatile organic compounds in soil [1]. The second generation instrument incorporates significant improvements in several areas and is nearly ready for field deployment. This instrument has been extensively characterized in the laboratory. In these tests, we have found anomalies in quantitation that might arise during field use. Once these problems - which may occur with any ion trap based field instrument - are resolved, the second generation GC/ITD will be tested and demonstrated in the field. The second generation transportable GC/ITD will be described in this manuscript. Some comparisons will be made to the first generation instrument where appropriate.

INTRODUCTION

We describe and compare two modular field-deployable gas chromatograph/ion trap detector systems for characterization of hazardous waste sites. Extraction of the analyte from the matrix occurs in the *sampling module*. Although the sampling module could be readily adapted for extraction of volatile organic compounds from air [2], the focus of this work has been soil and water analysis. A separations module, i.e., a gas chromatograph, provides separation of the extracted VOCs. A Finnigan MAT ion trap detector (ITD) provides a simple and reliable mass analyzer on which to base field instrumentation [3]. The ITD serves as a universal *detection module*. A turn-key operating system has been developed for this instrument. This operating system, which incorporates additional hardware and software, allows the instrument to be operated by personnel with minimal technical background. Because the instrument operates under nearly full computer control, very little operator interaction is required. The first generation instrument (GC/ITD-1) was developed using a purge and trap gas chromatograph built in our laboratory; commercially available equipment was used wherever possible in the second generation transportable instrument (GC/ITD-2).

EXPERIMENTAL

Ion Trap Detector

The ion trap detector was used in conventional fashion and without modification in GC/ITD-2. An SRI Instruments 8610 gas chromatograph was connected directly to the ITD transfer line. Electron impact ionization was used with the Finnigan Version 4.10 software with automatic gain control (AGC) [4]. The Finnigan Programmer's Option Package was used to generate FORTH subroutines and keystroke sequences. The ion trap was tuned using perfluorotributylamine (FC-43) as a tuning and mass calibration standard with the automated tuning procedures contained in the ITD software.

A schematic diagram of GC/ITD-2 is shown in Figure 1. Automation software consists of the host interface

software, the extended FORTH Finnigan ITD software, and keystroke sequences (i.e., macros) added to the ITD software. The SRI Model 8690 purge and trap device and Model 8610 gas chromatograph are controlled via the Microstar Laboratories DAP 1200/4 data acquisition processor. In this fashion, all components required for the second-generation transportable GC/ITD are readily and inexpensively available.

Although no special considerations were given to reducing the size, weight, and power requirements of GC/ITD-2, it easily fits into the back of a 4X4 vehicle and can be generator powered. GC/ITD-2 is self-contained in a housing approximately 60 cm on each side. This housing contains the gas chromatograph, ion trap detector, sampling system, and a 6.8-l cylinder of ultrapure helium. The mechanical backing pump for the ion trap vacuum system was mounted next to the housing. The instrument weighs ca. 80 kg and requires less than 1.5 KVA of power.

Modifications of the Finnigan ion trap were required for use in GC/ITD-1. The conductance-limiting interelectrode spacers and the open-split interface were eliminated. A wide-bore capillary column was directly coupled to the ion trap and the standard 50 l s^{-1} turbomolecular pump was replaced with a 240 l s^{-1} pump to maintain the ion trap at the proper pressure with the higher gas load imposed by the direct coupled column. A system based on the Hitachi HD637B05ZOF microprocessor was designed and built to control the sampling and chromatographic hardware.

Surrogates and Samples

Water standards and surrogates were prepared by adding the Purgeable Mixture A (200 µg ml^{-1} of each of 13 VOCs) and Purgeable Mixture B (200 µg ml^{-1} of each of 11 VOCs) (Supelco, catalog nos. 4-8851 and 4-8852, respectively) to HPLC grade water (J.T. Baker). Aqueous solutions of acetone, 2-butanone (methyl ethyl ketone), and 4-methyl-2-pentanone (methyl isobutyl ketone) were also prepared and added at the appropriate concentration. Standards at 1 part-per-million (ppm), 100 part-per-billion (ppb), 10 ppb, and 1 ppb concentrations were prepared by dilution of a stock solution containing the A & B Purgeables and three ketones at the 2 ppm level. Standard solutions were refrigerated to prevent evaporation of the VOCs. Fresh stock solutions and standards were prepared at approximately 3 day intervals. Fluorobenzene was used as an internal standard at the 32 ppb level in the aqueous standards and surrogates. A 10 ppm standard of fluorobenzene (Aldrich) in reagent grade methanol was prepared and used as the spike solution. Water, methanol, and the fluorobenzene/methanol solution were periodically analyzed with GC/ITD-2 as a check for impurities.

Purge and Trap Chromatography

For water analysis, a 5 ml aliquot of the standard or surrogate was loaded into a Pyrex glass tube (12.5 cm length by 16 mm i.d.). The sample was heated to 80°C during purging with helium at a flow rate of 60 ml min^{-1}. Sample recovery under these purge conditions is shown in Figure 2. Trap effluent during the purge cycle is diverted away from the analytical column and vented.

After the sample purge, the adsorbent trap (50/50 Graphpak GB and Chromosorb W) was ballistically heated to 375°C from ambient temperature at a rate of 1800°C min^{-1} and flushed with helium at the carrier flow rate of 3 ml min^{-1} (carrier gas velocity 21 cm s^{-1}). The analytical column is a "VOCOL" fused silica capillary column (30 m length by 0.53 mm i.d.) with a 3.0 µm film (Supelco, cat no. 2-5320M). The oven temperature for the chromatography column was held at 30°C during the purge cycle. Following heating of the adsorbent trap, the oven temperature was ramped at 20°C min^{-1} to 40°C, held for 1 minute, then ramped at 4°C min to a final temperature of 150°C. The adsorbent trap is continually flushed with helium during the chromatographic run; the chromatographic oven is heated to 250°C for system cleanout after data acquisition.

RESULTS

A list of the volatile organic compounds used in these studies (the A & B purgeables and ketones) and the reconstructed ion chromatogram (RIC) from the purge and trap analysis of 5 ml of water containing 100 ppb of these 27 compounds is shown in Figure 3. Working calibration curves from 1 ppb to 100 ppb of 1,1,2-trichloroethane in 5 ml of water are shown in Figure 4. The value of the average slope of these three lines is 0.82 +/- 0.02 and the correlation coefficient for these data is 1.00. This calibration curve was obtained using the Finnigan Automatic Gain Control (AGC) software. The use of the automatic gain control does not in itself ensure that the ion trap will not operate under space-charge conditions. At higher sample concentrations (microgram levels) the AGC should be manually tuned to prevent mass spectral degradation due to space-charging. Although the calibration curve for 1,1,2-trichloroethane is quite good, calibration curves for other compounds can exhibit non-linearity, especially at lower concentration levels. For these compounds, relative sensitivity factors will vary as a function of concentration as shown in Figure 5. This non-linearity can be partly explained by the occurrence of ion/molecule reactions of analyte molecules with ions from water (H_2O^+, H_3O^+) and methanol (CH_3O^+, CH_3OH^+, and others). In the AGC mode, the Finnigan ion trap detector is pre-programmed (in the instrument's firmware) to store all ions above m/z 20 (ionization DAC value of 125). However, water ions below m/z 20 can remain in the ion trap during and after ionization and are able to react with analyte ions

during the analysis sequence. A plot of relative intensity of H_3O^+ ions (m/z 19) as a function of the mass storage level during ionization is shown in Figure 6. These data were obtained with a Finnigan Ion Trap Mass Spectrometer (ITMS), which does allow the operator to select the storage level (DAC value) during ionization. With the Finnigan ITD, the storage level during ionization is fixed in the AGC mode (i.e., it is not user adjustable) and it is likely that the non-linearities displayed in Figure 5 will be observed with any purge and trap GC/ITD system. It is also possible for analyte ions to react with neutral water and methanol molecules. The creation of protonated water molecules, H_3O^+, via reactions of analyte ions (shown in the upper chromatogram) with water background in the ion trap detector, is demonstrated in Figure 7. We estimate water loss during our purge cycle to be about 1-2 mg min^{-1}. Moisture may either adsorb or simply condense on interior surfaces of the sampling system and subsequently be introduced to the ion trap during trap desorption. It is important to remember here that nanogram levels of analyte are being measured and that seemingly insignificant amounts of moisture in the ion trap (for example, water introduced by venting the instrument to transport it from one area to another) can affect the reliability of quantitation. An effective solution to this problem will require modification of the ITD. We are presently developing methodologies to reduce the ion/molecule chemistry that occurs in GC/ITD-2. These new techniques should improve response linearity for most of the VOCs in this study.

The chromatographic retention times obtained with GC/ITD-2 are very reproducible. Table 1 shows the precision of retention times for several compounds at concentration levels from 1 pbb to 100 ppb. We have found that changes in retention time are often accompanied by changes in mass spectral peak distribution and intensity. However, because of the excellent retention time reproducibility shown here, retention time measurement of the internal standard (fluorobenzene) can be a readily observed metric of performance during field analysis and provides a real-time check on instrument performance. A retention time control chart is shown in Figure 8. The three out-of-control points occurred following scheduled power outages in our laboratory.

Compounds are identified on the basis of their chromatographic retention time *and* their experimentally obtained mass spectrum via an automated identification routine. Mass spectral library matches are highly accurate on a "first-hit" basis for nearly all compounds in the A & B Purgeable and ketone mixture with GC/ITD-2. Exceptions are toluene and those compounds that coelute from the chromatograph (1,1-dichloroethylene and methylene chloride; benzene and 1,2-dichloroethane). Coeluting compounds can often be identified with some mass spectral interpretation. At this time, this capability is not programmed into our automated library search routines and, in fact, such interpretation might be better left to those reviewing the data after the field work is completed. Table 2 shows the accuracy of library matches with GC/ITD-2. The "ID Hit" is the rank of the correct compound identification in a list of the 10 most probable compounds selected by the library search routine. The purity value provides an indication of how closely related the sample mass spectrum is to the library spectrum on a scale of 0 - 1000. A purity of 800 or higher implies a very good match between the two. Even though some of the identifications shown in Table 2 do not have high purity values, the purity values obtained so far have been quite reproducible. This reproducibility provides a means to screen library search data for consistency. For example, *cis*-1,3-dichloropropene is identified on a "second-hit" with a purity value of about 400. If an analysis of an unknown mixture were to identify a compound as *cis*-1,3-dichloropropene with a significantly higher purity value, say 800, that identification might be suspect even though the purity value suggests otherwise. In general, we have found that the number of "first-hit" identified compounds is higher with GC/ITD-2 than with GC/ITD-1. This is most likely due to better regulation of the helium buffer gas partial pressure in GC/ITD-2 where the conductance limiting spacers are used and the ion trap is coupled to the chromatography column via the open-split interface.

DISCUSSION

The design of this transportable instrument, coupled with the flexible control system provided by the Microstar Laboratories DAP1200 data acquisition processor, is well suited to problems in field analysis. The ability to address and control ancillary instruments, such as sampling devices, via the host computer provides great flexibility for different analytical problems. Keystroke sequences can provide customized data reduction procedures for different applications.

The combination of the data acquisition processor, Forth interface software, and Forth keystroke sequences added to the ITD software allow the instrument to be operated in a turnkey fashion. That is, in the intended mode of operation for the transportable GC/ITD, the operator only needs to select the appropriate operational procedures from the menu. Figure 9 shows the menu by which the instrument is controlled. Once selected, each item proceeds automatically. For example, one can choose to calibrate the instrument ("Trap Setup") or to generate an analytical report ("Quantitation"). If "Acquisition" is selected from the menu, a sub-menu is displayed to provide optional analysis procedures, e.g., to analyze for a suite of VOCs in soil or to monitor a single compound in groundwater.

At this time, an analysis with GC/ITD-2 requires about 60 minutes. We have recently purchased the SRI

Model 8680 Purge and Trap Device; that device should allow us to significantly reduce the analysis time required by GC/ITD-2. Detection limits with GC/ITD-2 have not been determined. These limits cannot be reliably estimated until the quantitation anomalies described above are resolved. The response of GC/ITD-2 to many compounds at the 1 ppb level is quite good and we expect that detection limits will be below the part-per-billion level for laboratory standards. However, it is quite likely that the ultimate detection limits for the instrument will be limited by the nature of the sample in the field.

The gas chromatograph/ion trap detector (GC/ITD) configuration described here has other advantages over commercially available transportable gas chromatograph/quadrupole mass spectrometers [5]. Ion trap detectors are inherently simple. The ion trap does not suffer from the complexity added by external ion sources and ion lenses. The ion trap electrode assembly is small and rugged although the radio-frequency and power transformers, gas supplies, data system, and other equipment can offset the size advantage. When operated as an ion trap detector (that is, as a simple single-stage mass analyzer), no direct current (dc) potentials are applied to the trap electrodes. Without dc potentials applied to the trap electrodes, charging phenomena are minimized as the electrodes become dirty. Another advantage derives from the inherently high sensitivity of the ion trap detector. The ITD is roughly 10 to 100 times more sensitive than a conventional transmission quadrupole [6]. This sensitivity advantage can be pushed even further with the addition of axial modulation to the ion trap [7]. Finally, the ion trap can provide mass spectrometry/mass spectrometry capabilities (MS/MS) [8] far more simply than tandem quadrupole instruments, which require at least two independent quadrupole mass filters [9]. The advantages added by axial modulation and MS/MS capabilities do however require more expensive versions of the Finnigan ion trap than the Ion Trap Detector used in this work; these are the Finnigan ITS-40 Ion Trap System and the Ion Trap Mass Spectrometer (ITMS).

The configuration of GC/ITD-2 has advantages in several areas over the configuration of GC/ITD-1. The first advantage is a cost savings. Savings are realized through the use of commercially available equipment. The time and costs associated with the development, construction, and trouble-shooting of chromatographic hardware and the custom interface were eliminated. GC/ITD-1 also required an expensive turbomolecular pump and mechanical modification of the Finnigan vacuum manifold. The second advantage is reliability. The gas load imposed by the removal of the conductance limiting spacers and the high flow rates in GC/ITD-1 resulted in reduced lifetimes for the ionizing filaments and the electron multiplier. The DAP1200 processor also appears to be more compatible with the Finnigan operating system than the custom interface and computer "hang-ups" have been eliminated. The third advantage is the ease with which future instruments may be built. The construction of GC/ITD-2 by other laboratories should be quite straightforward due to the extensive use of commercially available equipment. In general, copies of instruments that use custom designed and built hardware are more difficult to build with the same performance of the original instrument vis-a-vis instruments that are based on proven "off-the-shelf" hardware. Finally, the Hitachi processor used in GC/ITD-1 is no longer available and therefore not suitable for new designs.

CONCLUSION

Work is currently in progress to fully characterize the second generation instrument in the area of quantitation accuracy. Once quantitation methods are developed and tested in the laboratory, detection limits for a wide number of compounds of environmental significance can be determined. Analysis time will be reduced. Tests with soil samples will be performed. We do not anticipate significant problems in the purge and trap analysis of soils since the SRI Purge and Trap devices used in this instrument have been developed for both soil and water samples. New containment for GC/ITD-2 is being designed; the present containment is designed to minimize instrument footprint but it does make minor maintenance operations cumbersome to carry out.

The ion trap detector provides many advantages as a mass analyzer in this application. It is simple to maintain and operate. The high sensitivity of the ion trap and the inherent universality of the modular mass spectrometer system are perhaps the most important features for a field analytical instrument. The instrument provides high specificity for compound identification due to the two-dimensional information provided by chromatographic retention time and mass spectral library identification. Mobile ion trap mass spectrometers operating in the MS/MS mode have been successfully applied for the direct, continuous or near-continuous analysis of permanent gases and condensable vapors [10]. Ion trap mass spectrometer systems have also been developed for rapid screening of volatile organics in environmental matrices by MS/MS techniques [11]. Such instruments can provide highly complementary information to that obtained from a transportable GC/ITD system. Both types of instruments will find widespread use in environmental restoration activities. Other instruments used in field applications, such as a gas chromatograph [12] or Fourier-transform infrared spectrometer [13], do not provide the combination of sensitivity, specificity, and universality demonstrated by the transportable ion trap instrument.

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Mobile Environmental Monitor (MEM) Bruker Instruments, Manning Park, Billerica, MA.
PETRA, VG Gas Analysis Systems, Aston Way, Chesire, England.
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SpectraTrak, Viking Instrument Corp., Reston, VA.

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Table 1.

Reproducibility of Retention Times

Compound	t_R* (1 ppb)	t_R (10 ppb)	t_R (100 ppb)	Average t_R**	%rsd
Methyl Ethyl Ketone	23.3	23.5	23.4	23.4	0.3%
1,1,1-Trichloroethane	25.0	25.0	25.0	25.0	0.07%
Carbon Tetrachloride	25.7	25.8	25.7	25.7	0.1%
Benzene	26.4	26.4	26.4	26.4	0.1%
Fluorobenzene	27.1	27.1	27.1	27.1	0.1%
Trichloroethylene	28.2	28.3	28.2	28.2	0.2%
1,2-Dichloropropene	28.9	28.9	28.9	28.9	0.1%
Bromodichloromethane	29.6	29.6	29.6	29.6	0.1%
Toluene	32.4	32.4	32.3	32.3	0.1%
1,1,2-Trichloroethane	33.6	33.6	33.5	33.5	0.1%
Tetrachloroethylene	34.4	34.3	34.4	34.3	0.2%
Dibromochloromethane	35.2	35.2	35.2	35.2	0.2%
Chlorobenzene	37.2	37.2	37.2	37.3	0.2%

* Retention times in minutes. The start of the purge cycle is time t = 0.
** Average of 9 runs from 1 ppb to 100 ppb.

Table 2.

Reproducibility of Library Matching

Compound	ID Hit	Purity*	%rsd
Methyl Ethyl Ketone	1	931	<1%
1,1,1-Trichloroethane	1	599	5%
Benzene**	1	759	7%
Trichloroethylene	1	801	2%
Bromodichloromethane	1	861	2%
c-1,3-Dichloropropene	2	413	6%
Toluene	-		
Tetrachloroethylene	1	657	6%
Chlorobenzene	1	826	5%
Bromoform	1	856	4%

* Average of 3 analyses at 100 ppb.
** Coelutes with 1,2-dichloroethane.

Figure 1. A Schematic Diagram of the Second Generation Transportable Gas Chromatograph/Ion Trap Detector.

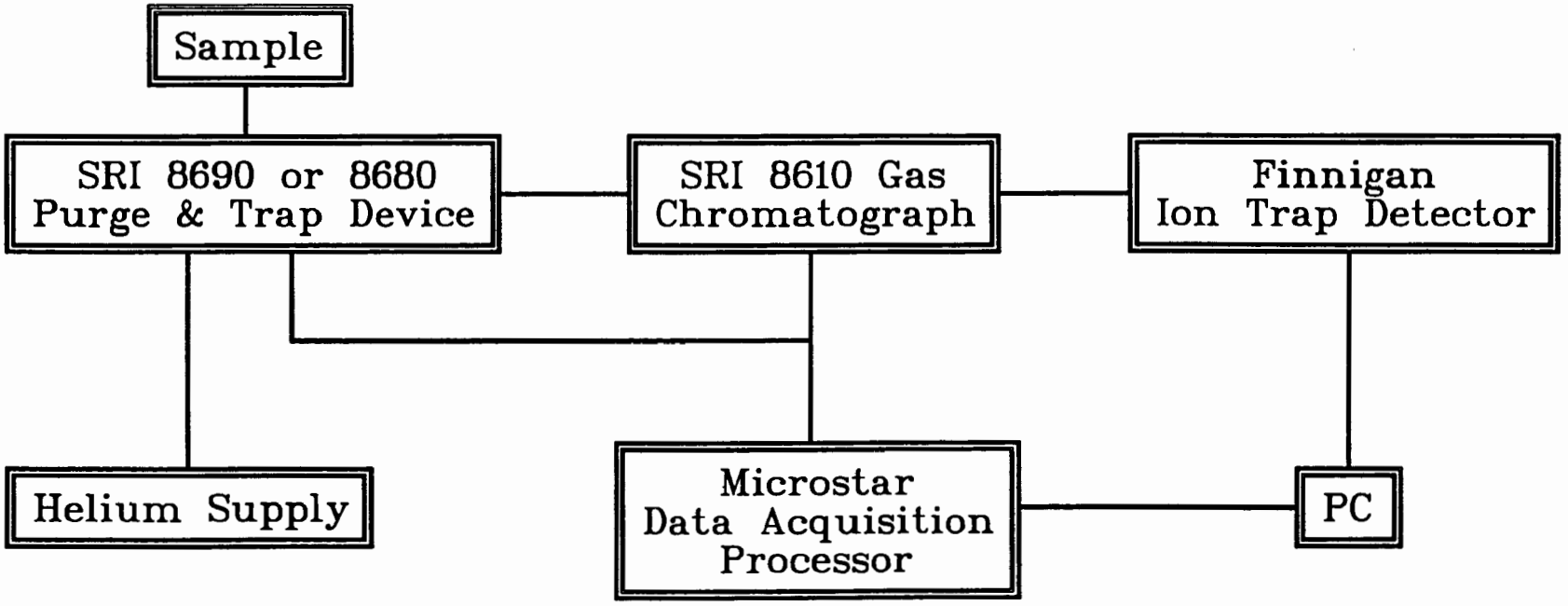


Figure 2.

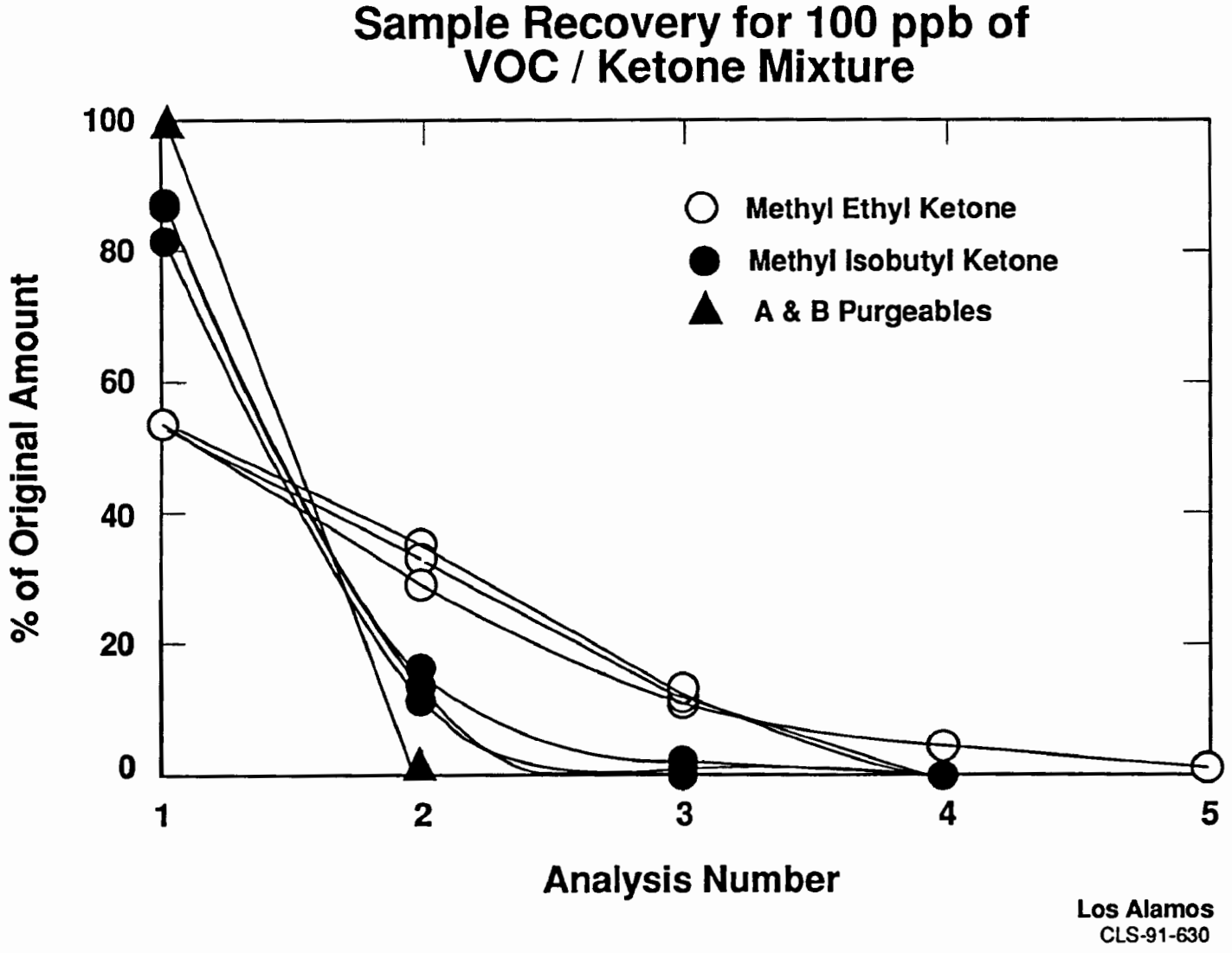
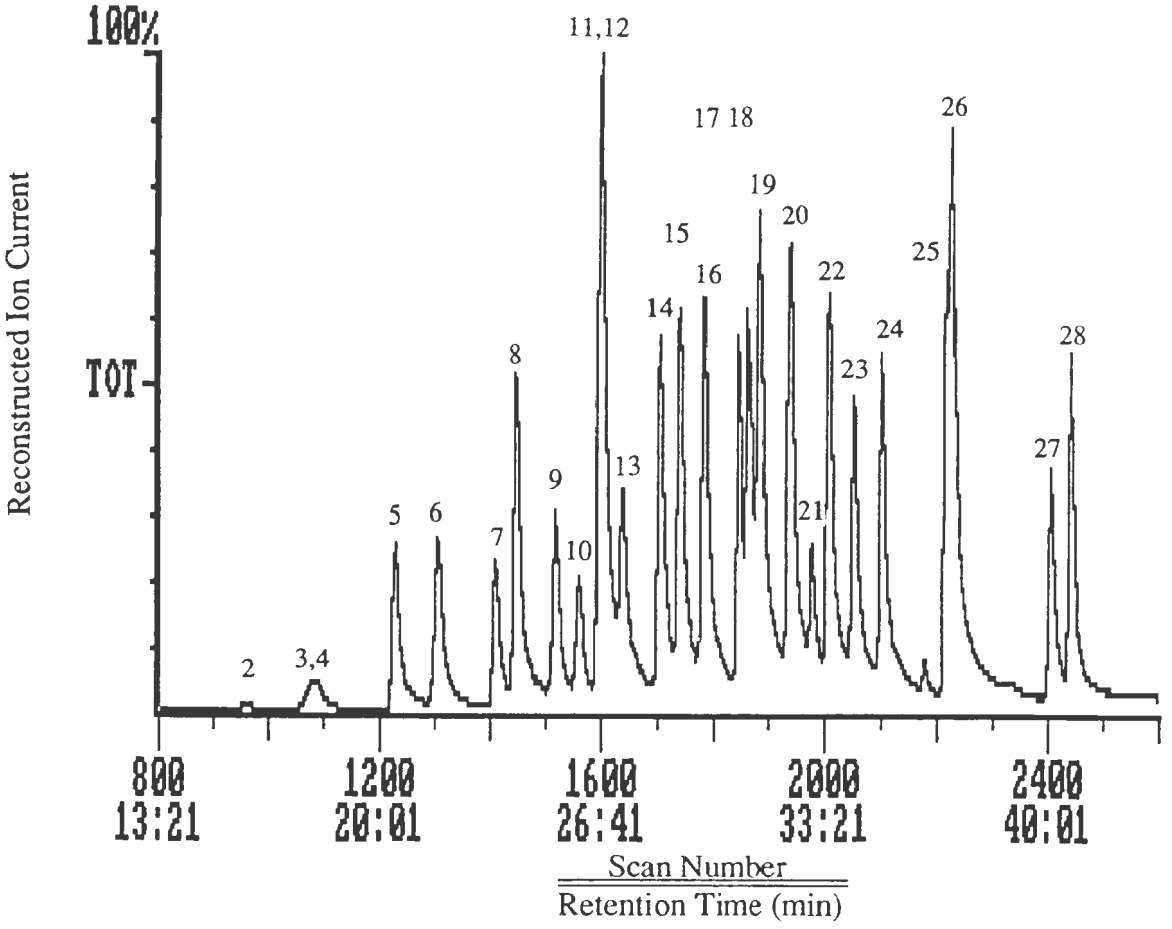

Sample Recovery for 100 ppb of
VOC / Ketone Mixture
100
80
60
40
20
0
% of Original Amount
1
2
3
4
5
Analysis Number
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
A & B Purgeables
Los Alamos
CLS-91-630

Figure 3. Reconstructed Ion Chromatogram from the Purge and Trap Analysis of 5 ml of Water Containing 100 ppb each of 28 Volatile Organic Compounds.



1. Acetone (not observed)
2. Trichlorofluoromethane
3. 1,1-Dichloroethylene
4. Methylene Chloride
5. t-1,2-Dichloroethylene
6. 1,1-Dichloroethane
7. Methyl Ethyl Ketone
8. Chloroform
9. 1,1,1-Trichloroethane
10. Carbon Tetrachloride
11. Benzene
12. 1,2-Dichloroethane
13. Fluorobenzene
14. Trichloroethylene
15. 1,2-Dichloropropene
16. Bromodichloromethane
17. 2-Chloroethyl Vinyl Ether
18. Methyl Isobutyl Ketone
19. *c*-1,3-Dichloropropene
20. Toluene
21. *t*-1,2-Dichloropropene
22. 1,1,2-Trichloroethane
23. Tetrachloroethylene
24. Dibromochloromethane
25. Chlorobenzene
26. Ethyl Benzene
27. Bromoform
28. 1,1,2,2-Tetrachloroethane

Figure 4.

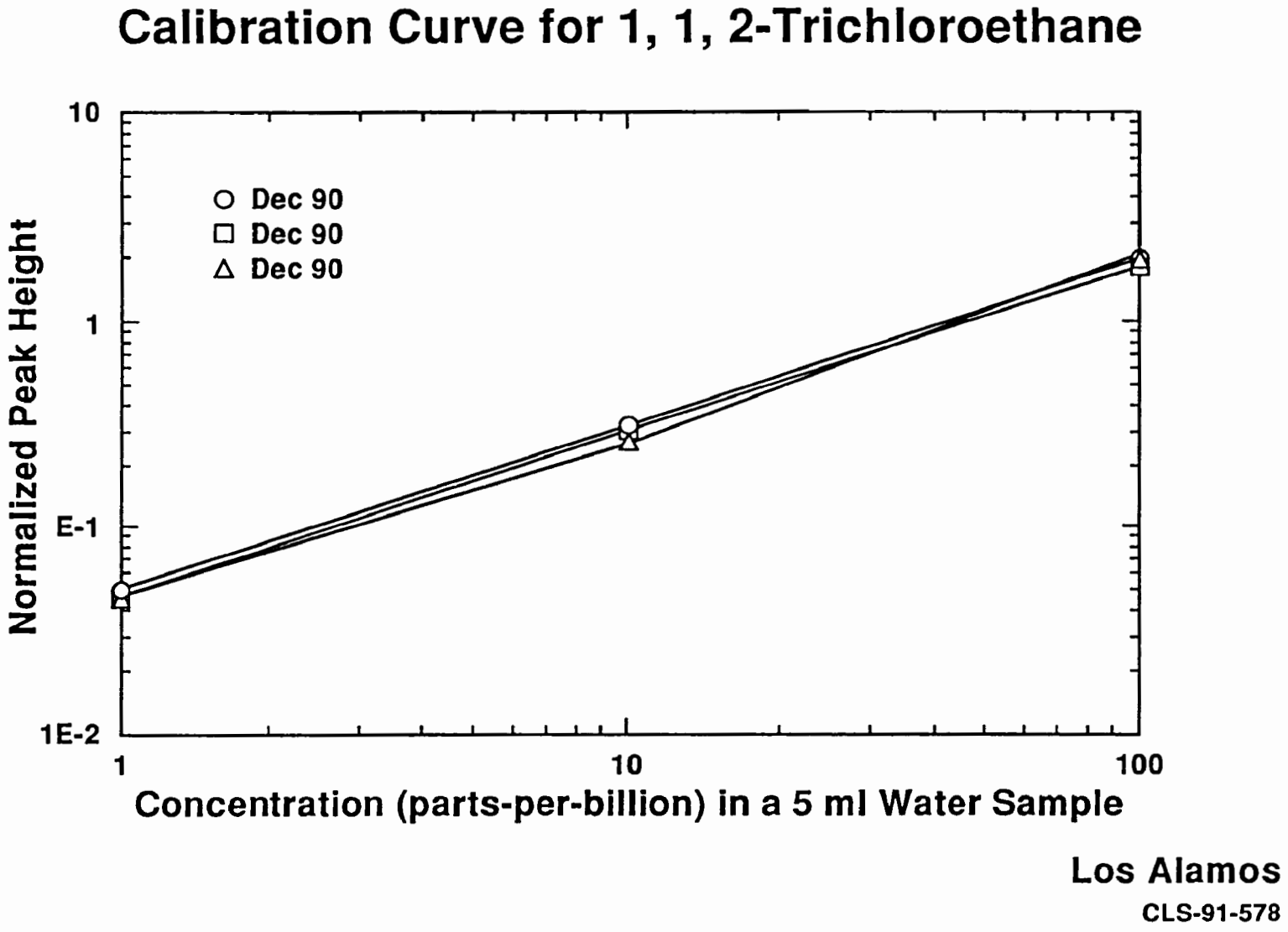

Calibration Curve for 1, 1, 2-Trichloroethane
Normalized Peak Height
10
1
E-1
1E-2
Dec 90
Dec 90
Dec 90
1
10
100
Concentration (parts-per-billion) in a 5 ml Water Sample
Los Alamos
CLS-91-578

Figure 5.

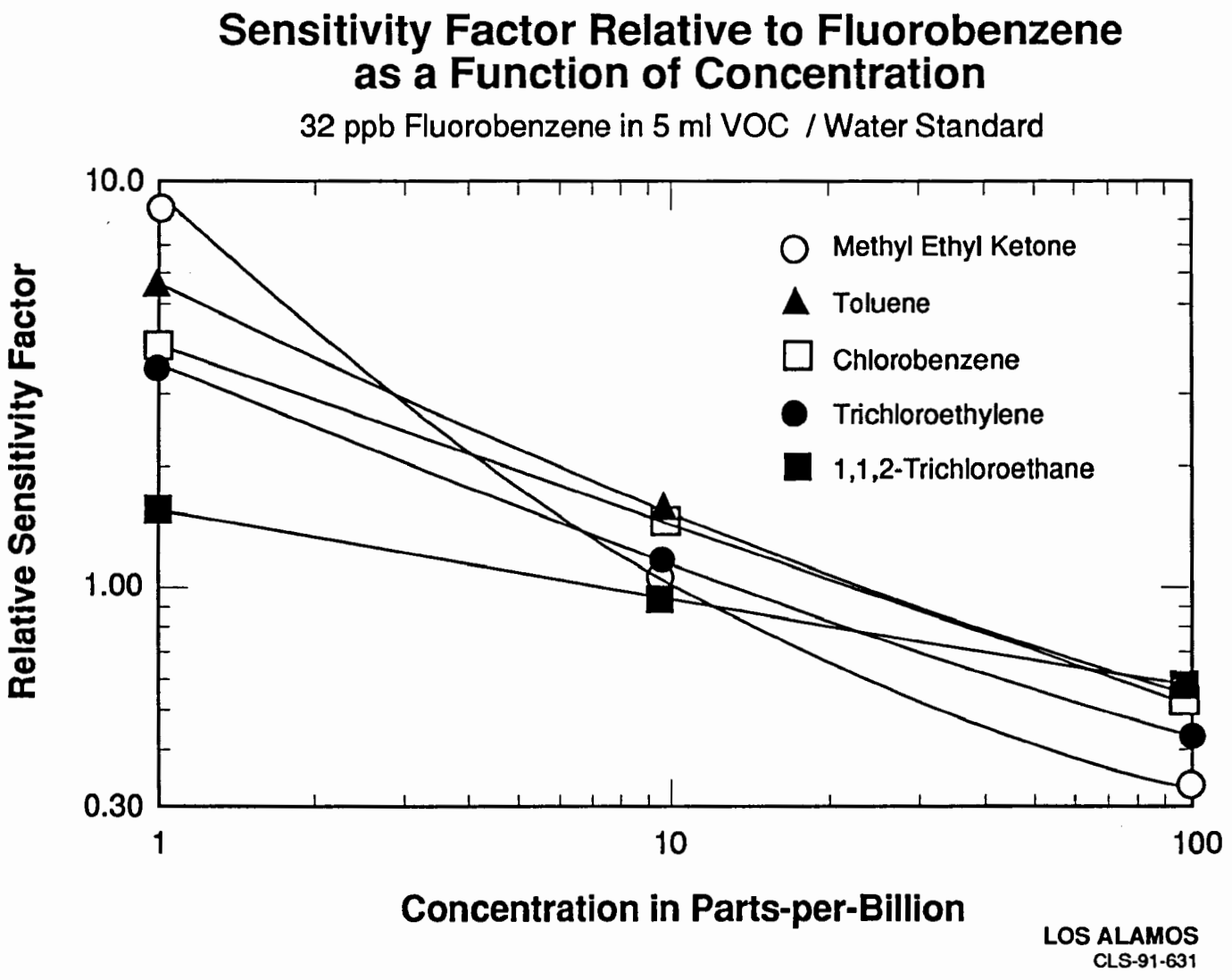

Sensitivity Factor Relative to Fluorobenzene as a Function of Concentration
32 ppb Fluorobenzene in 5 ml VOC / Water Standard
Relative Sensitivity Factor
10.0
1.00
0.30
1
10
100
Concentration in Parts-per-Billion
Methyl Ethyl Ketone
Toluene
Chlorobenzene
Trichloroethylene
1,1,2-Trichloroethane
LOS ALAMOS
CLS-91-631

Figure 6.

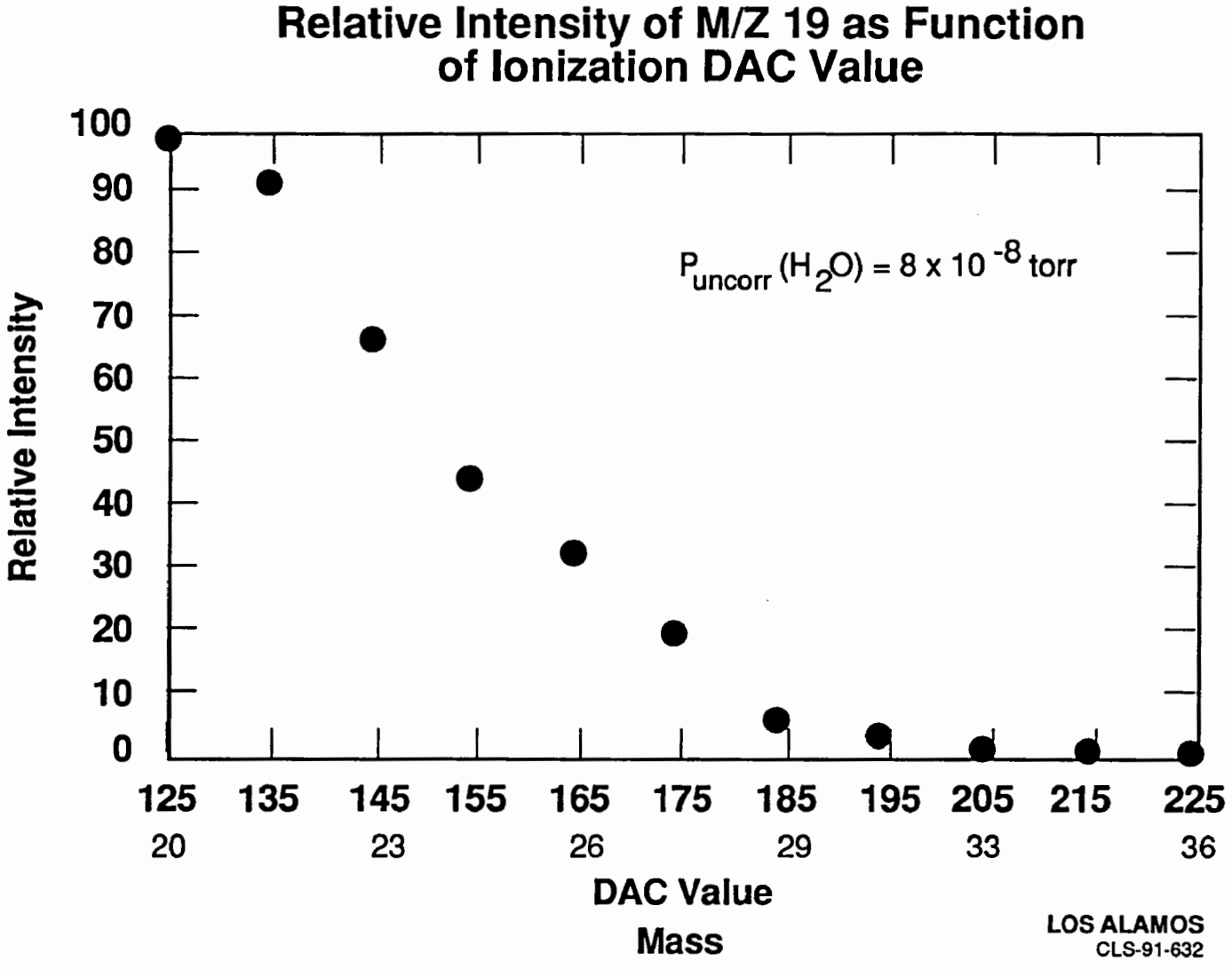

Relative Intensity of M/Z 19 as Function of Ionization DAC Value
Relative Intensity
100
90
80
70
60
50
40
30
20
10
0
P_{uncorr} (H_2O) = 8 x 10^{-8} torr
125 135 145 155 165 175 185 195 205 215 225
20 23 26 29 33 36
DAC Value
Mass
LOS ALAMOS
CLS-91-632

Figure 7.

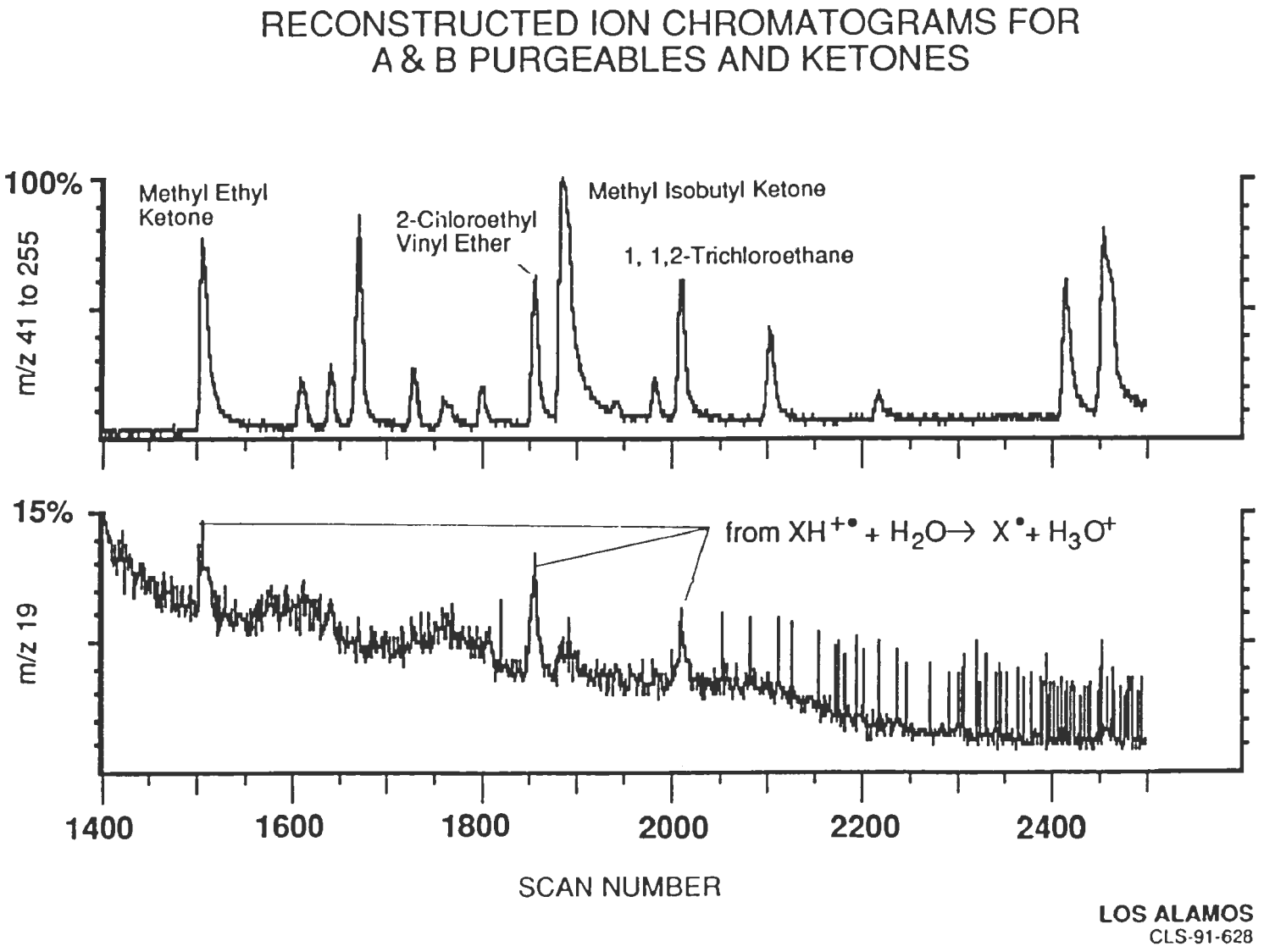
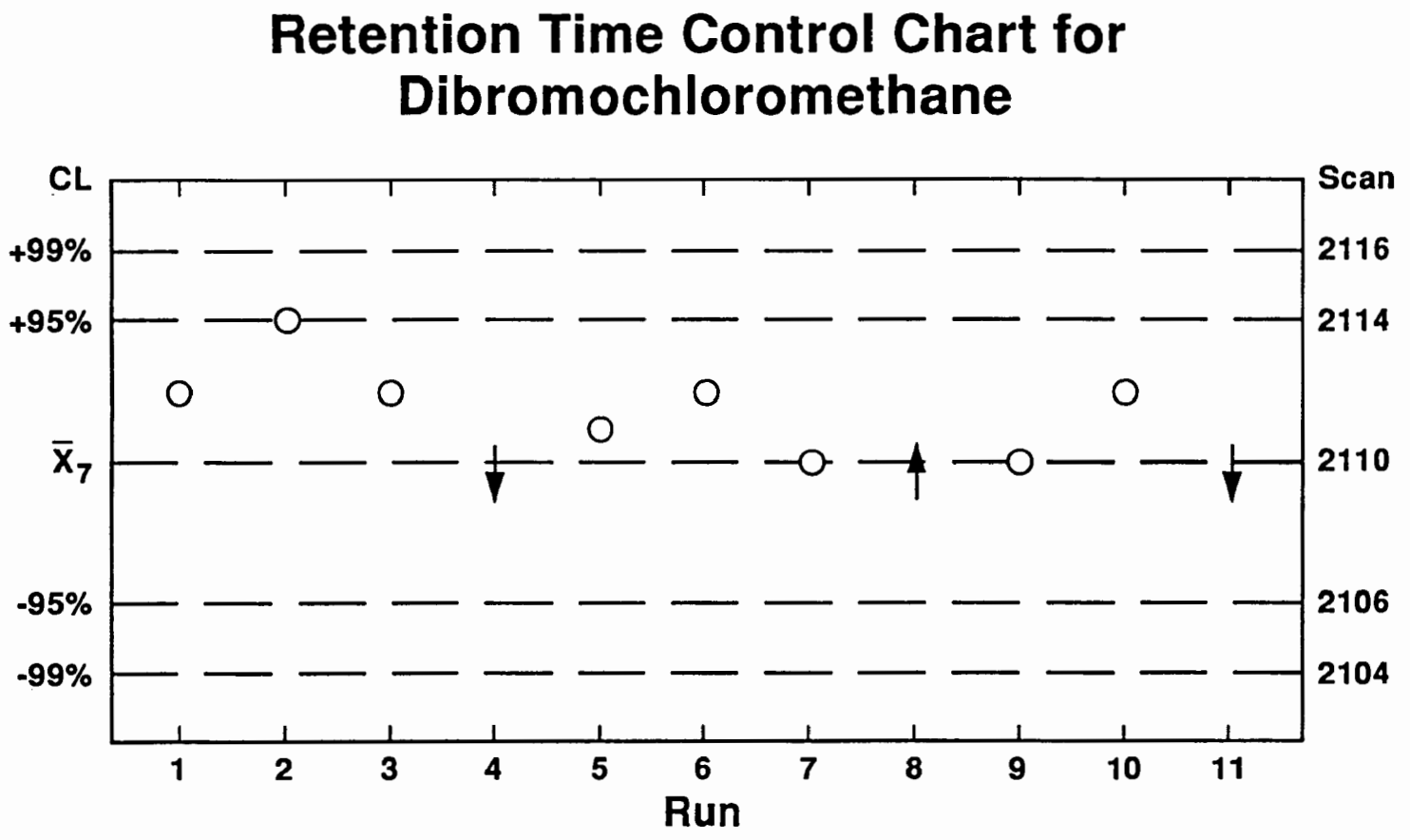

RECONSTRUCTED ION CHROMATOGRAMS FOR
A & B PURGEABLES AND KETONES
100%
m/z 41 to 255
Methyl Ethyl
Ketone
2-Chloroethyl
Vinyl Ether
Methyl Isobutyl Ketone
1, 1,2-Trichloroethane
15%
m/z 19
from XH+• + H2O→ X•+ H3O+
1400
1600
1800
2000
2200
2400
SCAN NUMBER
LOS ALAMOS
CLS-91-628

Figure 8.



Los Alamos
CLS-91-580

Figure 9.

Instrument Control Menu

SELECTION MENU

1) Trap Setup	(SETUP)
2) Bakeout	(BAKEOUT)
3) Acquisition	(ACQMENU)
4) Trap cool down	(TRAPCOOL)
5) DAP reset	(DAPCLR)
6) Quantitation	(QUANT)

9) Quit Menu

ENTER SELECTION NUMBER:

DISCUSSION

RUSSELL SLOBODA: Once you finished prototype work, what was the average length of time when you turned off the motor and the vehicle driving the trailer off the site and when your calibration could actually be done?

CHRISTOPHER LEIBMAN: Start again you mean? Actually we have a fairly good size turbo pump, the 240 liter/second turbo pump. That represents one of the modifications. It pumps out fairly quickly and we're back in business within a day. We drive up to the site at night, and let the unit pump down; that's been our practice. Clearly that's something we're going to have to look at very hard.

RUSSELL SLOBODA: Do you need power throughout the night for one day's events?

CHRISTOPHER LEIBMAN: The way it is currently configured, yes.

RUSSELL SLOBODA: Can you peel off the back of the system and then shut things off and then turn it on the next day?

CHRISTOPHER LEIBMAN: We've considered that. But the power requirements when the instrument is in the standby mode just aren't considerable. The GC's off and the turbo's up to speed, so there's very little load. The one thing I would like to also add is, I have this demonstration on a diskette. I suspect it will run a little more smoothly on your instrument than in this form. But if you would like to see any data after this presentation, write and let me know.

BRIAN ECKENRODE: I was wondering about your success on the library searching. For example, I noticed you had one spectrum, tetrachloroethylene, that had peaks beyond the molecular ion. How is that affecting your ability to get a hit in the library?

CHRISTOPHER LEIBMAN: We've done quite well in terms of the library searching, the library matching. We're looking both based on retention time and the mass spectra. So while it may see those other ions in the mass spectrum, it's only looking for the presence of certain target ions. Operated in that mode, the coelution does not pose a problem.

PHIL HEMBERGER: You had mentioned going to a hydrogen generator. Is that also to supply buffer gas to the ion trap?

CHRISTOPHER LEIBMAN: Yes. And in fact some interesting work has been done in that area. Scott McClucky and Gary Clish and O'Krish have looked at the presence of hydrogen in the ion trap, and what they've observed is an enhancement in sensitivity by a factor of two.

PHIL HEMBERGER: With hydrogen you would expect much different collision of cooling of the ions then would be provided by helium. The fragmentation patterns should also change. Do you anticipate that you're going to have to build your own library?

CHRISTOPHER LEIBMAN: I think you need to look at the search algorithm that we're using. The library we're using to conduct the search is one we create. So when we go through the chromatogram and identify each of the peaks, we essentially then identify that fragmentation pattern. So if it changes with different collision gases so be it. It's taken into account in the way we set up our calibration files. But, a very good point.

TRANSPORTABLE GC/ION TRAP MASS SPECTROMETRY FOR TRACE FIELD ANALYSIS OF ORGANIC COMPOUNDS

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Abstract

A transportable purge and trap/GC/MS based on the Finnigan Ion Trap Detector (ITD) has been developed at Los Alamos National Laboratory for the identification and quantification of volatile organic compounds present at chemical waste sites. This instrumentation is being evaluated for use to support environmental surveillance and the characterization/clean-up of hazardous waste sites. A custom purge and trap/GC sampling system was integrated with a modified ITD to achieve instrument operation consistent with field activities. The sampling system is controlled by an ancillary microprocessor designed at Los Alamos National Laboratory. The instrument is extensively automated and can be operated with minimal training. Instrument operation transparent to the field user has been achieved by integrating sampling system control software with the operating software of the ITD.

The instrumentation and associated methods parallel those outlined in method 8260, SW-846. Qualitative and quantitative analysis for the 68 target compounds and the associated internal standards and surrogates is completed in an automated sequence that is executed every 25 minutes. Sample purging, analysis, data reduction, and preliminary report generation proceeds automatically. The instrument can be operated in a continuous mode, pausing only for sample loading and data file specification. All data are archived on floppy disk for subsequent review by a skilled analyst.

Part-per-trillion detection limits can be attained for many compounds from either 5 gram soil or 5 milliliter water samples.

Introduction

The development and use of field transportable analytical instrumentation can significantly reduce the cost associated with environmental surveillance and restoration activities. Field analytical support minimizes the analytical data turnaround time, which can expedite site characterization and provide analytical data to field personnel for guidance of ongoing work. Clean-up personnel can be used more efficiently since these teams will not have to be released and reassembled weeks later after receipt of analytical results from a remote laboratory.

Field analytical support can directly impact the expense of environmental clean-up by reducing the cost-per-analysis. Cost for sample packaging, shipment, receiving and management are eliminated if analyses are performed on site. Field analytical support improves the chances that schedules and monetary constraints associated with remedial activities are met.

Performing analyses on-site can enhance the quality of analytical data generated. Field analyses reduce the possibility that samples will be compromised from transport and handling. Reduced sample handling and the analysis of samples within minutes of collection minimizes the potential loss of volatile components. Near real-time data can also be used to direct subsequent sampling efforts. Additionally, initial site characterization can help delineate the sampling grid used for collection of samples to be sent to a remote laboratory.

A transportable purge and trap/GC/MS has been developed at Los Alamos National Laboratory to provide field analytical support for environmental restoration activities. The instrument is based on a Finnigan Ion Trap Detector (ITD)[1], a rugged and simple mass spectrometer. This transportable GC/ITD has been designed specifically to support field operations and to provide analytical data of sufficient quality to meet higher level data quality objectives. Our focus has been to attempt to meet the quality control criteria outlined in chapter 1 of SW-846 and to use procedures which parallel method 8260, SW-846.

Experimental

Purge and Trap/Gas Chromatograph

A custom purge and trap/GC was fabricated for sampling volatile organics in water or soil samples. The purge and trap/GC has two sampling loops, each loop consisting of a needle sparger and an adsorbent resin trap. A schematic of this sampling system is shown in Figure 1. In position A, simultaneous with the purging and concentration of one sample onto trap B the contents of trap A are desorbed onto the capillary column. Subsequent to the analysis of trap A, the ten port valve (Valco Instruments Co.) is rotated to position B

and the contents of trap B are desorbed onto the capillary while purging/concentration occurs on the other sampling loop. Backpressure regulation via a split maintains column carrier gas flow. Splitless injection is performed for 20 seconds during adsorbent trap desorption. This is sufficient for quantitative transfer of trapped target analytes while serving to minimize water transfer to the analytical system. Additionally, the capillary column is maintained at 10 °C during desorption. This serves to cryofocus target analytes onto the head of the column while allowing any water to pass unretained.

The adsorbent traps are packed with equal amounts of 2,6-diphenylene polymer and silica gel. Traps are heated to 200°C at a rate of 500°C/min. Heater jackets are provided for the 5 milliliter sparger tubes and maintain a purge temperature of 35 °C. The temperature programmable GC oven can be programmed with up to 35 multiple ramps and is capable of sub-ambient operation. All sample transfer lines are deactivated fused silica and are heated to 85 °C. All valves, heaters and the GC oven associated with this sampling system are controlled by a dedicated microprocessor. A 30m x 0.32mm i.d. DB-624 (J&W Scientific) fused silica capillary column with 1 um film thickness was used. The capillary column was directly coupled to the ITD via a heated transfer line.

In addition to soil or water sampling, soil gas analysis can be accomplished by replacing the needle spargers with an adsorbent trap thermal desorption unit. Soil gas or air samples are collected on an adsorbent trap using an air sampling pump. The air sampling tubes are then transported to the instrument and placed in a heater assembly whereby trap contents are thermally desorbed onto the primary adsorbent traps shown in Figure 1. Conversion from soil/water analysis to air analysis can be accomplished within 5 minutes. Instrument operation is modified via the computer to accommodate the air sampling trap desorption/analysis.

Mass Spectrometer

A Finnigan MAT Ion Trap Detector[1] was used with the following modification. The supplied transfer line and open split interface were eliminated. The 50 L/sec turbomolecular pump was replaced with a 240 L/sec turbomolecular pump. The larger pump was required to handle the increased gas load realized from the direct coupling of the capillary column to the ITD. The larger turbomolecular pump also reduces pump down time following system venting.
Electron impact ionization was used; the ionization period was regulated using Finnigan supplied automatic gain control software.

Data System/Automation

A Zenith Supersport 286 laptop computer was used for data acquisition and instrument control. All aspects of mass spectrometer and sampling system operation were controlled through the dedicated laptop computer. Finnigan supplied ITD control software (version 4.10) with the programmer's option served as the platform for system automation. FORTH subroutines and keystroke sequences were incorporated with the Finnigan supplied software to automate ITD data acquisition, quantitation, and report generation. Communication to the sampling system microprocessor was through the serial port of the laptop computer. Sampling system control was achieved using assembly language programs. Parameters for sampling system event sequencing and heater or GC oven temperatures were written into the Finnigan ITD software using the programming option.

Physical Requirements

The total instrument dimensions are 17.5" x 23.5" x 26" (H x W x D) exclusive of the laptop computer. The instrument can be deployed in a vehicle equipped with compressed gas supply and a small liquid nitrogen dewar if cryogenic operation is required. A portable generator or line power is required. Power consumption is less than 1.5 kW. For field test to date, the instrument has been deployed in a 12 foot trailer.

Methods/Operational Sequence

The methods used with the transportable purge and trap/GC/ITD parallel those outlined in method 8260, SW-846[2]. Following instrument pump down and warm up of all heated zones, filament continuity and water concentration in the ITD are checked. Mass calibration is verified using perfluorotributylamine (PFTBA). Depending on the end use of field generated data, different levels of quality control can be used. An ITD tuning check can be performed using 4-bromofluorobenzene (BFB) to ensure that abundance criteria recently specified in method 524.2 is met. Figure 2 shows ion chromatogram derived from the molecular ion of 4-bromofluorbenzene obtained by purging a solution containing 50 ng 4-bromofluorobenzene. The mass spectrum obtained at the scan indicated by the cursor shown in Figure 2, is shown in Figure 3. This mass spectrum meets the abundance criteria specified in method 8260, SW-846. Following tune verification, a calibration curve can be established or continued adherence to the calibration curve can be checked using a midpoint standard. The midpoint standard check can also be used to update retention times on a daily basis. Currently our target list comprises the 68 target compounds shown (with their corresponding internal standards and surrogates) in Table 1. Following analysis of a blank, sample analysis is performed in a continuous mode, pausing only for sample loading and data file specification. Data acquisition is followed automatically by data reduction. Target compounds are identified by 1) elution of sample component at the appropriate elution window and 2) comparison of the sample mass spectrum with the standard reference mass spectrum. Standard reference mass spectra are obtained from the analysis of calibration mixtures. If any targeted compounds are detected, a hardcopy preliminary report is generated immediately. All data are archived on machine readable media for subsequent review by a skilled analyst.

Results/Discussion

We have successfully deployed the transportable GC/ITD at waste sites at Los Alamos National Laboratory. To date field trials have been completed without significant instrument failures. The qualitative and quantitative analysis for the 68 target compounds and the associated internal standards and

surrogates is accomplished in the field in an automated sequence executed every 25 minutes. A portion of the total ion chromatogram obtained in the field from 5 mls of a 50 ppb water standard is shown in Figure 4. Retention times for the target compounds reflected in Figure 4 are given in Table 1. Chromatographic development is completed within 16 minutes.

The need to obtain the chromatographic resolution displayed in Figure 4 is dependent on the site specific data quality objectives established. If only screening is required or the target list is more limited, chromatographic development can be reduced by using a steeper GC oven temperature ramp for faster elution. An example of instrument operation in the fast screening mode is shown in Figure 5, representing a chromatogram obtained from the internal standards/surrogates spiking mixture used in this work.

During field trials, co-located samples were taken for comparisons between the transportable GC/ITD and a laboratory based GC/quadrupole mass spectrometer. Table 2. shows the comparison between an analysis performed at a waste site with the GC/ITD and results obtained from the remote laboratory. The results shown in Table 2. reflect a 1 to 100 dilution (high level-methanol extraction method)[2]. Difference between the field results to those obtained at the remote laboratory may reflect the loss of volatile components during sample transport.

Low part-per-trillion detection limits have been achieved for some compounds from 5g soil or 5 mls water samples with this instrumentation. An extracted ion current profile of m/z 98, the quantitation ion of toluene d8 (a surrogate), obtained from a 20 ppt solution of the compounds listed in Table 1. (100 picograms/component in 5mls) is shown in Figure 6. The signal to noise ratio for m/z 98 in this chromatogram is approximately 10:1. The complete background subtracted mass spectrum for toluene d8 is shown in figure 7. No toluene d8 was detected in the blank which preceded the ion chromatogram shown in figure 6. Low part-per-trillion detection limits cannot be routinely achieved in the field. However, the high sensitivity of the instrument increases the degree of confidence in the automated mass spectral identifications performed in the field for a higher working concentration range. Our targeted working concentration range for field studies is from 100 ppt to 100 ppb for most compounds.

Conclusion

A transportable GC/MS for the qualitative and quantitative analysis of volatile organic compounds present at chemical waste sites has been developed at Los Alamos National Laboratory. System components have been integrated to produce an instrument which is extensively automated and can be operated with minimal training. Protocols for field technicians with subsequent data review by a skilled analyst ensure data quality. A high degree of specificity for compound identification is achieved with retention time and mass spectral information. The instrument is fast, analysis for the 68 target compounds outlined in method 8260, SW-846[2] can be achieved in 25 minutes. For screening, the chromatographic performance can be reduced to reduce analysis time. Additionally, part-per-trillion detection limits have been demonstrated for many compounds with this instrument.

References

1) Stafford, G.C., Kelley, P.E., Syka, J.E.P., Reynolds, W.E., and Todd, J.F.J. "Recent Improvements in and Analytical Applications of Advanced Ion Trap Technology " Int. J. Mass Spectrom. Ion Processes, 60, Special Issue, Sept., 1984, 85.

2) "Test Method for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Ed., Update I, Method 8260. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Acknowledgements

C.P.L. wishes to acknowledge the contributions of P.H. Hemberger, T.M. Cannon, and M.A. Wolf during the initial development of this instrumentation.

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TABLE 1.

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

	Ret. Time (min: sec)
Pentafluorobenzene	5:45
Dichlorodifluoromethane	:04
Chloromethane	:18
Vinyl Chloride	:28
Trichlorofluoromethane	1:18
1,1-Dichloroethene	2:00
Trichlorotrifluoroethane	2:03
Iodomethane	2:10
Carbon Disulfide	2:09
Acetone	2:08
Methylene Chloride	2:43
Acrylonitrile	3:13
trans-1,2-Dichlorethene	3:09
1,1-Dichloroethane	3:59
Vinyl Acetate	4:18
2,2-Dichloropropane	4:59
cis-1,2-Dichloroethene	5:02
2-Butanone	5:09
Bromochloromethane	5:28
Chloroform	5:28
1,1,1-Trichloroethane	5:34
Carbon Tetrachloride	5:45
1,1-Dichloropropene	5:46
Benzene	5:58
1,2-Dichloroethane-d4 (surrogate)	5:56
1,2-Dichloroethane	6:01
1,4-Difluorobenzene	6:24
Trichloroethene	6:36
1,2-Dichloropropane	6:48
Dibromomethane	6:54
Bromodichloromethane	7:04
2-Chlorovinylether	7:20
trans-1,3-Dichloropropene	7:26
Toluene d8 (surrogate)	7:38

	Ret. Time (min: sec)
Chlorobenzene d5	8:56
4-Methyl-2-pentanone	7:36
Toluene	7:42
cis-1,3-Dichloropropene	7:55
1,1,2-Trichloroethane	8:05
Tetrachloroethene	8:10
1,3-Dichloropropane	8:13
Chlorodibromomethane	8:25
2-Hexanone	8:19
1,2-Dibromomethane	8:31
Chlorobenzene	8:58
1,1,1,2-Trichloroethane	9:04
Ethylbenzene	9:07
m,p-Xylene	9:15
o-Xylene	9:39
Styrene	9:41
Bromoform	9:52
Isopropyl Benzene	10:04
1,4-Dichloroethane-d4	11:36
4-Bromofluorobenzene (surrogate)	10:15
Bromobenzene	10:24
1,2,3-Trichloropropane	10:29
1,1,2,2-Tetrachloroethane	10:26
n-Propylbenzene	10:33
2-Chlorotoluene	10:39
4-Chlorotoluene	10:46
1,3,5-Trimethylbenzene	10:46
t-Butylbenzene	11:09
1,2,4-Trimethylbenzene	11:12
S-Butylbenzene	11:24
1,3-Dichlorobenzene	11:31
1,4-Dichlorobenzene	11:38
p-Isopropyltoluene	11:34
1,2-Dichlorobenzene	12:03
n-Butylbenzene	12:04
1,2-Dibromo-3-Chloropropane	13:03
1,2,4-Trichlorobenzene	14:11
Napthalene	14:21
Hexachlorobutadiene	14:27
1,2,3-Trichlorobenzene	14:54

TABLE 2.

COMPARISON OF FIELD ANALYSIS TO LABORARORY BASED ANALYSIS*

Compound	Field	Laboratory
1,1,1-Trichloroethane	1900 ppb	1340 ppb
Tetrachloroethene	1800 ppb	1500 ppb
2-Butanone	140 ppb	40 ppb
Trichlorotrifluoroethane	2950 ppb	810 ppb

*100x Dilution Required Prior to Anaylsis

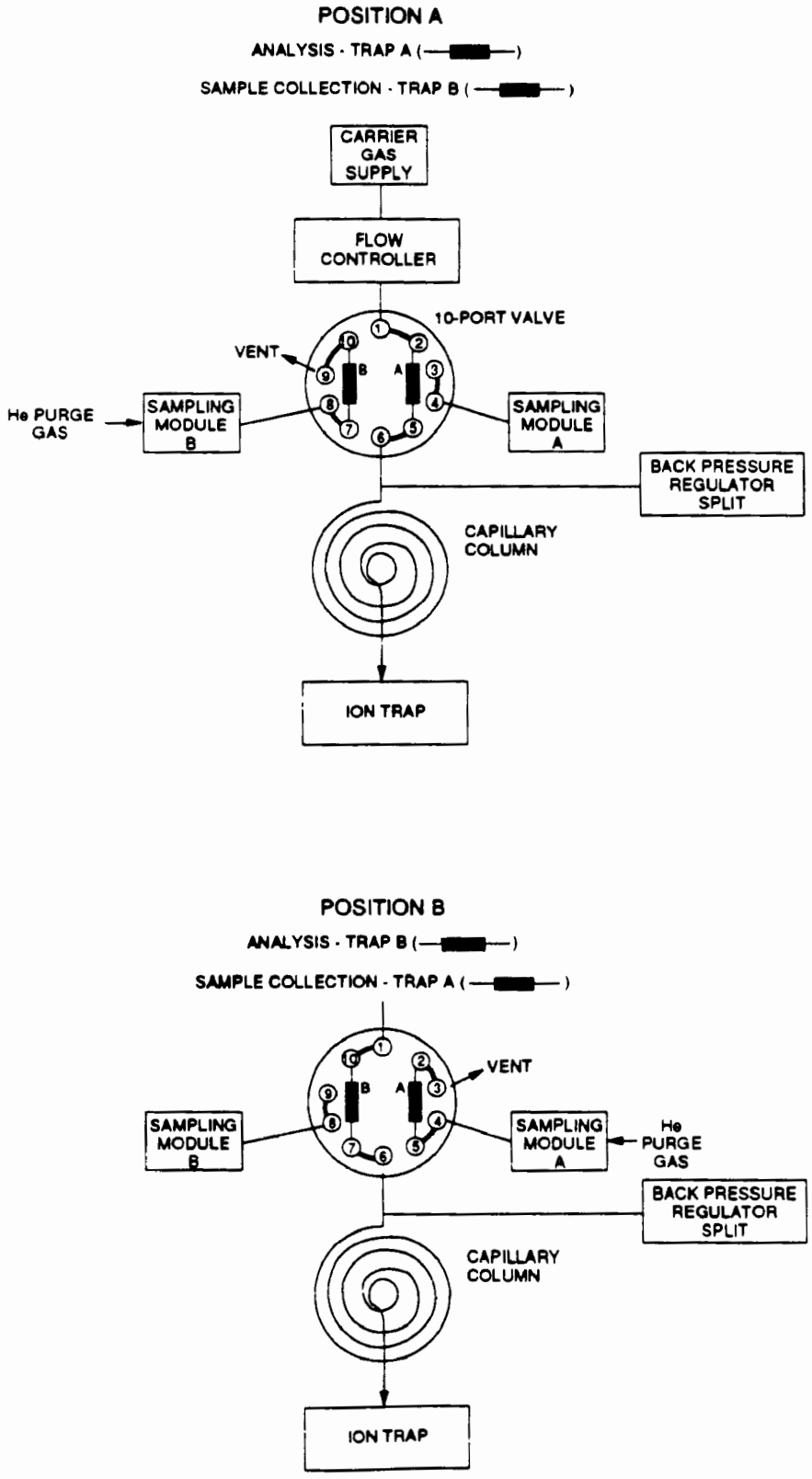

Figure 1. Schematic of Transportable GC/ITD Sampling System.

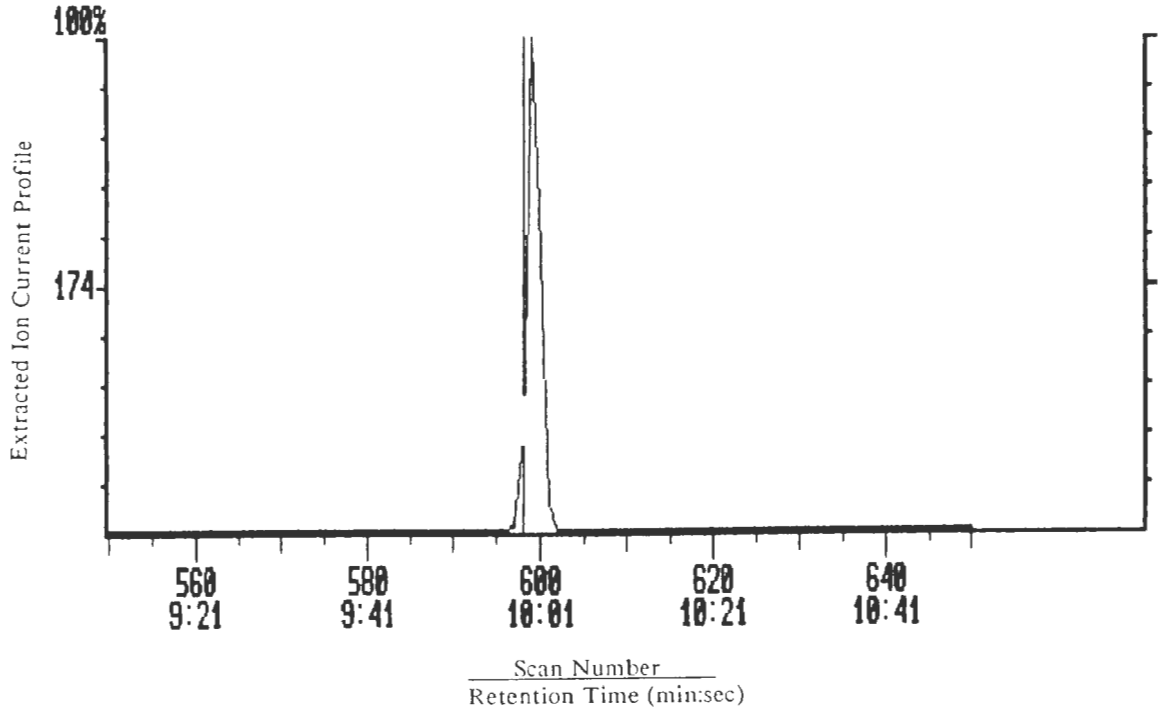

Figure 2. Extracted Ion Current Profile Derived from Molecular Ion of 4-Bromofluorobenzene (50ng).

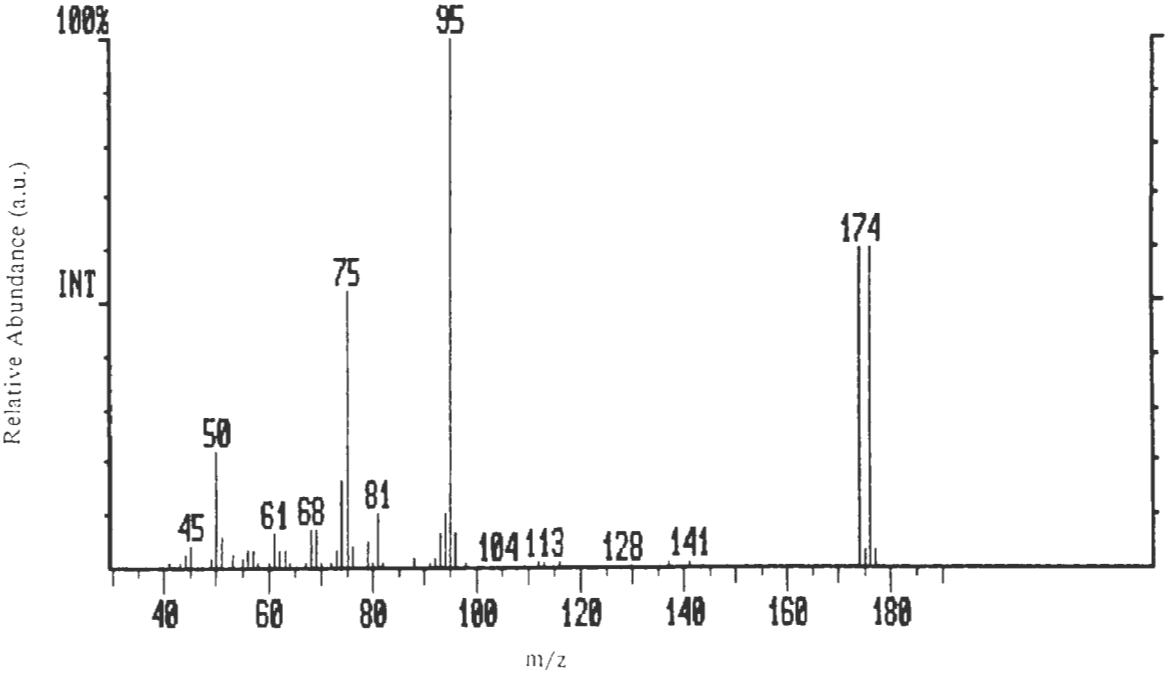

Figure 3. Mass Spectrum of 4-Bromofluorobenzene Which Meets Tune Criteria.

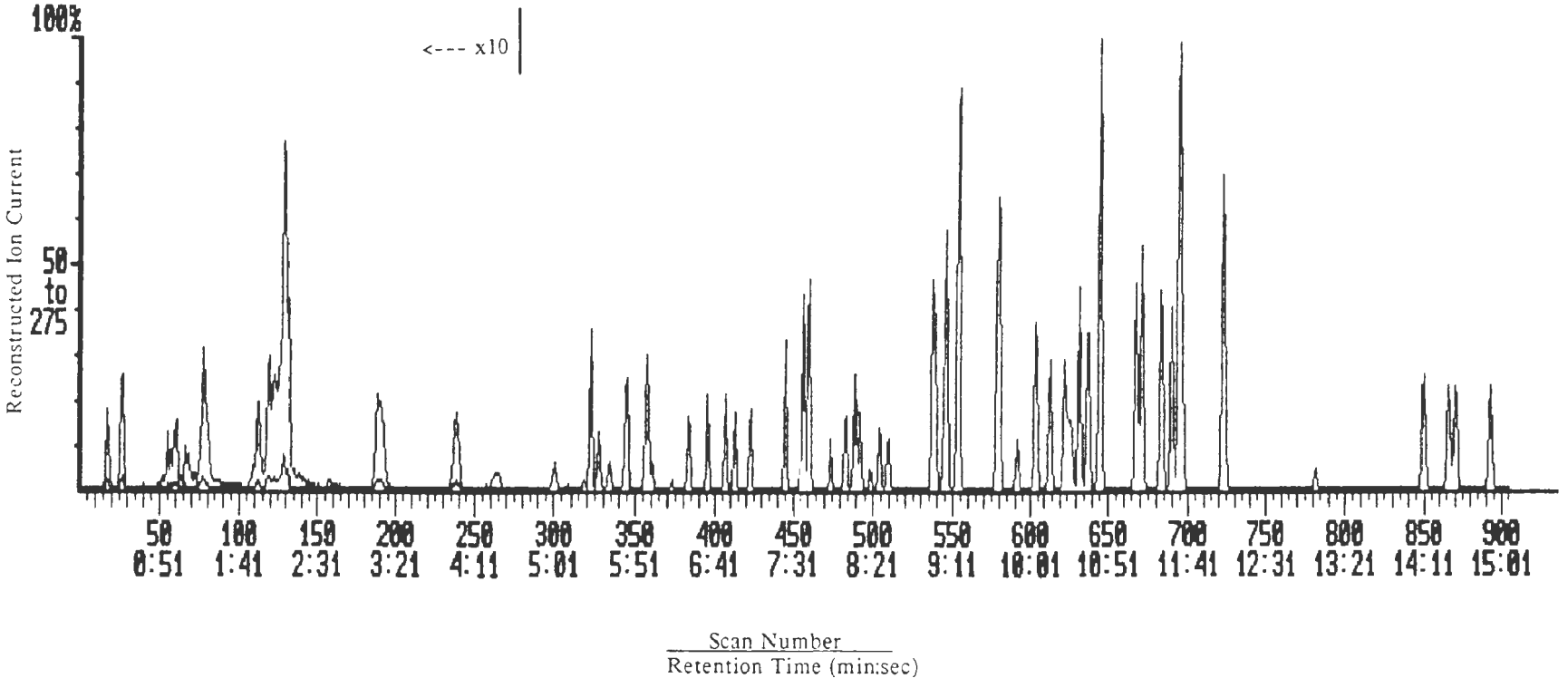

Figure 4. Total Ion Chromatogram Obtained in the Field from 50 ppb Standard.

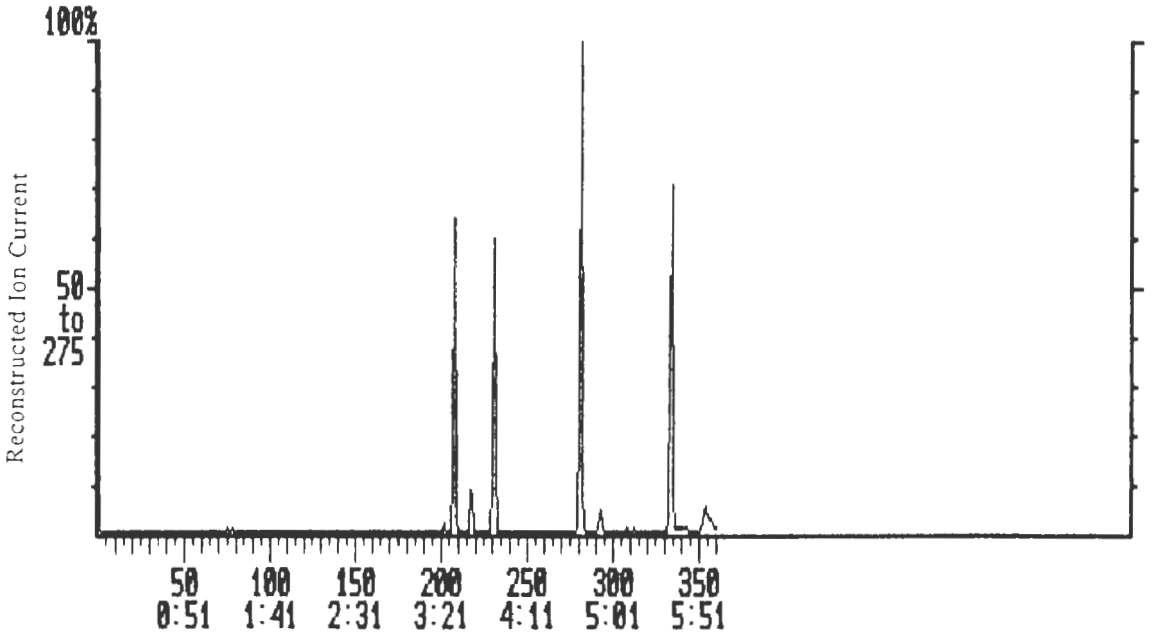

Figure 5. Total Ion Chromatogram of Internal Standards Obtained in Fast Screening Operational Mode.

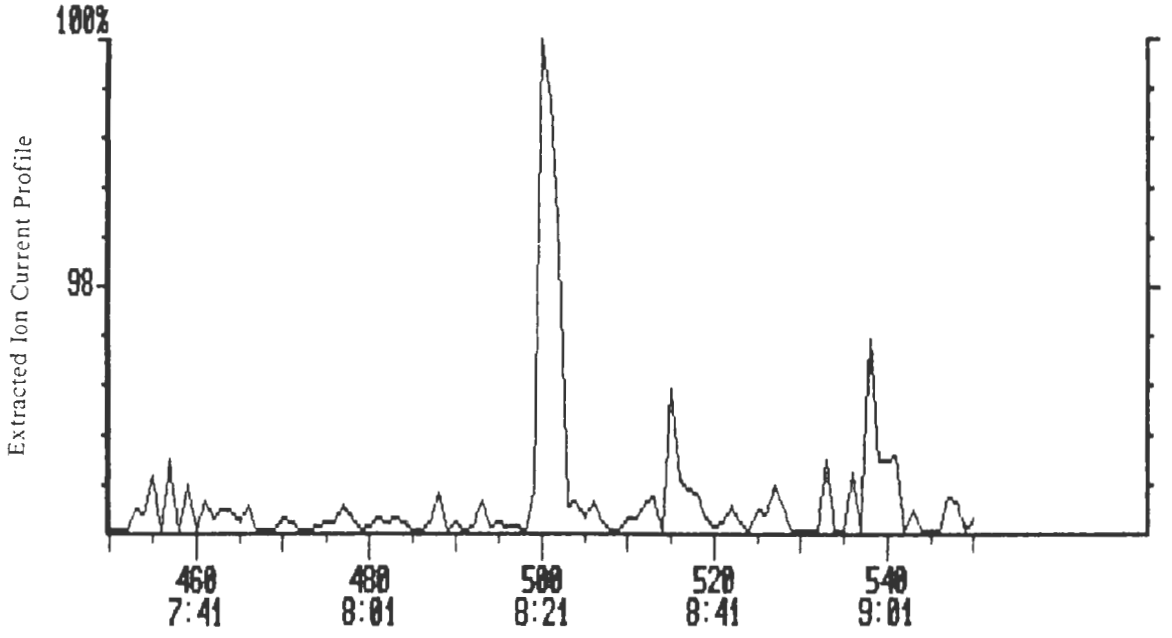

Figure 6. Extracted Ion Current Profile of Toluene d8 Molecular Ion from 20 ppt Standard Solution (100 picograms/5 mls water).

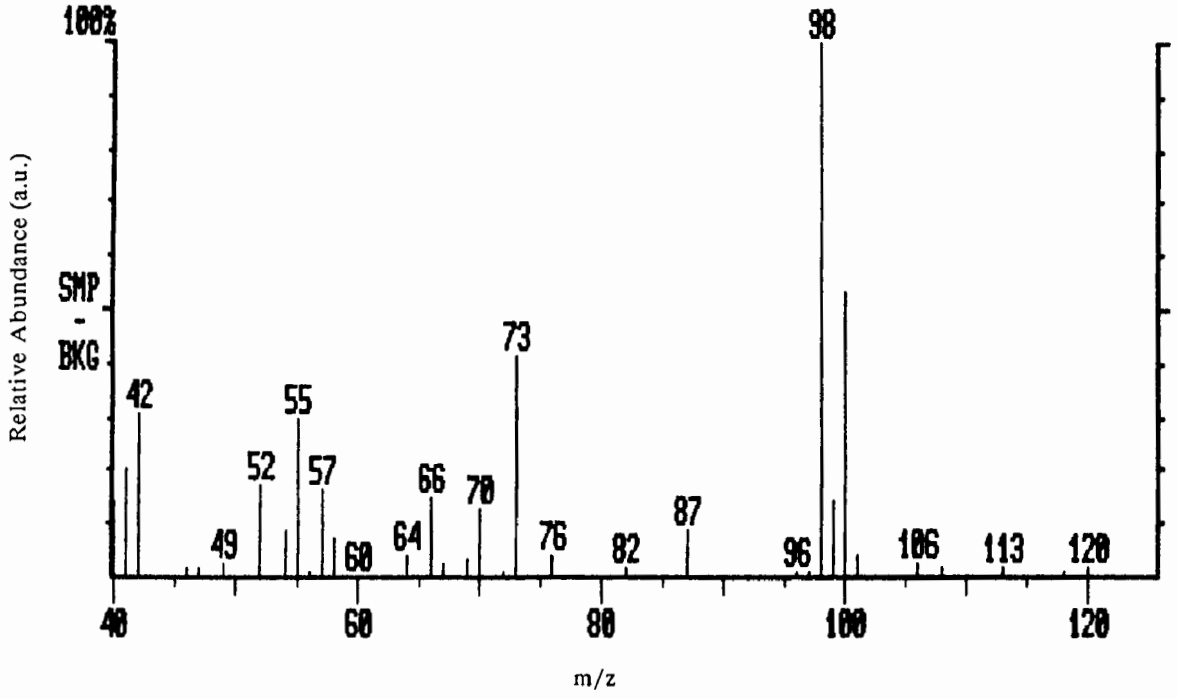

Figure 7. Background Subtracted Mass Spectrum Obtained from 20 ppt Standard Solution.

The Use of Field Gas Chromatography to Protect Groundwater Supplies

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Abstract

The Use of field instrumentation to detect the presence of volatile chemicals in the environment has undergone rapid and dramatic change in the past fifteen years. This paper will give a brief overview of this development and indicate some of the promising uses to which this equipment can be put in the service of groundwater protection.

The use of non-specific detectors to determine the presence of volatile organics in the environment is really a preliminary phase of field gas chromatography. Such instruments can determine low ppm levels of most volatiles and are now equipped with on-board data-logging capability.

Portable gas chromatographs are obviously more useful for identification and quantitation of mixtures of volatile organic contaminants. While there are many different instruments on the market, only a limited number meet the qualifications of true portability, ruggedness and high sensitivity that are frequently required in field studies. The capabilities and limitations of several field instruments will be described in some detail.

The remarkable sensitivity of some field gas chromatographs enables a field chemist to detect very low levels in ambient or vadose zone soil gas surveys (low ppb levels on a wt/wt basis). Also, the use of headspace analysis in the field provides ppt sensitivity for volatile organics in water. These techniques provide a field analyst with an ability to detect contamination in potable water even when levels are well below any need for health concerns.

The above techniques and equipment provide the basis for a truly preventive strategy to protect groundwater supplies. Some discussion of the various stages useful in developing and implementing a groundwater protection strategy will be discussed.

Introduction

Contamination of groundwater in the 1970's was primarily a matter of concern for bacterial, odorous or visible constituents deemed undesireable for potability. With the advent of sensitive detection equipment, attention began to focus on the presence of organic contaminants as well. It did not take long to realize that in most areas of the country groundwater contamination was principally caused by volatile, low-solubility solvents and hydrocarbons. Now it is widely acknowledged that the greatest threat to groundwater is from fuel leaks and other solvent losses to the ground and water table.

Total Organic Analysers

Field measurement of volatile organics at waste sites began historically with the use of portable total organic vapor detection equipment.(1) Typical examples of this equipment were the HNu PM 101, Century Systems OVA and the AID PID

analyser. Using either photoionization or flame ionization as the detection principle, these instruments were able to detect most volatile organics at about the 1-5 ppm range. Despite their obvious lack of specificity, such equipment is still widely used to detect the presence of volatile organics from fuel leaks, spills and improper disposal of solvents in pits, ponds and lagoons.(2-5)

Depending on the nature of the detector, some instruments were much more sensitive to certain classes of volatile organics. For example, the PID detector can detect about 1 ppm of benzene and chlorinated ethylenes, but only about 40 ppm of the chlorinated alkanes. In fact, some PID detectors of an early design (HNu and AID) had almost no sensitivity to chloroalkane molecules. This was based on a paper on photoionization theory as first proposed by Driscoll of HNu.(6) When Photovac introduced their total PID detector it was apparent that this detector, while still operating with lamps at 10.2 or 10.6 ev, could readily detect compounds with ionization potentials above the rated energy of the lamp. While no theoretical explanation of this vastly heightened sensitivity has been published, users have known for years that 111 TCA can be detected with the Photovac gas chromatograph.

About three years ago a significant advance on the total analysers appeared on the market in the form of data-logging capability. First came the "Smart Portable" from Thermo Environmental Instruments (formerly AID) which was followed closely by the Photovac "Microtip". Now field data could be stored in computer memory and dumped via an interface cable to a computer for later display in either tabular or graphic format.

Field Gas Chromatographs

The limitations of non-specificity soon led investigators to taking small field-designed gas chromatographs with them for field studies.(1,7) In the 1970's this usually meant either the Century OVA equipped with an ambient temperature gas chromatographic column or the isothermal unit by AID.(8) Both instruments had the advantage of careful attention to field needs: they were ruggedly designed, had a good track record for field usefulness and contained unique features that made for versatility in addressing a wide range of field problems. For Example, the AID unit could accept five different detectors in the same gas handling and electronics package. The Century unit contained features that allowed a field chemist to rapidly screen samples using a total analysis mode and at any time switch into the gas chromatographic mode when the detector showed the presence of volatile organics in the sample stream. (1)

Headspace Analysis

To demonstrate the usefulness of field chromatography, consider screening water samples by analysing headspace above collected drinking water samples. These samples can be rapidly screened by simply injecting 200 ul of headspace gas into the GC septum and observing the total response of the detector in the backflush configuration. When the backflush peak exceeds some low limit, the presence of ppb levels of dissolved volatiles is indicated.(1) At this point a sample can be injected into the septum using the GC configuration and rapid analysis with rather good resolution can be achieved for the typical list of volatiles found in contaminated ground water. Identification is performed by comparing peak retention time to known standard mixtures in the field. Quantitation is achieved by comparing the unknown peaks to known standards with identical retention times.(9) Where retention times are ambiguous, it is a simple matter to change the column and repeat the sample and standard to determine retention times again on a different packed column.

Soil Gas Analysis

In addition to field headspace analysis, a second powerful tool to aid in field investigations was the technique known as "Soil Gas Analysis". It was principally the remarkable sensitivity of the Photovac PID detector that made this method of vapor detection so widespread. Now it was possible to detect typical aromatics or chlorinated alkenes at the ppb (wt/wt) level in air.(10,11) With this increased sensitivity, many investigators began to determine the presence of volatiles from spills or underground tank leaks by the simple expedient of measuring their concentration in the vadose zone. (12-14)

Soil gas analysis, coupled with headspace analysis provides the field

investigator with tools to locate and track under-ground plumes or tank leaks and determine rapidly their impact on local ground-water. There are certain features of the Photovac GC which enable an experienced field analyst to do this work more effectively. First, the instruments are typically supplied with two columns so that the field analyst can not only perform reliable identifications using the two-column technique but he can also use a short column in one position to speed up screening of samples.(15) Second, the use of inexpensive zero-grade compressed air eliminates the typical problem of sample matrix interference with the early part of the chromatogram since the carrier gas is now identical to the usual sample matrix, ambient air or headspace above soil or aqueous samples. (12) Third, the use of an isothermal oven containing a wide-bore capillary column has greatly enhanced the resolution of field gas chromatography.

When discussing the necessity for high resolution in field work, this observation has been made frequently by experienced field investigators. Most field contamination incidents do not involve a large number of volatile compounds. In fact, it is more common to find two to five volatiles in the typical field study. Even in this situation, only one or two compounds predominate at a site and are the principal reason for the investigation and remediation.(16) Where a larger number of gas chromatographic peaks are found the experienced field chemist will immediately suspect the presence of some type of hydrocarbon fuel. In these cases it is much easier to continue the investigation by merely observing the pattern and relating it to a type of fuel (e.g. gasoline, diesel, jet fuel etc.). Even number two fuel oil has enough of a volatile fraction to be rather readily detected in underground tank leaks and spills.(17,18)

Groundwater Protection Strategy

Using some of the above observations and equipment, it is possible now to devise a practical strategy for groundwater protection which has much more of the "prevention" aspect than the "reactive" component so often found in environmental contamination incidents.(19)

The first consideration in a real protective strategy would be the unusual sensitivity of today's field gas chromatographs. For example, the Photovac has a sensitivity to volatiles in air in the range of parts per billion (pg/cc). (11) Consider a volatile like benzene dissolved in groundwater. The benzene will partition into the headspace of a closed vial with a distribution coefficient of about 1 at room temperature. (20) This means that if benzene was present in the aqueous phase at the ppb level, it is present in the vapor phase at the ppm level. But we have said that the Photovac PID is capable of detecting one ppb of benzene in air. It follows that when water concentrations are in the ppt range, it is still possible to detect them using the headspace technique.

Consider now the fact that many if not most public water supplies drawing on ground water are surrounded by test borings or other experimental wells often drilled when the original supply was under consideration for exploitation. Where this is not the case, it is a relatively simple matter to place such test wells in strategic locations upgradient of the supply wells so that they can be used as an early warning monitoring field. Instead of regular testing of production wells, these test wells can and should be regularly tested for possible signs of early incursion of contaminant plumes into the production well field. When subsequent tests show the presence of increasing levels (even at the ppt level) of volatiles like aromatics from gasoline leaks or chlorinated hydrocarbons from other sources, it is time to investigate potential sources. The mere fact of increasing levels, low though they may be at the present time, is clear evidence that the water supply is under threat of future higher contamination which might eventually render it unfit for consumption.

In the early investigation stage of this process, soil gas analysis often can and will play a key role. Establishing soil gas sampling profiles will often show clearly whence the contaminant plume originates. Because of the low levels of contamination present in the perimeter of the production well field, there is still adequate time to lay out a plan to find and stop the source of contamination. In this exercise great care must be taken that not only the source be removed, but also the contaminated soil beneath the source be remediated as soon and as efficiently as possible to stop any further discharge of contamination

to the aquifer. For this purpose there are now many alternatives. Among the most practical is vacuum extraction.(21, 22)

Vacuum Extraction Technique

Vacuum extractions is a method of choice for removal of volatiles from soil for several reasons. First, it addresses the problem at the point where volaltile organic contamination directly enters the aquifer. Second, vacuum extraction can rapidly and effectively remove precisely that fraction of the organic contamination which is most volatile and water soluble. In fact, volatility and water solubility of hydrocarbons go hand in hand. Hexane is about 13 ppm water soluble, octane is 0.6 ppm soluble and n-dodecane is only 4 ppb water soluble. Thus, spills involving fuels less volatile than number 2 fuel oil have very little tendency to dissolve in rain water and reach the aquifer. Even a product layer of these heavier hydrocarbon fuels will only contribute very low levels of organic contamination to the underlying groundwater. On the other hand, the very soluble aromatic fraction of gasoline, diesel and fuel oil has sufficient volatility that it is rapidly removed from the soil by vacuum extraction.

It has been the experience of many who use this removal technique of vacuum extraction that once the bulk of the more volatile constituents are removed from the spill site, normal bacterial action is enhanced and rapidly consumes the higher boiling constituents which cannot be removed from soil by vacuum extraction.(23) The combination of enhanced aeration and reduced volatile content in the soil is precisely the set of conditions which most favor natural degradation of the residual hydrocarbons from any fuel contamination situation.

Interceptor Well Installation

The last step in a prevention oriented clean-up strategy should be to install interceptor wells in the path of the groundwater contamination plume. For this purpose, it is imperative that careful depth profiling of contamination in the aquifer precede any attempt to install interceptor or barrier wells. The literature is replete with studies which indicate that groundwater plumes are usually confined in their vertical and horizontal dimensions by the natural geological features and the wide range of permeabilities of aquifer materials.(24) By careful placement of screens in the interceptor wells a contamination plume can be cost-effectively removed from the aquifer while permitting clean water from other parts of the aquifer to continue to supply the production well.

Field GC and Groundwater Protection

Routine field monitoring of the test wells and withdrawn and aerated water by a field chromatograph will insure that the water supply remains in a potable condition. At the same time vacuum extracted volatiles can be monitored to prevent air pollution. The use of real-time monitoring will prevent inadvertant environmental damage during the cleanup.

Spray Aeration Technique

Regarding techniques to aid in restoring the quality of water removed from the plume zone, I wish to discuss a method developed several years ago in Miami by Paul Wood.(25) Wood's technique was spray aeration as an alternative to the more conventional stripping towers. In his system, water is sprayed upward in a box the dimensions of which are not critical as long as about 14 ft in height is used. At the base of the box is a tank to receive the sprayed water. A second pump and spray head is placed in series in a second box to form a two-stage system of spray aeration. Wood measured an average 90% efficiency per aeration stage. It is then a simple matter to place enough stages in series to remove dissolved volatile organic contamination down to whatever level is satisfactory for recycling back into the aquifer.

Contrasting Wood's spray aeration with stripping towers, the following five points should be made. 1) Spray aeration is considerably less expensive to build and maintain. 2) Biofouling of the aeration system is almost non existent. Compare this to the continual buildup of large bacterial colonies in stripping towers. 3) Buildup of oxide films on the stripping tower coils is absent in the spray aeration box. 4) Concentration of removed volatiles is much higher in the natural draft exhaust than in the large volume-high flow rate coming from a stripping tower. 5) The highly concentrated exhaust stream of the aeration box is more easily captured and can be more cost-effectively

prevented from becoming an air pollution problem.

Field GC and Spray Aeration

Once more, the use of a portable gas chromatograph to monitor the performance of the vapor handling system is obvious. Data can be obtained in real time to monitor the efficiency of spray aeration using headspace analysis of inlet and finished water. Vapor concentration of the volatiles from the aeration tower discharge can also be monitored in real time to assist in designing and operating a vapor recovery system. Where vapor recovery is necessary, systems such as the CRS technique (26) will also benefit from ongoing field monitoring for optimization of performance.

Conclusions

In conclusion, we have seen that the availability of inexpensive, sensitive and rugged field gas chromatographs can make a substantial contribution towards a practical groundwater protection strategy. There are now many examples in the northeast where these ideas have been applied at the local municipal and county level.(17,19) With the limited resources of federal programs and the dwindling funding of state programs, this move towards local self-help is not only welcome but long overdue. Such a strategy, under the guidance and technical overview of state and federal programs promises to be a cost-effective way to insure the future purity of groundwater resources. There is also a growing awareness that such inexpensive techniques as field gas chromatography are sorely needed in many other countries where emerging environmental awareness cannot keep pace with limited budgets, but where a high level of dependence on groundwater is a practical necessity.

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FIELD SCREENING PROCEDURES FOR DETERMINING THE PRESENCE OF VOLATILE ORGANIC COMPOUNDS IN SOIL[1]

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ABSTRACT

Many field screening procedures have been used to detect the presence of volatile organic compounds (VOC) in soils but almost none have been documented and verified. Users of these procedures have not really known whether their objectives in screening were met. A reliable VOC screening procedure could significantly reduce the number of samples currently being submitted to laboratories, thereby reducing costs and improving site characterization. The Environmental Protection Agency's Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV) has therefore sponsored a research effort to evaluate and improve headspace methods for screening soils for VOC in the field. The research involved comparing several extraction procedures using soils from actual waste sites, and determining the agitation and mixing necessary to achieve equilibrium. Headspace was analyzed using a relatively simple portable gas chromatograph with a short column. The results were variable and show that several procedures should be attempted and the results evaluated before selecting a screening procedure.

INTRODUCTION

A recent study by the Office of Technology Assessment and the National Academy of Sciences has indicated that the U.S. Environmental Protection Agency (EPA) should be collecting 10 times as many samples as is the current practice under the Resource Conservation and Recovery Act (RCRA) and Superfund. Considering that the approximately 80 laboratories in EPA's Contract Laboratory Program (CLP) are already operating at full capacity, that there will be no extension of clean-up deadlines and no increase in funding, there will have to be major changes in the programs to increase efficiency. One way of increasing efficiency is to reduce the number of samples being analyzed under CLP protocols that show no or only very low contamination levels. At present, 80% and 90% of the samples submitted to CLP laboratories for analysis of volatile and semivolatile organics, respectively, fall in this category (personal communication, Dave Bottrell, EMSL-LV). One means of reducing the numbers of such samples is to screen samples prior to submission for CLP analyses. In theory, 80% of the volatile samples being submitted to CLP laboratories could be eliminated or the CLP productive capacity could be expanded by a factor of 5 if adequate screening methods for VOC were available.

Specific examples would be the Department of Energy's (DOE) Hanford Site and Savannah River Plant, where about 126 soil or sediment samples were collected and analyzed for volatile organics as part of the DOE Environmental Survey (1, 2). Of the samples collected, approximately 59% equaled or exceeded the Contract Required Detection Limit (CRDL) for one or more volatile compounds. Many of these samples were flagged with a B, indicating blank contamination.

Only 29% of the samples had positive detections above the CRDL and no B flag. Therefore, in theory, somewhere between 41% and 71% of the samples could have been rejected if screened in

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the field to CRDL limits. If it costs DOE $250-$500 for each VOC analysis, the savings could have been $13,000-$44,000 for analytical services, which does not include costs for data management and report preparation.

This research was designed to evaluate several headspace methods for screening soil samples in the field for the presence of VOC. The objective was to determine whether or not to send a sample to a CLP laboratory for gas chromatography/mass spectrometry (GC/MS) analysis.

BACKGROUND

The term "volatile organic compounds" refers to a group of chemicals that readily pass from a solid or liquid form to the gaseous phase (volatile) and are composed of carbon-based molecules (organic). Many VOC, toxins, carcinogens, or mutagens, are hazardous to the health of human and nonhuman organisms and are common environmental contaminants. Volatile organics (Table 1 for EPA list of VOC) are particularly significant because they constitute 15 of the 25 most frequently identified substances at 546 superfund sites (3).

A standard operating procedure for field screening of VOC could decrease the demand for CLP analyses, and at the same time result in improved characterization of hazardous waste sites. More samples could be collected and screened, thus increasing the size of the area characterized at a site, the intensity of that characterization, and maximizing the usefulness of those samples sent to the laboratory for analysis. Near real time data would permit the field sampler to redesign the sampling effort while still in the field to characterize "hot spots" and plumes. Other potential uses include preliminary input for risk-assessment studies, monitoring for efficacy of clean-up actions, and research on the transport of VOC in soils (4).

Laboratory Analysis of Soils. EPA Method 8240 (5) for VOC in soils uses an inert gas to purge (11 min.) VOC from a mixture of 5 g of soil and 5 mL of water into a Tenax[2] trap. The VOC is thermally desorbed and swept into the GC/MS for analysis. The "high-level method" involves extraction of 1 g of soil with 10 mL of methanol (including spiking solution) by hand shaking for 2 min., transfer of an aliquot of the extract to a purge and trap device, and analysis by GC/MS.

Laboratory Screening of Soils by Headspace Analysis. EPA Method 3810 (5) allows rapid screening of large numbers of samples. Ten g of soil are placed in two 125-mL septum-seal glass vials and one is spiked with calibration standards. The two vials plus a third containing only the standards are allowed to equilibrate in a 90°C water bath for 1 hour. Then, 2 mL of headspace is withdrawn and injected into a GC. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The sensitivity of the method depends upon the equilibria of VOC between the vapor and dissolved phases.

Field Screening. The most commonly used procedures for field screening soil samples involves analyzing headspace with an organic vapor analyzer such as a Photovac TIP, HNU PI-101 or Century Systems OVA-108. These instruments respond to flame or photo ionizable materials in air. They are very portable, easy to use but do require relatively large sample flow (0.25-1 L/min.) and have detection limits in the lower ppm range. Very little data have been published on their effectiveness as field screening devices for determining the presence of VOC in soils.

To improve detection limits and reduce sample size, some field personnel have used portable gas chromatographs which are up to 3 orders of magnitude more sensitive and only require headspace samples of 1-2 mL or even low μL quantities. Much more has been published on the use of such devices for screening and analysis of soil headspace in the field. Most screening methods for soil samples are based on headspace methods used for water samples.

Cheatham (6) effectively used a close support laboratory to provide rapid assessment of presence or absence of organic contamination. The study used two portable HNU 301 GCs equipped with a photo ionization detector (PID) connected in series with a flame ionization detector, or an electron capture detector. The method gave unacceptable resolution of the indicator compounds when no column packings were used. So, direct headspace and purge and trap techniques were studied using packed columns. Samples were prepared by sealing 10 g of soil in tared 100 mL serum bottles, which were placed in a 90° water bath and allowed to equilibrate approximately 1 hour, after which time the headspace gas was analyzed. Samples were submitted to a CLP laboratory for confirmation. The results were of sufficient quality to increase the accuracy of the site

[2] Mention of specific products and/or manufacturers in this document implies neither endorsement or preference, nor disapproval by the U.S. Government, any of its agencies, or EG&G Idaho, Inc., of the use of a specific product for any purpose.

TABLE 1. CLP ANALYTICAL DATA FOR TEST SOILS

TARGET COMPOUNDS	SAMPLE								
	KC804203 (µg/kg)	KC804214 (µg/kg)	LA61201 (µg/kg)	LA82301 (µg/kg)	LA82302 (µg/kg)	SR52702 (µg/kg)	Batch 1 (µg/kg)	G-4 (µg/kg)	PARK LOT (µg/kg)
Acetone	0	0	95	180	260	1200	0	0	0
Benzene	66	45	0	0	0	220	0	3	0
Bromodichloromethane	0	0	0	0	0	0	0	0	0
Bromoform	0	0	0	0	0	0	0	0	0
Bromomethane	0	0	0	0	0	0	0	0	0
2-Butanone	0	0	0	120	440	220	0	0	0
Carbon disulfide	0	0	0	0	0	17	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0	0	0
Chlorobenzene	0	0	0	0	0	0	0	0	0
Chloroethane	0	0	0	450	300	0	0	0	0
Chloroform	0	0	0	59	320	0	0	0	0
Chloromethane	0	0	0	0	0	0	0	0	0
cis-1,3-dichloropropene	0	0	0	0	0	0	0	0	0
Dibromochloromethane	0	0	0	0	0	0	0	0	0
1,1-Dichloroethane	0	0	0	510	1100	0	0	0	0
1,2-Dichloroethane	0	0	0	0	0	0	0	0	0
1,1-Dichloroethene	0	0	0	140	210	0	0	0	0
1,2-Dichloroethene (total)	24	26	0	6200	5800	10	0	0	0
1,2-Dichloropropane	0	0	0	0	0	0	0	0	0
Ethyl benzene	170	160	0	3	0	200	0	0	2
2-Hexanone	0	0	0	0	0	0	0	0	0
Methylene chloride	0	0	0	190	160	65	0	0	0
4-Methyl-2-pentanone	0	0	0	0	0	0	0	0	0
Styrene	0	0	0	0	0	0	0	0	0
1,1,2,2-Tetrachloroethane	0	0	0	0	0	0	0	47	138
Tetrachloroethene	0	0	0	0	0	40	5	2	36
Toluene	84	62	0	47	72	1300	0	1	0
trans-1,2-dichloroethene	0	0	0	0	0	0	0	0	0
trans-1,3-dichloropropene	0	0	0	0	0	0	0	0	0
1,1,1-Trichloroethane	0	0	62	160	1200	0	37	2	3
1,1,2-Trichloroethane	0	0	0	9	32	0	0	0	0
Trichloroethene	0	0	0	33	55	16	0	4	30
Vinyl acetate	0	0	0	0	0	0	0	0	0
Vinyl chloride	31	0	0	24	26	1100	0	0	0
Xylenes (total)	870	860	0	0	0	380	0	0	0
m-xylene	0	0	0	0	0	0	0	0	0
o-xylene	0	0	0	0	0	0	0	0	680

characterization and improve plume mapping. The quick turnaround time (~2 hours) allowed the field staff to better understand the site and select sampling locations using known data rather than "best guess", thus optimizing the limited project budget.

Clark, et al. (7) used a method developed by Spittler in which 10 mL of soil was added to a tared 40-mL VOA vial containing 20 mL of water and 20 µL of 2% mercuric chloride. In the lab, the vials were warmed to room temperature, shaken for 1 minute, and the headspace analyzed using a Photovac model 10A10 GC. Headspace sample volumes varied from 10 µL to 1 mL. The method was used to screen samples prior to GC/MS analysis to avoid overloading the GC/MS and to provide an indication of the presence or absence

of organics. Use of the method has reduced expensive GC/MS time and greatly reduced lost analysis time in the laboratory. When screening showed no organics, Clark thought it safe to assume that no priority pollutants were present at the ppb level, but that there might be exceptions.

Griffith (8) and Spittler et al. (9) spiked soil with three known VOC and placed aliquots of that soil in water. The soil/water mixture, contained in a glass vial, was placed in a water bath and allowed to equilibrate. The air above the water was then analyzed for VOC using a Century Systems Model 128 GC portable organic vapor analyzer. Results showed good recovery of the compounds introduced to the soil specimens. The method was tested under field conditions with duplicate samples sent to an independent laboratory. Comparison of field and laboratory results showed good correlation for the aromatic compounds under study.

OBJECTIVES

The objective of this research was to evaluate eight headspace procedures for determining the presence or absence of volatile organic compounds (CLP list) in soil at less than ppm detection limits. The intent was to be able to screen soils for the presence of VOC and to decide whether the samples need further analysis by CLP methods or could be considered clean, (i.e., contain insignificant levels of VOC.)

To achieve this objective, a variety of information was required. First, an extraction technique was needed that would maximize the concentration of volatile compounds in the headspace (more important for instruments without low detection limits), in a reasonable period of time, using practical field procedures. This extraction procedure should be fast (minutes), efficient (90% of equilibrium), and easily accomplished under field conditions. Secondly, a suitable analytical device was required for detection of VOC in headspace. A Photovac 10A10 field portable GC with a PID was selected although other instrumentation could be substituted.

APPROACH

This study was designed to build upon previous studies. While a quantitative approach is reasonable for water, many uncontrollable factors make soil headspace analysis much more complicated. This study was not designed to investigate theory but to develop empirical evidence on the utility and limitations of soil headspace analysis using "naturally" contaminated soils.

The first step was to compare a variety of soil extraction methods to maximize headspace concentration of volatiles when used on "naturally" (as opposed to spiked) contaminated soils. The second step was to determine the "best" method of achieving 90% of headspace equilibrium using the extraction method identified in Step 1. The third step (not conducted) would have been to use the screening procedure in the field on samples that would also be analyzed by GC/MS. The methods and procedures are compared to each other, as well as to a modified Method 3810 (5) in which the 10A10 was substituted for the prescribed analytical instrumentation.

TABLE 2. EXPERIMENTAL TREATMENTS

1	1 g of soil in 29.5 mL of water in a 40 mL VOA vial
2	5 g of soil in 27.5 mL of water in a 40 mL VOA vial
3	20 g of soil in 20.0 mL of water in a 40 mL VOA vial
4-6	same as above with a saturated NaCl solution
7	10 g of soil in a 125 mL septum cap bottle heated to 90°C in a water bath for 1 h.
8	5 g of soil in 5 mL of methanol followed of 0.6 mL of methanol to 29.5 mL of water in a VOA vial

STEP 1: COMPARISON OF SIX EXTRACTION METHODS TO ACHIEVE MAXIMUM HEADSPACE CONCENTRATION. The first tests were to determine maximum headspace concentration after vigorous agitation using the treatments listed in Table 2. The first treatment was suggested by Spittler and has been investigated by Griffith (8) and Spittler et al. (9). A salt solution was selected for testing since it is well known that adding salts to water samples can increase headspace concentration (salt also can be used as a nonhazardous preservative). Treatments 1-6 and 8 were planned around 10 mL of headspace in volatile organic analysis (VOA) vials. Treatments 7 and 8 were included for comparison to a standard laboratory screening procedure (Method 3810) (5) and a solvent extraction method (Method 8240, "high level" method which uses methanol as the extracting solvent) (5).

The importance of achieving maximum concentrations in the headspace was to improve the detection limit. While a GC/MS may not be as sensitive as the Photovac 10A10 to some compounds, a much larger sample can be actually analyzed by using the Tenax sorbent in Method 8240. Essentially all the VOC contained in the 5 g sample are placed in the instrument using Method 8240 while with headspace techniques, only a small fraction of the VOC are injected. Thus, to approach CLP detection limits for as many compounds as possible, the objective was to maximize static headspace concentration.

Obtaining fresh soil samples with good analytical data was a problem, so archived samples, known to have contained volatile contaminants, were used. Although the samples were quite old they still had detectable concentrations of VOC, so their age did not matter. The interest was in how efficient the extraction procedures were and how long it took to reach equilibrium (Step 2, below).

The headspace was sampled with standard syringes (2-40 μL injections) and analyzed using the Photovac 10A10 which had a 10.6 eV PID. Ultra zero air was used as the carrier gas. While it was not possible to specifically identify or quantify the VOC present, it was the relative concentration among the treatments that was important.

The sources of the soil samples are given below and the contaminants originally reported present are listed in Table 1. Some of the VOC have high ionization potentials and thus are difficult to detect with the 10.6 eV PID.

Batch 1	provided by EPA and collected from the Times Oil Superfund site in Tacoma, Washington.
G-4	laboratory column sample provided by EPA.
KC804203	subsurface soil sample collected from under a pond at the DOE's Kansas City Plant.
KC804214	very similar to the above.
LA61201	soil collected from a canyon wall at DOE's Los Alamos
2LA61202	National Laboratory.
LA82301	sludge samples from an inactive septic tank at DOE's Los
LA82302	Alamos National Laboratory.
Park Lot	EPA provided sample from Tacoma, Washington.
SR52702	subsurface soil sample collected from an oil basin at DOE's Savannah River Plant.

These bottles of soil were to be homogenized and cored to obtain the required aliquot which would be added to a tared vial containing the extractant. This proved impractical and a laboratory scoop was used to accomplish the transfer as quickly as possible. Vials were weighed again to obtain the actual amount of soil. Tap water was used for the extractions since headspace blanks showed no major interference. Extractant volume was measured using a graduated cylinder (most practical for field work).

If it is assumed that the VOC are totally desorbed from the soil in the extraction tests, the 20 mL soil test should result in a 29.5 times higher concentration in water than 1 mL soil (20 times more organic in about 1/3 less water). While salts in an aqueous medium will reduce the solubility of VOC in water thus increasing headspace concentration in a two phase system, their effect on headspace concentration in a soil-water-air equilibrium is not readily predictable.

To rapidly achieve static equilibrium, a Spex Mill was used to violently agitate the soil water mixture for 5 min. Headspace was analyzed using a 6 in. SE-30 column at ambient temperature. Because the treatment's effectiveness was expected to vary greatly for different soils and VOCs, it was deemed preferable to test several soils once rather than perform repeated tests on the same sample. The limited volume of each sample was also a factor. It was expected that violent shaking for 5 min. would approximate equilibrium (or at least be as rigorous as any practical field extraction technique).

STEP 2: TIME TO REACH EQUILIBRIUM. The second step was to minimize the time it takes for soil, water, and headspace to reach near equilibrium (goal was to obtain at least 90% of equilibrium conditions in headspace) using practical field procedures. "Naturally" contaminated soils were again used instead of spiked soils because a common criticism of spiking is "easy on, easy off".

The four extraction procedures listed in Table 3 were compared with 5 min. of agitation on the Spex Mill. The null hypothesis was that there is no difference in extraction rate among the treatments.

TABLE 3. EXTRACTION PROCEDURES

1	Violent hand shaking for 1 min.
2	Agitation in a sonic bath for 5 min.
3	Agitation using a vibrator for 1 min.
4	Combinations of the above and repeated analysis over time

STEP 3: COMPARISON TO CLP PROCEDURES. The final evaluation of the selected extraction procedure identified in Steps 1 and 2 was to be a field trial of the recommended procedures. This would involve making a decision as to whether volatiles were present or not and then evaluating those decisions based on laboratory analytical data (ideally using an improved Method 8240 where 5 g samples were sealed in the field and never opened in the laboratory). This step still needs to be conducted.

Water and NaCl blanks were also prepared and treated as samples. A benzene in water standard was run as a retention time and instrument response check. No significant attempts were made to identify contaminants or quantify concentrations. The number of samples analyzed varied, but ideally, duplicate samples with duplicate injections were used. Peak height data were measured and recorded by hand. The raw data were normalized before statistical analysis to eliminate differences in actual versus planned soil weight, attenuation setting, and volume of sample injected into the GC. An example of a normalized data set is presented in Table 4 which shows: sample number, treatment (D= duplicate sample), nominal amounts of soil and extractant used, and normalized peak heights with replicate injection data.

TABLE 4. NORMALIZED PEAK HEIGHT DATA FOR ANALYZED SAMPLES

TREATMENT, NOMINAL AMOUNT OF SOIL (g), and EXTRACT (mL)	NORMALIZED HEIGHT, PARK LOT SAMPLE (cm)									
	PEAK 1	PEAK 1R	PEAK 2	PEAK 2R	PEAK 3	PEAK 3R	PEAK 4	PEAK 4R	PEAK 5	PEAK 5R
Treatment Ambient										
5.0 0	0.78		0.35		1.02		0.00		2.04	
5.0 0 D	0.85		0.39		0.89		0.00		2.09	
Treatment H20										
5.0 27.5	0.69	0.91	0.25	0.69	1.23	2.26	0.00	0.00	1.79	1.86
5.0 27.5D	0.77	0.70	0.25	0.25	1.99	1.75	0.00	0.00	1.65	1.44
1.0 29.5	0.17	0.00	0.35	0.00	0.42	0.00	0.00	0.00	1.83	0.00
1.0 29.5D	0.21	0.25	0.18	0.69	0.46	0.71	0.00	0.00	1.49	1.59
Treatment Heated Bot										
10.0 0	20.16	21.09	7.44	12.40	21.71	23.26	0.00	0.00	10.85	10.85
10.0 0 D	20.73	26.97	8.23	12.21	23.57	29.81	0.00	0.00	12.49	15.05
Treatment Heated Wet										
10.0 10	14.59	18.16	11.02	13.62	20.75	27.24	0.00	0.00	3.89	4.86
10.0 10 D	9.70	14.71	3.44	7.51	12.52	18.78	0.00	0.00	3.76	5.01
Treatment Methanol										
5.0 5.0	1.23	1.07	0.61	0.61	4.70	4.09	0.61	0.51	1.84	1.58
5.0 5.0 D	0.53	0.00	0.42	0.00	5.56	0.00	0.53	0.00	2.12	0.00
Treatment NaCl										
5.0 27.5	0.91	0.81	0.40	0.30	1.28	0.99	0.00	0.00	1.78	0.99
5.0 27.5D	0.79	1.02	0.31	0.40	1.67	2.01	0.00	0.00	0.94	1.11
1.0 29.5	0.21	0.00	0.18	0.00	0.48	0.00	0.00	0.00	1.66	0.00
1.0 29.5D	0.29	0.00	0.41	0.00	0.53	0.00	0.00	0.00	1.57	0.00

RESULTS

Initial work showed major problems with conducting the standard laboratory procedures (treatments 7 and 8, heated headspace and methanol extraction). After some early eluting peaks, a massive tailing peak was produced which masked all other data. It was thought that the level of methanol in the headspace was interfering with the analysis and that condensed water may have produced a similar effect. Therefore, early experiments eliminated these treatments. Later, the procedures were tried again with better results in some cases.

Statistical Methods

The normalized data were analyzed with analysis of variance (ANOVA) techniques to test for statistically significant treatment effects (a treatment is a specific extracting method and soil amount combination). In many cases the effect of the amount of soil extracted was acceptably linear, but in some cases the relationship did not appear linear. Therefore the results were also analyzed with the soil amount log-transformed to better linearize the response. It was found that the log-transformation did not change the results. Because the treatments might have different effects when used on the different soil samples, the analyses were run separately for each sample.

For each experimental run with a given treatment, from four to six peaks were measured and used. There were high correlations among the peak heights for a given treatment, i.e. if a treatment affected peak 1 height, it similarly affected all the other peaks. To take advantage of this correlation, a Multivariate Analysis of Variance (MANOVA) was used to analyze the treatment effects. The soil amount was treated as a covariate in the analysis. The analyses were done using the GLM procedure of the SAS® (10) statistical software package.

For the experiments using soil types KC804203, KC804214, and LA61201, there were no true replicates analyzed, therefore it was impossible to directly estimate the experimental error or natural variation. Instead, subsampling or measurement error was used as a lower bound estimate of experimental error, and all analytical results for these samples should be viewed conservatively.

Statistical Results of Extraction Tests

Sample SR52702

Sample SR52702 was a subsurface soil sample collected from an oil basin at a depth of 6-12 in. Table 1 shows that the sample contained 12 VOC when analyzed by GC/MS for the DOE Environmental Survey. In appearance, the soil was heterogeneous with black specks and rocks. Because of concern for sampling error, the contents of the sample jar were dumped into a beaker, the rocks removed and the aggregate broken up as much as possible to improve homogeneity prior to subsampling. Some VOC were certainly lost in this process but there were enough left to use for testing.

The MANOVA involved comparison of treatments 1-6 (treatments 3 and 6 used 10 g instead of the planned 20 g of soil due to limited amount of soil available) and showed that the NaCl and water treatments did not result in significantly different peak heights (Wilks' Lambda F=2.2, p=0.23)[3]. However, the amount of soil (1, 5, and 10 g) had a statistically significant effect on the peak heights, with larger soil amounts resulting in higher peaks (Wilks' Lambda F=12.8, p=0.01). The height of the 10 g peaks were from 1.6 to 3.4 times higher than the 1-g water extract peaks.

Sample Batch 1

The Batch 1 sample was collected by EMSL-LV personnel from the Times Oil superfund site in mid March, 1989. The sample was very dense, black, and contained small pebbles. The chromatograms showed 2 large peaks of very early eluting compounds (possibly including vinyl chloride). Because they were so large and early, they could not be separated and measured accurately with the 6-in. column and only the later 4 peaks were analyzed.

The analysis of treatments 1-6 showed that the NaCl and water extractions did not result in significantly different peak heights (Wilks' Lambda F=3.2, p=0.14). The amount of soil used had a statistically significant effect on peak heights, with larger soil amounts resulting in higher measured peaks (Wilks' Lambda F=80.6, p=0.0004). The 20-g samples produced peaks 15 to 48 times larger than the 1-g water extract samples. It is interesting to note that the effect the amount of soil had depended on the extractant used.

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[3] The Wilks' Lambda statistic tests whether the treatments have significantly different effects on the measured peak heights. The p-values given are the probability that the observed results are simply due to chance, and not due to treatment effect.

Sample KC804203

The experiment included all eight treatments (data for the 20-g NaCl treatment was lost) but the methanol extract was diluted 100:1 instead of 50:1. The analysis (5 peaks) showed that the different extraction methods resulted in significantly different peak heights (Wilks' Lambda F=5.6, p=0.003). The water extract gave consistently higher peaks, with NaCl second highest. The methanol extracting and the heated dry treatment gave generally lower peaks than the other two treatments.

The amount of soil used also had a statistically significant effect on the peak heights (Wilks' Lambda F=157, p=0.0001). For all the peaks, the greater the amount of soil used, the higher the measured peak, i.e. there was a positive correlation between amount of soil used and the peak height. For the water extraction, the 20-g extract increased peak heights from 2 to 6 times compared with the 1-g extracts. For the five peaks measured, methanol produced from 0.2 to 0.5 times the response compared to the 1-g water extract. Methanol appears to be relatively more efficient in recovering the late eluting peaks (higher boiling compounds). For the heated dry bottle, response varied from 0.5 to 0.8 times the comparable peaks height for the 1-g water sample.

Sample KC804214

This experiment included all 8 treatments but there were no replicate injections or duplicate samples. Therefore the statistical tests were not very powerful or accurate. Additionally, the results for the 5- and 20-g water extraction appear to be outliers (peak heights for both treatments were very similar, contrary to the NaCl data). The analysis (6 peaks) using all the data showed that the extraction methods did not result in significantly different peak heights ($p > 0.3$). Also, the amount of soil used did not seem to affect peak heights ($p > 0.1$). However, visual interpretation of the data, excluding the outliers, showed results very similar to sample KC804203.

Sample LA61201

The experiment included all 8 treatments but about 20 g of soil was used for the heated bottle (Treatment 7) instead of the planned 10 g (the normalizing program therefore cut peak heights in half for data analysis). The analysis of all 6 peaks showed a fairly significant extraction treatment effect (Wilks' Lambda F=11.9, p=0.03). The results were mixed though, with water giving very much higher peak 2 readings, and NaCl giving somewhat higher peak 6 measurements. Overall, water and NaCl extracts produced comparable peak heights for the same soil amount, methanol produced smaller early eluting peaks than the 1-g water or NaCl extractions, but the last peak was 2.9 times larger. The greatest peak heights were achieved using the heated dry bottle (11-66 times than the 1-g water extract).

The amount of soil used also had a very significant effect on the peak heights (Wilks' Lambda F=2678, p=0.0001). For all the peaks, the greater the amount of soil used, the higher the measured peak. Peak heights were from 4-12 times higher using 20 g of soil than 1 g.

Sample LA82301

The experiment involved only treatments 1,2,4, and 5 (1- and 5-g extractions using water and NaCl) because of the small soil volume available. The analysis of 7 peaks showed that the different extraction methods resulted in significantly different peak heights (Wilks' Lambda F=240.5, p=0.05). The NaCl extraction gave consistently higher peaks than the water (up to about 3 times greater peak height).

The amount of soil used also had a very significant effect on the peak heights (Wilks' Lambda F=3304, p=0.01). The 5-g treatments generally produced 3-5 times higher peaks than the 1-g water treatment.

Sample G-4

The analysis of data (4 peaks) from treatments 1-6 showed no significant difference in peak heights for the water and NaCl extractions (Wilks' Lambda F=2.1, p=0.2). The amount of soil used had a statistically significant effect on peak heights for the water treatments, with larger soil amounts resulting in higher measured peaks (Wilks' Lambda F=31.7, p=0.001). The 20-g water extraction peaks were 2-6 times larger than the 1-g peaks. It was interesting that this soil effect was not apparent with the NaCl extractant. These data, however, are suspect since they had to be reanalyzed several days after initial extraction due to analytical problems.

Sample PARK LOT

The experiment included treatments 1, 2, 4, 5, 7, and 8 (the 20-g water and NaCl treatments were omitted due to limited soil volume available) plus a modification of the heated bottle (Treatment 7) technique (10 mL of water added to bottle). Additionally, a 5-g sample was placed in a VOA vial at ambient room temperature. The analysis of data (Table 4) from treatments 1-6 showed no statistically significant differences between the water and

NaCl extractions (Wilks' Lambda F=0.95, p=0.6). However, the heated bottle (treatment 7, listed as "Heated Bot" in Table 4) produced the greatest peak heights followed by the same treatment with 10 mL of added water ("Heated Wet" in Table 4), and methanol. Interestingly, the VOA vial with 5 g of dry soil at ambient temperature ("Ambient B" in Table 4) provided greater peak heights than the 1-g water and NaCl extractions.

The amount of soil (1 versus 5 g) did somewhat affect the measured peak heights, with larger soil amounts resulting in higher peaks (Wilks' Lambda F=90, p=0.002).

Statistical Results of Equilibrum Tests

Sample 2LA61201

Step 2 experiments for this soil included the treatments in Table 3. Additionally, since Step 1 data on treatments 7 and 8 were limited (heated bottle and methanol) those treatments were included to supplement Step 1 data.

Sample 2LA61201 was extracted using hand shaking, the Spex Mill, vibration and sonication as well as the same treatments over a period of 2+ hours. Statistical analysis of the data showed there were some differences in the treatment effects (Wilks' Lambda F=4.2, p<0.001), but only for 2 of the 5 peaks analyzed. To help compare treatment effects, both Duncan's multiple range test and Scheffe's multiple comparison were calculated at the 0.05 significance level. While there were some differences, no treatment clearly emerged as superior. Although not tested statistically, it appears that initial extraction using the Spex Mill is more efficient since peak heights increased less over time that with the other treatments. The Spex Mill initially provided the highest average peak height for all 5 peaks; up to 2-3 times higher in some cases. After a couple of hours, all treatments show very similar results.

The heated dry bottle extraction produced much greater peak heights than the reference method of 1 g of soil extracted by the Spex Mill. The response was about 8-34 times greater for the 5 peaks analyzed. A methanol extraction treatment was also conducted but the results were unusable due to interferences from the methanol.

Sample LA82302

The Step 2 treatments for this soil included hand shaking for 1 min., Spex Mill shaking for 5 min., sonication for 5 min. after hand shaking for 1 min., and vibration treatment for 1 min. after hand shaking for 1 min. The samples from the hand shaking and sonication treatments were shaken again by hand after 3 hours and reanalysed. The MANOVA results indicated that there were some significant differences (Wilks' Lambda F=2.9, p=0.04).

The individual ANOVA analysis for 3 of the 4 peaks analyzed showed no statistically significant differences in treatment effects in spite of some peaks being twice the size of those in other treatments. For one peak, the initial Spex Mill treatment was superior all other treatments (p=0.006). For all peaks, the vibration treatment produced the lowest peaks. No other obvious patterns appeared that would suggest one treatment was better than the others.

Both a heated bottle and methanol treatment were run at the same time to supplement the Step 1 data. The methanol results showed gross interferences from the methanol even though a fresh bottle of HPLC grade methanol was used. The heated bottle treatment produced significantly greater peak heights for all peaks than any of the treatments discussed above (p<.01). Compared to the initial hand and Spex Mill extractions, the heated bottle method produced 5-13 times higher peaks than the initial 1-g soil sample extracted with water using the Spex Mill.

CONCLUSIONS

The comparison of six treatment combinations of soil amount and extracting solution (water or NaCl), showed variable results. While NaCl extractions produced significantly larger peaks for one test sample, that was the only data demonstrating clear superiority. Even then, the differences were only a factor of about 3. The conclusion is that water is generally a superior extractant to the saturated NaCl solution for soil headspace analysis.

The tests of the effect of extracted soil amounts, clearly showed that larger quantities of soil extracted into the same volume of headspace produces higher headspace concentrations. For the 5- and 20-g soil samples, one would expect a 5 and 29 fold increase in headspace concentration over a 1-g sample if all soil contaminants were transferred to the water (ideal but not possible). Table 5 shows the effect of sample size on VOC headspace concentration, by sample. The 20 g sample produced from 3.6 to 24 times greater response than the 1 g sample extracted with water using the Spex Mill. Overall, the increase was about a factor of 6.5 improvement calculated using a geometric mean. The 5 g soil samples provided between 1.8 and 7.8 times greater response with a geometric mean of 3.3. While increased soil

amounts do increase headspace concentration, the increase is usually not as great as theoretically possible.

The methanol extraction data shown in Table 6 shows that methanol is sometimes superior (factor of 4.2) and sometimes inferior (factor of 0.3) to the water extraction using 1 g of soil and the Spex Mill. Overall, there was little reason to select methanol over water (geometric mean = 1.1). The disadvantages of methanol extraction for field screening are that it involves the transport, use, and disposal of a hazardous chemical, and requires the additional field steps of quantitatively transferring an aliquot to a VOA vial after settling. Methanol may also interfere with analysis on some instruments and it may be difficult to obtain clear supernatant from some samples. The advantages are that the extraction step is quick, the sample in methanol should be relatively stable, composite samples can be collected, the same sample used for field screening can be sent to a laboratory for analysis, and the extraction method is based on a standard EPA analytical procedure.

Dry heated head space analysis method using 10 g of soil was sometimes far superior to the 1-g soil/Spex Mill treatment for maximizing peak heights. As shown in Table 6 the relative headspace concentration for the heated bottle treatment compared to the 1 g water extraction varied from 0.7 to 48 times greater, with a geometric mean of 6.8. The disadvantages of the heated bottle approach are the time requirement of heating for 1 hour, the need for a water bath (requiring electrical power) and possible analytical problems related to condensed water in the analytical device. Some GC columns do not work well with saturated vapor samples.

For extracting samples in the field, violent shaking such as provided by the Spex Mill is efficient but not possible without a power supply. Hand shaking for 1 min. seems slightly inferior initially, but with time, headspace concentration becomes the same as with Spex Mill extraction.

The overall recommendation is that several procedures should be evaluated and compared using site specific contaminated soils. A standard operating procedure that helps a user select the best screening procedure for the intended use should be developed. Also, documentation on the effectiveness of screening procedures versus standard quantitative methods is needed so that screening effectiveness can be evaluated including a rough estimation of detection limits.

TABLE 5. RELATIVE HEADSPACE CONCENTRATION OF VOC for 20, 5, and 1 g soil samples extracted with water

Sample Size	Batch 1	G-4	KC804203	KC804214	LA61201	LA82301	Park Lot	SR52702	Arithmetic Mean	Geometric Mean
20 g	24	3.6	3.6	5.1	7.2	--	--	2.4*	8.7	6.5
5 g	7.8	3.5	1.8	5.6	2.9	3.8	2.3	1.8	3.7	3.3
1 g	1	1	1	1	1	1	1	1	1	1

*Sample size was 10 g., not included in means.

TABLE 6. RELATIVE HEADSPACE CONCENTRATION OF VOC for Heated Bottle and Methanol Treatment Compared to 16 Soil/Sample Extracted Water

SAMPLE	KC804203	KC804214	LA61201	2LA61201	LA82302	PARK LOT	Arithmetic Mean	Geometric Mean
Heated Bottle	0.7	2.0	28	26*	7.6	48	17	6.8
Methanol	0.3	1.6	0.8	--	--	4.2	1.7	1.1
1 g soil/H_2O	1	1	1	1	1	1	1	1

*Not included in means.

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DISCUSSION

RANDY GOLDING: What is the correlation between what might be perceived as standard accepted analytical practices and the results you get from these screening methods. What's their predictive value and which one is the best?

ALAN CROCKETT: I don't really have a good answer for you, I'm afraid. How predictive are they? That was to be step three which was never completed. I don't know right now how well the CLP data would correlate with the field screening data. That's why I'm asking people right now, who have the interest in following these procedures, to analyze their samples two different ways and publish the results.

THOMAS SPITTLER: Just one brief response to that, because we had used this water extraction for volatiles in soil for quite a few years in our own region, and I've been in touch with other people who have been doing it, particularly some of the people doing research at the University of Connecticut. They have found extremely good reproducibility and very high sensitivity in extracting volatiles out of soil. The only thing is most of this was done with synthetic soil samples. There's a group at the Cold Regions Research Lab in Hanover, New Hampshire, who have also done spiking of soil samples, and had done some very nice work on extracting volatiles from soil samples. Tom Jenkins is one of the two. I think he's got some very interesting insights on this problem of volatiles in soil analysis. It's a major issue because so many people are out there digging up tanks, trying to comply with state regulations on how much is too much contamination in soil. An incredible amount of lousy data is coming out of samples collected, shipped off to laboratories, and reported back months later only to find that what was obviously there when the sample was collected is no longer there when the sample is analyzed. That's a lesson in biodegradation and vapor loss, among other things.

COMPARISON OF FIELD HEADSPACE VERSUS FIELD SOIL GAS ANALYSIS VERSUS STANDARD METHOD ANALYSIS OF VOLATILE PETROLEUM HYDROCARBONS IN WATER AND SOIL

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ABSTRACT

Twelve sites in the state of Iowa were evaluated for hydrocarbon contamination associated with the use of existing underground storage facilities. Using driven probe technology; soil gas, groundwater and/or soil samples were taken from each sampling location. Each soil gas, groundwater and soil sample was analyzed on location using a field mobilized gas chromatograph. Each groundwater and soil sample was also analyzed by a contracted laboratory using the appropriate standard method. Correlations between the various analytical approaches were examined.

The correlation between field analytical results and the laboratory analytical results was 0.87 over four orders of magnitude for twenty-five samples. The correlation for toluene in soil gas samples versus toluene in soil samples was 0.81 over five orders of magnitude.

INTRODUCTION

In order to examine the utility of soil gas investigations and field analyses in evaluating the contamination at underground storage tank (UST) sites, temporary approval was granted to Tracer Research Corporation (TRC) to apply soil gas methods at several UST sites in Iowa. The results of the soil gas investigations were to be compared to analyses of soil and water samples collected at the same time. The results of this comparative study were to be used to establish appropriate action criteria for soil gas investigations used at UST site audits for insurance purposes.

BACKGROUND

The background section consists of two parts. First a brief description or definition of soil gas methodology and second a discussion of how the instrument that makes the total petroleum measurement (TPHC) works. This background is very important in understanding the first part of the results section.

Shallow Soil Gas Investigation - Methodology

Shallow soil gas investigation refers to a method developed by TRC for investigating underground contamination from volatile organic chemicals (VOCs) such as industrial solvents, cleaning fluids and petroleum products by looking for their vapors in the shallow soil gas. The method involves pumping a small amount of soil gas out of the ground through a hollow probe driven into the ground and analyzing the gas for the presence of volatile contaminants. The presence of VOCs in shallow soil gas indicates the observed compounds may either be in the ground near the probe or in groundwater below the probe. The soil gas technology is most effective in mapping low molecular weight halogenated solvent chemicals and petroleum hydrocarbons possessing high vapor pressures and low aqueous solubilities. These compounds readily partition out of the groundwater and into the soil gas as a result of their high gas/liquid partitioning coefficients. Once in the soil gas, VOCs diffuse vertically and horizontally through the soil to the ground surface where they dissipate into the atmosphere. The contamination acts as a source and the above ground atmosphere acts as a sink, and typically a concentration gradient develops between the two. The concentration gradient in soil gas between the source and ground surface may be locally distorted by hydrologic and geologic anomalies; however, soil gas mapping generally remains effective because distribution of the contamination is usually broader in areal extent than the local geologic barriers and is defined using a large data base. The presence of geologic obstructions on a small scale tends to create anomalies in the soil gas-groundwater correlation, but generally does not obscure the broader areal picture of the contaminant distribution.

Soil gas contaminant mapping helps to reduce the time and cost required to delineate underground contamination by volatile contaminants. The soil gas investigation does this by outlining the general areal extent of contamination.

How the Hydrocarbon Measurement is Made

To illustrate some of the advantages of soil gas hydrocarbon measurements, representative chromatograms produced during the comparative study at selected Iowa UST sites are presented with a brief explanation.

A chromatogram is a graph of the analytical signal output by the chromatograph. When a sample is analyzed using a gas chromatograph, it is injected into a tube through which a gas is flowing towards a detector. The sample is carried toward the detector by the flowing gas stream. Between the injection point and the detector is a long tube called a column that contains a powder or fluid that absorbs substances like gasoline vapors. Gasoline is a mixture of many different substances that are very similar. The column is most absorptive to substances with high boiling points such as xylenes (280 degrees F) and less absorptive to substances with low boiling points such as methane (-260 (below zero) degrees F). Thus low boiling or very volatile substances like methane flow rapidly through the column and high boiling or not so volatile substances like xylenes are retarded by the column and flow through the column more slowly.

When a substance exits from the column and is carried by the gas stream into the detector, it is burned in the flame (flame ionization detector) and an electrode senses an increase in combustible

substances in the flame and the result is an increase in voltage at the signal output.

The chromatogram is a plot of this voltage versus time. When nothing combustible is entering the detector the recorder draws a straight line (baseline) along the left side of the page. When a combustible substance such as methane enters the detector, the increase in voltage from the chromatograph causes the recorder pen to move until the substance is completely burned. The recorder pen then returns and stays at the baseline until the next combustible substance enters the detector. This triangular shaped deflection is called a peak. The point in time that the peak occurs indicates what kind of substance it is and the time is printed on the chromatogram next to the peak. The distance that the pen moves or how tall the peak is indicates how much of the substance entered the detector.

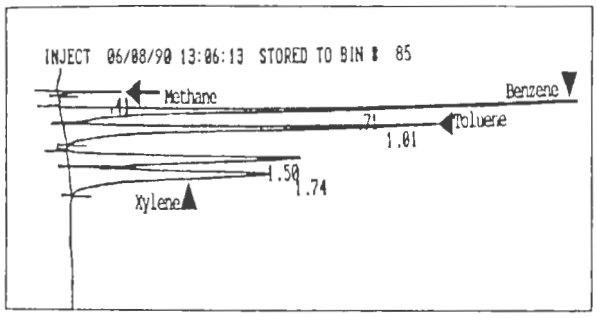

Figure 1. Standard mixture for calibration.

Figure 1 is a chromatogram of a mixture of methane, benzene, toluene, and xylene, all substances found in gasoline and most other petroleum fuels. Note the exit time for toluene is 1.01 minutes.

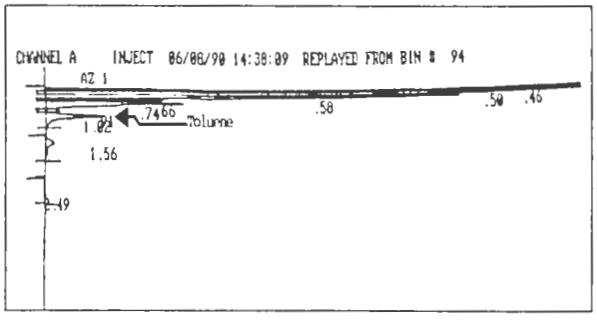

Figure 2. Gasoline vapors from a gasoline tank. NOTE: Most of the components of gasoline exit before toluene.

Figure 2 is a chromatogram of gasoline vapors taken from a gasoline tank.

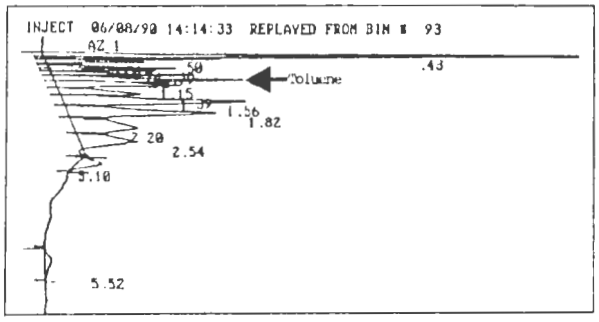

Figure 3. Kerosene vapors from a kerosene tank. NOTE: Most of the components exit after toluene. Kerosene is not as volatile as gasoline.

Figure 3 is a chromatogram of kerosene vapors taken from a kerosene tank.

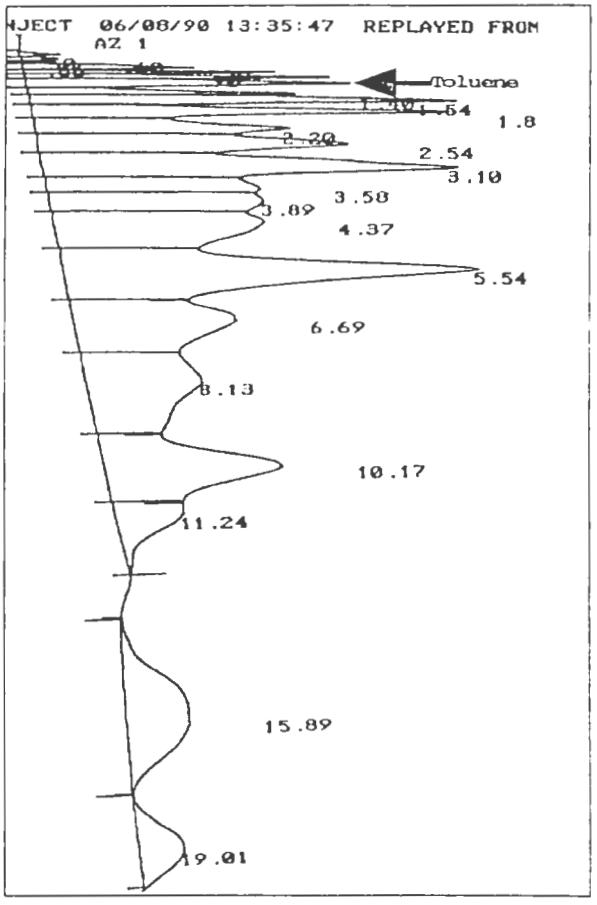

Figure 4. Diesel vapors from a diesel tank. NOTE: Almost all components exit after toluene. However, there are some volatile substances in diesel.

Figure 4 is a chromatogram of diesel vapors taken from a diesel tank. Only a small portion of the constituents of the diesel vapors exit before toluene.

Kerosene is more volatile than diesel and gasoline is more volatile than kerosene. These figures illustrate that the more volatile substances exit the column first and the less volatile substances exit the column later. They also serve to illustrate that diesel contains a substantial amount of relatively volatile substances.

PROCEDURES

The following describes in a general way the procedures used to acquire the data in this study.

Equipment

Tracer Research Corporation utilized a one-ton analytical field van that is equipped with one gas chromatograph and two computing integrators. In addition, the van has two built-in gasoline powered generators that provide the electrical power (110 volts AC) to operate all of the gas chromatographic instruments and field equipment. A specialized hydraulic mechanism consisting of two cylinders and a set of jaws was used to drive and withdraw the sampling probes. A hydraulic hammer was used to assist in driving probes past cobbles and through unusually hard soil.

Soil Gas Sampling Procedures

Sampling probes consist of 7-14 foot lengths of 3/4 inch diameter hollow steel pipe that are fitted with detachable drive tips. Once inserted to the desired depth, the above-ground end of the sampling probes were fitted with an aluminum reducer and a length of polyethylene tubing leading to a vacuum pump. Gas flow is monitored by a vacuum gauge to insure that an adequate flow is obtained.

To adequately purge the volume of air within the probe, 2 to 5 liters of gas is evacuated with a vacuum pump. During the soil gas evacuation, samples are collected in a glass syringe by inserting a syringe needle through a silicone rubber segment in the evacuation line and down into the steel probe. Ten milliliters of gas are collected for immediate analysis in the TRC analytical field van. Soil gas is sub-sampled in volumes ranging from 1 uL to 2 mL, depending on the VOC concentration at any particular location.

Soil Sampling Procedures

Soil samples were collected by pushing the soil gas probes into the ground without the detachable drive point, thus allowing soil to accumulate in the probe. The soil was removed by inserting a one-half inch diameter pipe through the probe to push the soil out. Approximately 10 grams of soil and 10 mL of water were placed in a 40 mL teflon sealed VOA bottle leaving approximately 20 mL of headspace. Each VOA was then shaken vigorously for 30 seconds before the headspace was analyzed. This allows for the desorption of volatile compounds into the headspace of the vial. Headspace vapor is sub-sampled in volumes ranging from 1 uL to 2 mL.

Groundwater Sampling Procedures

Groundwater samples were collected by driving the hollow probes with detachable drive points below the water table. Once at the desired depth the probe was withdrawn several inches to permit water inflow into the resulting hole. Once inserted into the ground, the above-ground end of the sampling probes were fitted with a vacuum adaptor (metal reducer) and a length of polyethylene tubing leading to a vacuum pump. A vacuum of up to 24 inches of mercury was applied to the interior of the probe and open hole for 1 to 15 minutes or until the water was drawn up the probe. The water thus accumulated was then removed by drawing a vacuum on a 1/4 inch polyethylene tube inserted down the probe to the bottom of the open hole. Loss of volatile compounds by evaporation is minimized when water is induced to flow into the very narrow hole, because it can be sampled with little exposure to air. The polyethylene tubing was used once and then discarded to avoid cross-contamination.

Groundwater samples were collected in 40 mL VOC vials that are filled to exclude any air and then capped with Teflon-lined septum caps. Groundwater samples were analyzed by injecting headspace in the sample container created by decanting off approximately half of the liquid in the bottle. Headspace analysis is the preferred technique when a large number of water samples are to be performed daily. The method is more time efficient for the measurement of volatile organics than direct injection. Depending upon the partitioning coefficient of a given compound, the headspace analysis technique can also yield greater sensitivity than the direct injection technique.

Field Analytical Procedures

A Varian 3300 gas chromatograph, equipped with a flame ionization detector (FID), was used for the soil gas, soil, and groundwater analyses. Compounds were separated by a 6' by 1/8" OD packed column with OV-101 as the stationary phase at 100°F in a temperature controlled oven. Nitrogen was used as the carrier gas.

Hydrocarbon compounds detected in soil gas, soil, and groundwater were identified by chromatographic retention time. Quantification of compounds was achieved by comparison of the detector response of the sample with the response measured for calibration standards (external standardization). Instrument calibration checks were run periodically throughout the day and system blanks were run at the beginning of the day to check for contamination in the soil gas sampling equipment. Air samples were also routinely analyzed to check for background levels in the atmosphere.

The GC was calibrated for soil and groundwater headspace analysis by decanting 10 to 20 mL off of the known aqueous standard so as to leave approximately the same amount of headspace that is in the field samples. The bottle is then resealed and shaken vigorously for 30 seconds. An analysis of the headspace in the vial determines the Response Factor (RF) which is then used to estimate soil or groundwater concentrations.

Detection limits for the compounds of interest are a function of the injection volume as well as the detector sensitivity for individual compounds. Thus, the detection limit varies with the sample size. Generally, the larger the injection size the greater the sensitivity. However, peaks for compounds of interest must be kept within the linear range of the analytical equipment. If any compound has a high concentration, it is necessary to use small injections, and in some cases to dilute the sample to keep it within linear range. This may cause decreased detection limits for other compounds in the analyses.

The detection limits for the selected compounds vary depending on the conditions of the measurement, in particular, the sample size. If any component being analyzed is not detected, the detection limit for that compound in that analysis is given as a "less than" value (e.g. ug/L). Detection limits obtained from GC analyses are calculated from the current response factor, the sample size, and the estimated minimum peak size (area) that would have been visible under the conditions of the measurement.

Laboratory Analytical Procedures

Groundwater samples were analyzed using analytical protocols outlined in EPA methods 5030 and 8015. A purge and trap step is used to strip the hydrocarbons out of the water.

Soil samples were analyzed by a method stipulated by the Iowa Department of Natural Resources referred to as OA-1. The method is substantially derived from EPA methods 5030 and 8015. Methanol is used to extract hydrocarbons from the soil. The Methanol extract is then diluted at least 25 to 1 in reagent water. The water is then analyzed in essentially the same manner as the groundwater samples.

Quality Assurance/Quality Control Procedures

Tracer Research Corporation's normal quality assurance procedures were followed in order to prevent any cross-contamination of soil gas, soil, and groundwater samples.

- Steel probes were used only once during the day and then washed with high pressure soap and hot water spray or steam-cleaned to eliminate the possibility of cross-contamination. Enough probes were carried on each van to avoid the need to reuse any during the day.
- Probe adaptors (TRC's special design) were used to connect the sample probe to the vacuum pump. The adaptor was designed to eliminate the possibility of exposing the soil gas stream to any part of the adaptor. Associated tubing connecting the adaptor to the vacuum pump was replaced periodically as needed during the job to insure cleanliness and good fit. At the end of each day the adaptor was cleaned with soap and water.
- Silicone tubing (which acts as a septum for the syringe needle) was replaced as needed to insure proper sealing

around the syringe needle. The tubing does not directly contact soil gas samples.

- Glass syringes were used for one sample only per day and were washed and baked out at night.
- Injector port septa through which samples were injected into the chromatograph were replaced on a daily basis to prevent possible gas leaks from the chromatographic column.
- Analytical instruments were calibrated each day by analytical standards from Chem Service, Inc. Calibration checks were also run after approximately every five sampling locations.
- Sub-sampling syringes were checked for contamination prior to sampling each day by injecting nitrogen into the gas chromatograph.
- Prior to sampling each day, system blanks were run to check the sampling apparatus (probe, adaptor, and 10 cc syringe) for contamination by drawing ambient air from above ground through the system and comparing the analysis to a concurrently sampled ambient air analysis.
- All sampling and sub-sampling syringes were decontaminated each day and no such equipment was reused before being decontaminated. Microliter size sub-sampling syringes were reused only after a nitrogen blank was run to insure it was not contaminated by the previous sample.
- Soil gas pumping was monitored by a vacuum gauge to insure that an adequate gas flow from the vadose zone was maintained. A reliable gas sample can be obtained if the negative pressure reading on the vacuum gauge was at least 2 inches Hg less than the maximum pressure of the pump.

RESULTS

Twelve UST sites were evaluated by comparative methods previous to May 29, 1990. In all cases the condition of the site determined by soil gas or field analytical measurements agreed with the results obtained from soil and water samples, if the soil gas action levels recommended by TRC were used to interpret the soil gas data and the current Iowa UST Board action levels were used to interpret soil or water data. When the data from soils or water indicated that the site was contaminated, the data from soil gas samples also indicated that the site was contaminated. In Iowa, a site is considered contaminated if the level of TPHC in soil is greater than 100,000 ug/Kg or the level of benzene in the groundwater is greater than 5 ug/L.

There was no existing standard or action level for soil gas or for field analytical methods. The action levels proposed for TPHC levels were 1000 ug/L, 10,000 ug/Kg, and 500 ug/L for soil gas, soils, and water, respectively.

In addition, the results of soil and water analyses using TRC field analytical methods were compared to results obtained using standard laboratory methods. The correlation between field measurements and laboratory measurements was good for water samples. The correlation between field measurements and laboratory measurements was not as good for soil samples. This result is not surprising, however, since water samples can be homogeneous and soil samples are not. In many cases the soil samples being compared were taken from the same bore hole but were taken from different cores. It is very likely that discrepancies between field and lab results for soils represent real differences between samples as much as disagreements between analytical methods.

Duplicate samples were also sent to two laboratories to check the inter-laboratory reproducibility. The agreement between TRC field methods and the samples sent to the two laboratories is as good as the agreement between the two laboratories.

Soil Gas Sampling Versus Soil Sampling: Sample Integrity

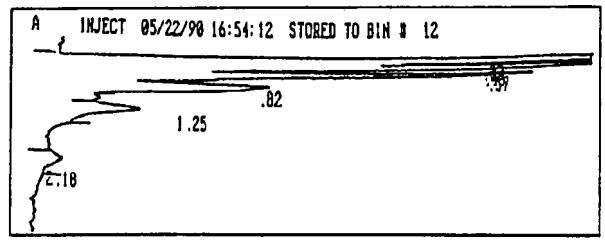

Figure 5. Soil gas sample #1 taken at a depth of 6 feet. NOTE: The early peaks are much larger than the later peaks, like fresh gasoline.

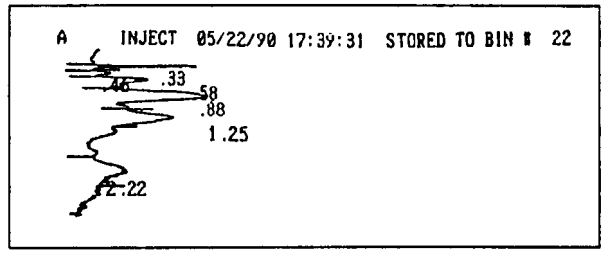

Figure 6. Soil sample #1 taken at a depth of 6 feet. NOTE: The early peaks are smaller than the later peaks. Most of the volatile substances were lost while handling the soil

Figure 5 is a chromatogram of a soil gas sample taken at a farmer's coop in north-central Iowa. Notice that the early peaks are much larger than the later peaks. Also notice that the chromatogram looks very similar to the chromatogram for fresh gasoline vapors (see Figure 2). Compare the chromatogram in Figure 5 to Figure 6 which is a chromatogram from the analysis of a soil sample taken from the same location within a few inches. Notice that the early peaks in Figure 6 are smaller than the later peaks. This is because most of the volatile compounds have been lost during the handling of the soil sample. Also the addition of water and agitation to the soil sample prior to headspace analysis increases the signal from lower volatility compounds.

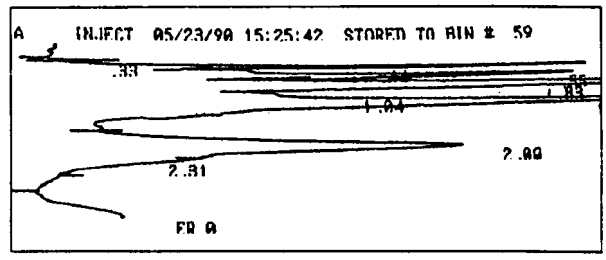

Figure 7. Soil gas sample #8 taken at a depth of 3 feet. NOTE: The early peaks are larger than the later peaks, like fresh gasoline.

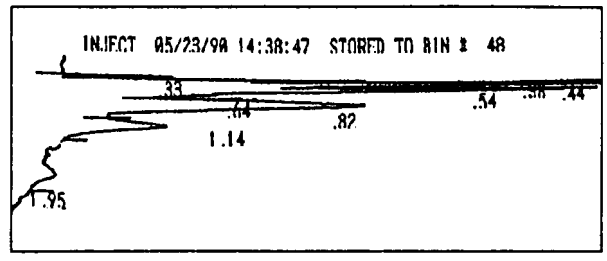

Figure 8. Soil sample #8 taken at a depth of 3 feet. NOTE: The early peaks are smaller than the later peaks. Most of the more volatile substances were lost while handling the soil.

A comparison of Figure 7 and Figure 8 illustrates the same principles. The chromatogram in Figure 7 is the result of the analysis of a soil gas sample from Sioux City, IA, and the analysis

in Figure 8 is the result of the analysis of a soil sample taken from the same location. Once again the analysis of TPHC in soil gas sample is more similar to that of fresh gasoline than that of petroleum product left in the soil sample after handling and exposure of the soil to ambient air.

Site By Site Comparison

The results from four of the twelve sites are presented here. These examples are intended to be representative of what occurred in the study.

■ *SIOUX CITY, IOWA*

This is a relatively new site where the UST's were recently installed. The site is fairly clean, except for isolated contamination near the elbows in the piping where the turn is made toward the pump islands (see Table 1 and Figure 9 at sampling location 8). A leak in the pipe is indicated. There is excellent agreement between the soil gas measurement and the analysis of soil samples at this site. Both would have located the problem. However, having the analytical laboratory on site allowed additional samples to be taken at locations 12, 13 and 14, which verified that location 8 is within a few feet of the release point of the hydrocarbon contamination.

TABLE 1
Sioux City, Iowa
05-23-90
CONDENSED DATA

SAMPLE	TRC TPHC SG ug/L	TRC TPHC SOIL ug/l	KEYSTONE TPHC SOIL ug/L
1-9'	<4	n/a	N/A
2-8'	<4	6	<5000
3-6'	<4	4	<5000
4-8'	0.7	<2	<5000
5-8'	<4	<2	<5000
6-10'	<4	<5	<5000
7-3'	<4	6	<5000
8-3'	5800	157000	516000
9-3'	<4	71	<5000
10-3'	2	<8	<50000
11-3'	50	17	<5000
Shaded valu			

es represent concentrations above action levels.

N/A = Not analyzed.
TRC samples analyzed by Tracer Research Corporation in mobile lab.
KEYSTONE samples analyzed by Keystone Laboratories Inc., Newton, IA.
THPC signifies Total Petroleum HydroCarbons.
SG signifies a soil gas sample.
SOIL signifies a soil sample.

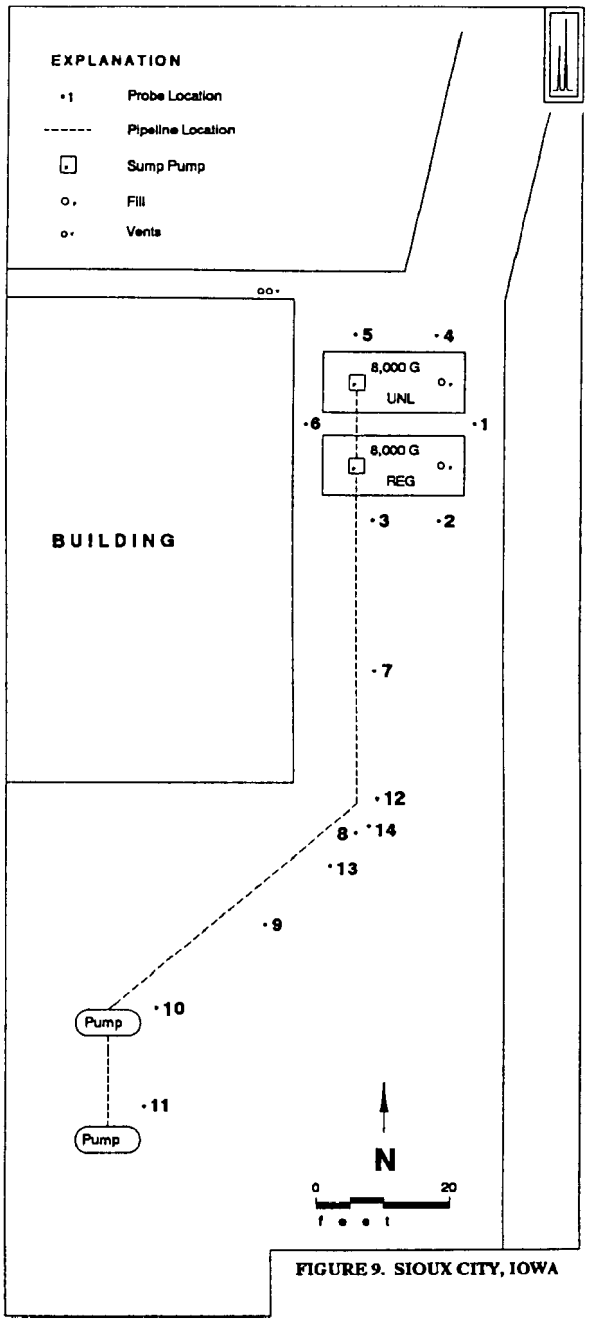

FIGURE 9. SIOUX CITY, IOWA

Figure 9. Facilities and sampling locations at a convenience store in Sioux City, Iowa. See Table 1 for Analytical results.

■ *OLWEIN, IOWA*

See Table 2 and Figure 10 for a summary of the results of this site investigation. The results from the soil gas investigation, the field analyses of soil samples, and the laboratory analyses of soil samples all indicate that contamination is not general throughout the site but is localized around the eastern end of the tank pit, the piping trench between the building and the pump islands and around the southern pump island. On the map in Figure 10, the largest indications of contamination are at sampling locations 4, 6, 7, and 9. Analysis of soil samples indicated problems at two locations where soil gas measurements did not, but analysis of soil gas samples indicated contamination problems in two locations where analysis of soil samples indicated no problem. At this site, the same conclusions are reached by using either investigative method as long as multiple sample locations are examined in reaching those conclusions.

TABLE 2
Olwein, Iowa
05-25-90
CONDENSED DATA

SAMPLE	TRC, TPHC, SG, ug/l	TRC, TPHC, SOIL, ug/l	KEYSTONE, TPHC, SOIL, ug/l
1-9'	<1	<8	<5000
2-9'	<4	<6	<5000
3-10'	2700	2200	<5000
4-9'	58	5400	1590000
5-9'	0.8	<13	<5000
6-9'	1500	16000	131000
7-3'	24000	96000	2620000
8-3'	5	100	549000
9-3'	5300	21000	3330000
10-3'	<4	34	<5000
11-3'	3300	310	<5000

Shaded values represent concentrations above action levels.
N/A = Not analyzed.
TRC samples analyzed by Tracer Research Corporation in mobile lab.
KEYSTONE samples analyzed by Keystone Laboratories Inc., Newton, IA.
TPHC signifies Total Petroleum HydroCarbons.
SG signifies a soil gas sample.
SOIL signifies a soil sample

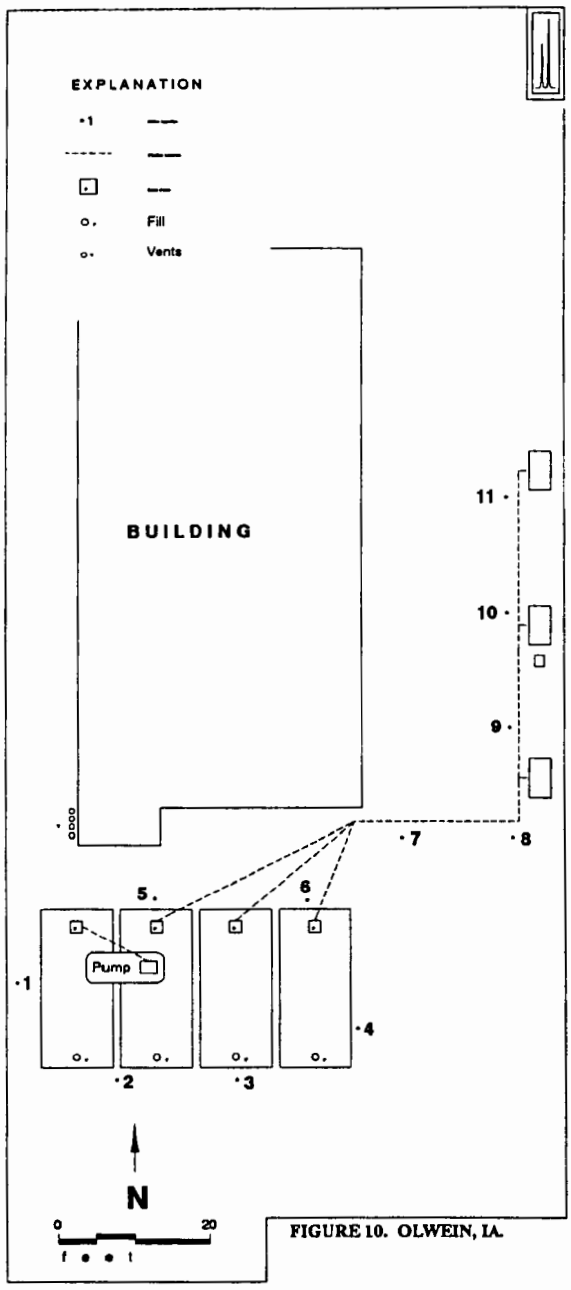

FIGURE 10. OLWEIN, IA.

Figure 10. Facilities and sampling locations at a gas station in Olwein, Iowa. See Table 2 for analytical results.

■ *GAS STATION, DES MOINES, IOWA*

Because the surface of this tank pit was covered with grass, which makes the tank pit a groundwater recharge area, and the backfill material is native clayey soil, the soil gas survey was not relied upon to survey this site. Soil samples were collected at depths equal to or greater than the tank bottoms. The samples were analyzed by the TRC field method for soils and by two different independent Laboratories. The agreement between the TRC results and the Laboratory results was as good as the agreement between the two laboratories (see Table 4 and Figure 12). This illustrates the variability of soil samples.

The result of the investigation is that the site is contaminated throughout the tank pit at the depth of the tank bottoms.

TABLE 4
Gas Station/Des Moines, Iowa
06-11-90
CONDENSED DATA

SAMPLE	TRC, TPHC GW-HS ug/L	NET TPHC GW ug/L	PACE TPHC GW ug/L
1	600	140	190

SAMPLE	TRC TPHC SOIL ug/Kg	NET TPHC SOIL ug/Kg	PACE TPHC SOIL ug/Kg
2	<0.5	<15,000	<10
3	1,200,000	860,000	40,000
4	62,000	43,000	34,000
5	263	<15,000	<10
6	290,350	26,000	984,000
7	200	<15,000	<10

Shaded values represent concentraitons above action levels.
TRC samples analyzed by Tracer Research Corporation in mobile lab.
PACE samples analyzed by Pace Laboratories, Coralville, IA.
NET samples analyzed by NET Midwest Laboratories, Cedar Falls, IA.
TPHC signifies Total Petroleum HydroCarbons.
SOIL signifies a soil sample.
GW signifies a groundwater sample.
GW-HS signifies a groundwater samle analyzed using a head space method.

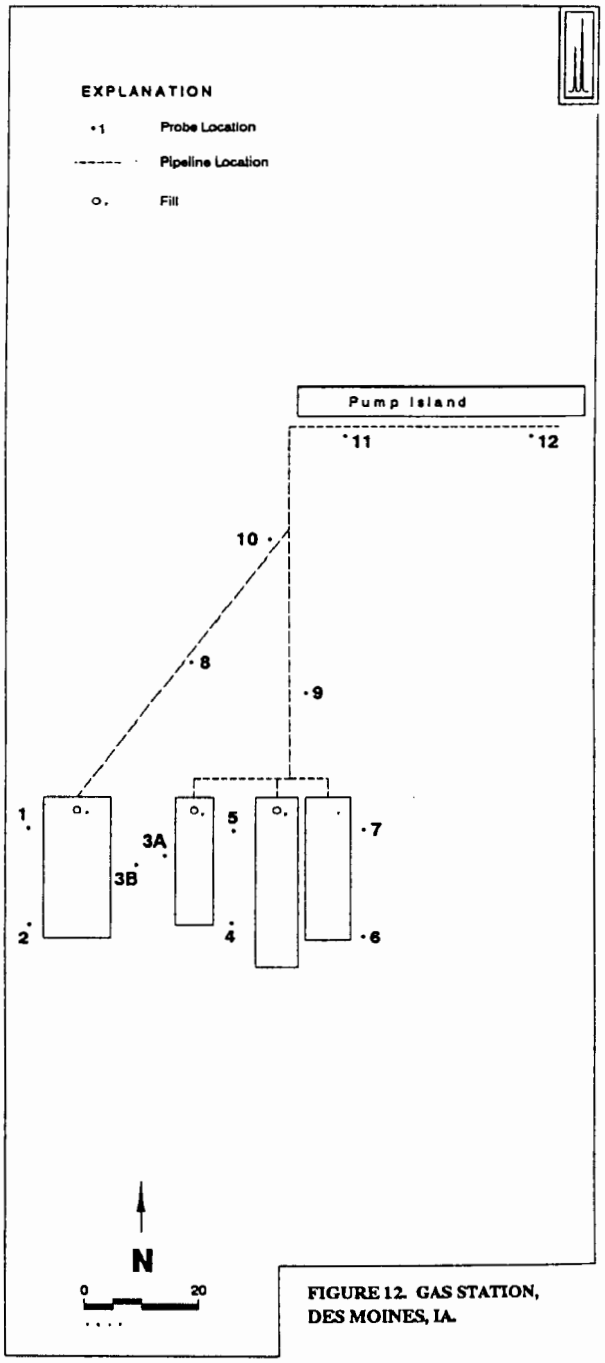

FIGURE 12. GAS STATION, DES MOINES, IA.

Figure 12. Facilities and sampling locations at a gas station in Des Moines, Iowa. See Table 4 for analytical results.

■ *CONVENIENCE STORE 2, DES MOINES, IOWA*

High levels of contamination were discovered at all sample locations at this site (see Table 3 and Figure 11). When contamination was discovered early in the investigation, the objective of the investigation changed to an effort to determine the extent of the contamination. It was discovered that the contamination extends mainly eastward from the north end of the tank pit and does not diminish at least to the border of the property. The extent of this contamination indicates that petroleum is being released underground currently and has been for some time. The very high levels of hydrocarbons in the soil gas (100,000 ug/L or greater) over a widespread area is typical of a significant ongoing contamination problem. This is also the ideal condition for the best correlation between different investigation approaches. The results at this site were unlike the results at almost all the other sites where isolated pockets of minor contamination were indicated.

TABLE 3
Convenience Store #2/Des Moines, Iowa
06-10-90
CONDENSED DATA

SAMPLE	TRC, TPHC, SG, ug/l	TRC, TPHC, GW-HS, ug/l	TRC, TPHC, SOIL, ug/kg	PACE, TPHC, GW-HS, ug/l	PACE, TPHC, SOIL, ug/kg
2	110,000		60,000		150,000
5	10,000	1,400		41	
6	25,000				
8	23,000				
11	44,000				
12	53,000				
13	84,000				
14	100,000				
15	130,000				
16	52,000				
17	100,000				

Shaded values represent concentrations above action level.
TRC samples analyzed by Tracer Research Corporation in mobile lab.
PACE samples analyzed by Pace Laboratories, Coralville, IA.
SG signifies soil gas sample.
SOIL signifies a soil sample.
TPHC signifies Total Petroleum HydroCarbons.
GW signifies a groundwater sample.
GW-HS signifies a groundwater sample analyzed using a head space method.

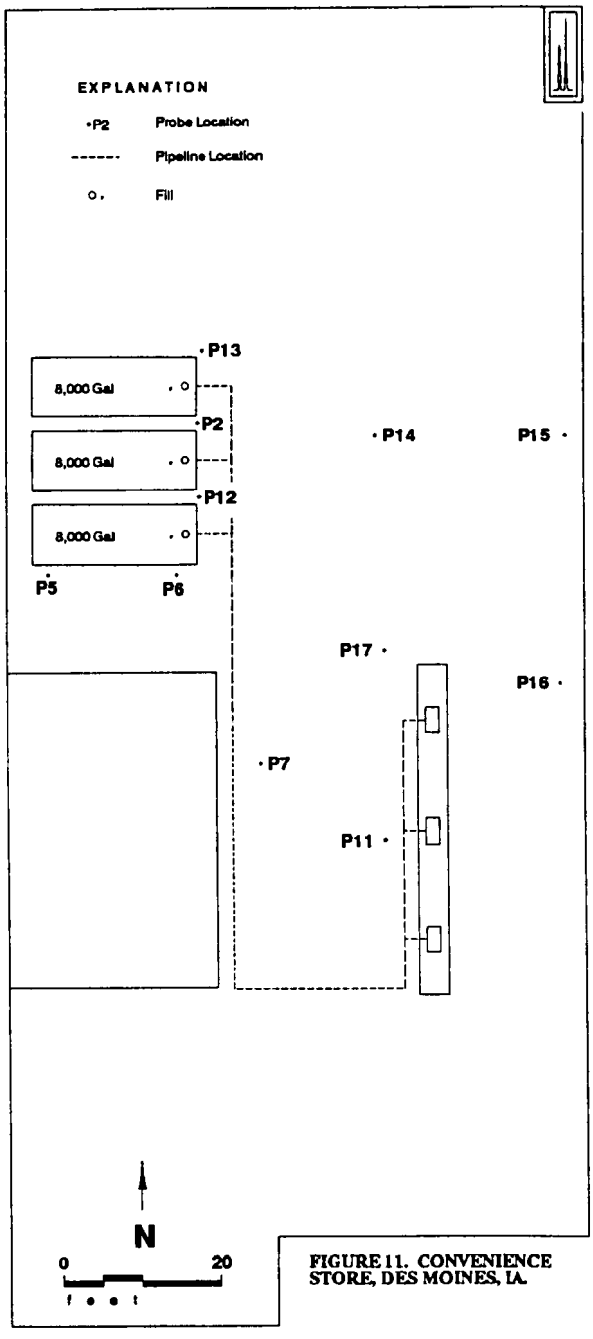

FIGURE 11. CONVENIENCE STORE, DES MOINES, IA.

Figure 11. Facilities and sampling locations at a convenience store in Des Moines, Iowa. See Table 3 for analytical results.

SUMMARY RESULTS

The following discussion is concerned with the general conclusions that can be drawn from the data discussed above.

Comparison of Field and Laboratory Analytical Results.

Figure 13 is a plot of the field analytical results versus the Laboratory analytical results for total petroleum hydrocarbons in water samples collected at the same sampling locations. The data are presented in log-log scaled plots because of the wide ranges of data values. Table 5 is a summary of a regression analysis of the data. The regression results are reported as logarithms. As can be seen in Figure 13, the agreement between the two methods is good. The correlation coefficient yielded by the data is 0.87.

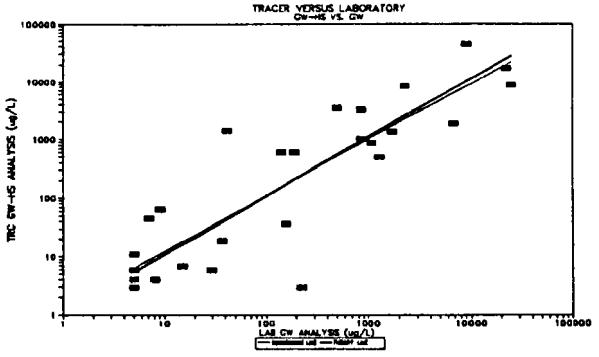

Figure 13.Comparison of field analytical results using a head space method with laboratory results using a standard method for hydrocarbons in water. See Table 5 for a list of linear coefficients and statistical results.

TABLE 5
LINEAR COEFFICIENTS AND STATISTICAL RESULTS OF A COMPARISON OF FIELD HEADSPACE ANALYSIS AND STANDARD METHOD ANALYZING OF HYDROCARBONS IN WATER

	REGRESSION RESULTS	STD. ERROR
Slope (theoretically = 1)	0.95	0.11
Intercept (theoretical = 0)	0.14	0.69
Correlation Coefficient (r)	.87	.10
Threshold value for statistical significance of r (at 99% confidence level)	0.28	

Also the theory line, which is generated by the assumption that the field results should be equal to the laboratory result (slope = 1, intercept = 0), is just as good a representation of the data as is the line generated by a linear regression analysis.

Some differences between field and laboratory water analyses and between field and laboratory soil analyses are parallel. In both cases the field analysis uses what is called a head space method, and also in both cases the laboratory analysis uses what is called a purge and trap method. For these reasons the TRC field analysis for soils should compare favorably with standard laboratory methods for soils if identical samples are analyzed.

The correlation between field and laboratory analyses of soil samples should not be expected to correlate as well as water samples. Soil samples are not typically homogeneous and, therefore, should not be rigorously considered as split samples. Very different samples can be collected form nearly the same location. After examining the data in Table 4, it can be seen that duplicate soil samples collected in this study are not reliably similar. Also, the laboratory method uses methanol to extract hydrocarbons from the soil. The field headspace analysis relies on water to wet the soil particles and displace the absorbed hydrocarbons. A methanol extraction of the hydrocarbons should be more efficient than a water displacement because the hydrocarbons are more soluble in methanol while the methanol is able to strongly wet the soil particle.

Figure 14 compares the field and laboratory analytical results. While there is more scatter than in the comparison of groundwater analyses the correlation is still strong (0.69 See Table 6). However, the line generated by a regression analysis of the data does not agree well with the theory line which assumes both results should be equal. The log mean value of the ratio of the laboratory analytical result divided by the field analytical result is 1.3, which indicates a ratio of 20. This could be related to the better extraction efficiency of the methanol.

If, as is the case for low level analyses, the soil sample is not extracted with methanol but is simply mixed with water and placed in the purge vessel, the field headspace method would yield results that are roughly equivalent to the standard laboratory method.

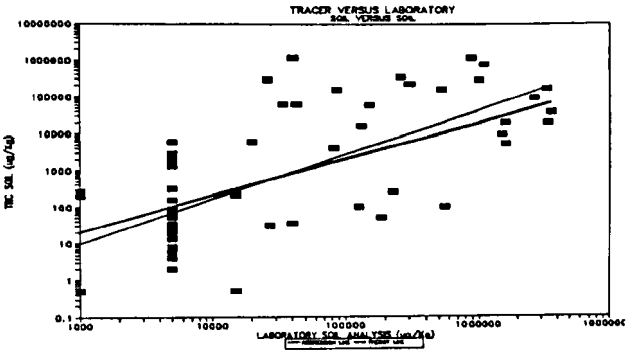

Figure 14. Comparison of field analytical results using a headspace method with laboratory results, using a standard methanol for hydrocarbons in soils. See Table 6 for a list of linear coefficients and statistical results.

TABLE 6
LINEAR COEFFICIENTS AND STATISTICAL RESULTS OF A COMPARISON OF FIELD HEADSPACE ANALYSIS WITH STANDARD LABORATORY ANALYSIS OF SIMILAR SOIL SAMPLES FOR HYDROCARBONS

	REGRESSION RESULT	STD. ERROR
Slope (theoretically = 1)	1.2	0.16
Intercept (theoretically = 0)	-2.7*	1.3
(Average of $\log \frac{\text{field result}}{\text{lab result}}$	1.3**	
Correlation Coefficient	0.69	0.09
Threshold value for statistical significance of r (at the 99% confidence level)	0.24	
* See Equation 3		
** See Equation 4		

Comparison of Soil Gas Measurements with Soils Analyses

If the correlation of hydrocarbons in sol gas is represented by Cg and the level of hydrocarbons absorbed to the soil and dissolved in the water, which is adsorbed to the soil is represented by C_s, the ratio of the two values could be represented by K.
Equation 1:

$$\frac{C_g}{C_s} = K \quad or, \quad C_g = KC_s$$

K is not an equilibrium constant, but if the system were at equilibrium, K would be proportional to the equilibrium constant. Note also that K contains many variable factors such as the surface area of the soil, the water content of the soil, the soil porosity and the soil temperature. Since the data is plotted in the log-log scale, the logarithm of Equation 1 becomes Equation 2:

$$\log \frac{C_g}{C_s} = \log K \text{ or } \log C_g = \log (KC_s)$$

Which is equivilent to Equation 3:

$$\log C_g = \log C_s + \log K$$

A set of hydrocarbon levels governed by a single ratio, K, plotted on a log-log scale would fall on a line with a slope of 1.0 and an intercept equal to log K. In this way the intercept from a regression analysis might be related to log K. See Tables 7-9.

An alternative method of obtaining log K would be to average the logarithms of the ratios of the soil gas and the soil hydrocarbon levels. Equation 4:

$$\text{Average } \log K = \sum_{1}^{n} \log \frac{C_{g(n)}}{C_{s(n)}}$$

Figure 15 is a plot of soil gas levels of total petroleum hydrocarbons with measurements of total petroleum hydrocarbons in soils taken from nearly the same locations. The correlation coefficient for the data set is 0.73, which is highly significant. Also, the slope of 0.81 is more than the std. error different from 1.0, but the theoretical slope of 1.0 is within the 95% confidence interval of the regression calculated slope.

There are many reasons why the correlation is not perfect. The ratio of the amount of petroleum hydrocarbons in the soil gas versus the amount adsorbed to the soil changes depending upon the soil type and water content. The ratio also depends on the type of fuel, length of time in the ground, or the distance between the sampling point and the original source of contamination. Hydrocarbons can be detected in soil gas at greater distances from the source than in soil samples. Also, the condition, species, and concentration of microbes in the soil have an effect. Finally, the amount of volatiles lost from soil samples during handling varies a great deal with soil types, water content, sampling operator, and analyst.

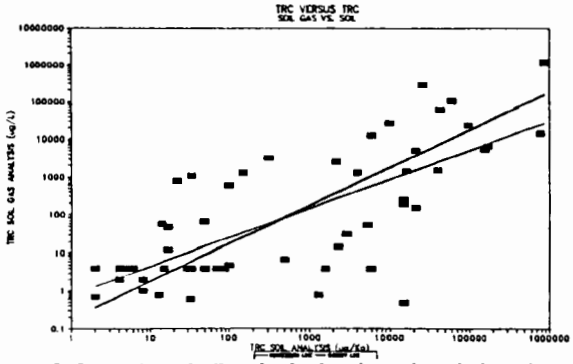

Figure 15. Comparison of soil gas levels of total petroleum hydrocarbons (TPH) with TPH levels in soil samples taken from nearly the same location. Both samples were analyzed in the field. See Table 7 for a list of linear coefficients and statistical results.

TABLE 7
LINEAR COEFFICIENTS AND STATISTICAL RESULTS OF A COMPARISON OF FIELD SOIL GAS ANALYSIS AND SOIL ANALYSIS BY A FIELD METHOD

	REGRESSION RESULT	STD. ERROR
Slope (theoretically = 1)	0.77	0.10
Intercept (log K)*	-.117	1.2
Average of log K**	-.74	
Correlation Coefficient (r)	.73	.10
Threshold value for statistical significance of r (at the 99% confidence level)	.27	
*See Equation 3		
**See Equation 4		

To illustrate the effect of some of these factors, consider Figure 16. This is a plot of the level of toluene in soil gas versus the level of toluene in soil samples. (Note that in this analysis toluene is not completely separated from the other hydrocarbons in the sample.) Toluene is a common component of gasoline that is less volatile than most of the components in gasoline (see Figure 2). It is therefore less susceptible to loss during sampling. Therefore, as expected, the correlation coefficient (0.81) for toluene in soil gas versus toluene in soils is better than for total hydrocarbons in these two kinds of samples (0.73).

Also, the slope of 1.0 calculated by the regression analysis is in excellent agreement with theory. The exact agreement is probably only circumstantial. The scatter in the data sets is best represented by the standard error of the intercept. The standard error of the intercept for the plot comparing toluene levels (0.82) is also reduced from 1.2, which is the standard error of the intercept for the comparison of total hydrocarbon measurements.

Figure 17 is a plot of total petroleum hydrocarbons in soil gas versus total petroleum hydrocarbons in soils as determined by keystone laboratories. The correlation coefficient (0.63) for the data set is highly significant and the slope of the regression line is in excellent agreement with expectation.

Although the scatter in each of these plots that compare soil gas levels to levels in soils is large, as great as 1.2 (remember that this is the error in log K) it is easily accounted for by allowing for the possible variation in soil surface area alone. In other words, clayey soils would tend to give rise to data skewed towards the X axis and sandy soils would tend to give rise to data skewed towards the Y axis.

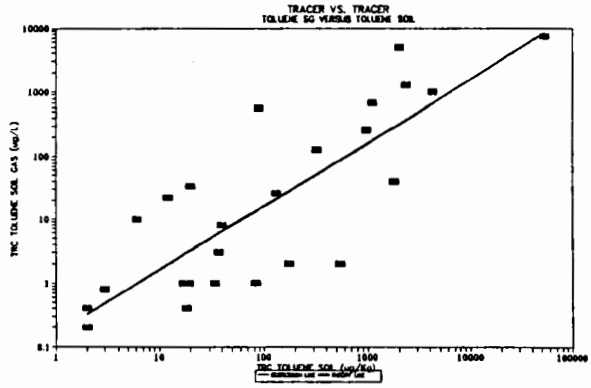

Figure 16. Comparison of soil gas levels of Toluene with Toluene levels in soil samples taken from nearly the same location. Both samples were analyzed in the field. See Table 7 for a list of linear coefficients and statistical results.

TABLE 8
LINEAR COEFFICIENTS AND STATISTICAL RESULTS OF A COMPARISON OF SOIL GAS LEVELS OF TOLUENE WITH TOLUENE LEVELS IN SOIL SAMPLES

	REGRESSION RESULTS	STD. ERROR
Slope (theoretically = 1.0)	1.0	0.15
Intercept (log K)*	-.079	0.82
Average log K**	-0.79	
Correlation Coefficient	0.81	0.12
Threshold value for statistical significance of r (at 99% confidence level)	0.33	
*See equation 3		
** See equation 4		

Appropriate Action Levels for Soil Gas

The cleanup action level for TPHC in soils in Iowa, and some other states, is 100,000 ug/Kg or 100 mg/Kg.

If a vertical line is drawn through the graph (Figure 17) at the value of 100,000 ug/Kg, it divides the data into two groups, those above the action level, called positives and those below the action level called negatives. From a total of 51 samples, 15 are positives. These soil samples are classified as contaminated above the action level.

If a horizontal line is drawn through the intersection of the vertical line and either the regression line or the theory line, it will intersect the Y axis of the graph in Figure 17 at a value of approximately 200 ug/L. This horozontal line divides the data into two sets. Those levels above the line are called soil gas positives and those below the line are called soil gas negatives.

When the analytical result for a sampling location falls above the action level for soils and for soil gas, both methods are in agreement. When the measured levels of TPHC falls below the action level for soils and for soil gas, once again both methods are in agreement. The frequency of agreement between field soil gas and laboratory soil measurements by this approach is 0.8.

If, however, the intent is to use the soil gas survey as a screening method, and the occurence of one or more contaminated samples causes a site to recieve a closer look, the discrepancies that cause the greatest concern are those in which soil gas analysis gives a negative results when soils analysis would have yielded a positive one. This might be called a false negative. An estimate of the frequency or probability of false negatives from the data in Figure 17 is 0.08. Finally, it should be noted that soil gas samples are less costly to collect and analyze than are soil samples. If therefore, multiple soil gas samples are analyzed, the chances of a continued false negative becomes $(0.08)^n$, in which n is the number of soil gas samples. Very quickly, the chances of obtaining a repeated false negative becomes vanishingly small ($(0.08)^2 = 0.006$, $[0.008]^3 = 0.0005$).

After this evaluation the action level for TPHC in soil gas was set at 1000 ug/L as a compromise between false negatives and false positives and to compensate for the fact that soil gas samples would be collected closer to the contaminated sources. The use of 1000 ug/L as the soil gas action level raises the frequency of false negatives for soil gas to 10% in the data set in Figure 17. The frequency of agreement of 0.8 is not affected.

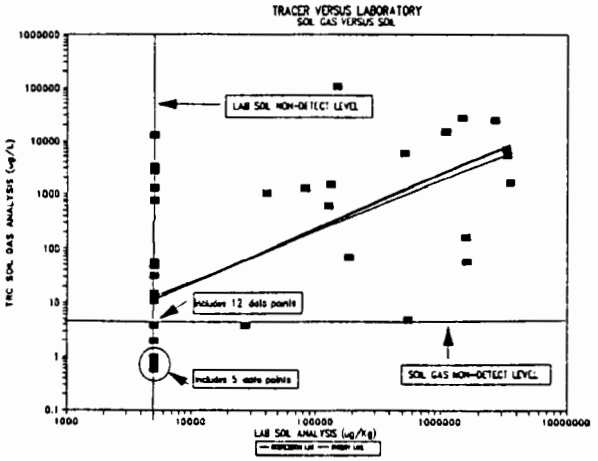

Figure 17. Comparison of soil gas levels of total petroleum hydrocarbons (TPH) with TPH levels in soil samples taken from nearly the same location. The soil samples were analyzed by a contract laboratory using OA-1 which is an Iowa modification of EPA method 8015. See Table 9 for a list of linear coefficients and statistical results.

TABLE 9
LINEAR COEFFICIENTS AND STATISTICAL RESULTS OF A COMPARISON OF FIELD SOIL GAS LEVELS OF TOTAL PETROLEUM HYDROCARBONS (TPHC) WITH TPHC LEVELS IN SOIL SAMPLES BY A STANDARD METHOD***

	REGRESSION RESULTS	STD. ERROR
Slope (theoretically = 1)	0.92	0.17
Intercept (log K)*	-2.3	1.2
Average log K**	-2.6	
Correlation coefficient (r)	0.63	.012
Threshold value for statistical significance of r (at 99% confidence level)	0.32	
*See equation 3		
** See equation 4		
***Method is OA-1 which is an Iowa modification of EPA 8025		

CONCLUSIONS

After a review of this data set it can be concluded that soil gas investigations are a useful complement to soil and water sampling approaches to site evaluations. It is important, though, to use appropriate action levels for soil gas measurements.

Reasonable and practical guidelines can be written to ensure that soil gas investigations be used at locations for which it is appropriate. For those locations where soil gas measurements are inappropriate, soil or water samples can be collected. It has been shown that the field headspace analysis of volatile petroleum hydrocarbons yields results that correlate very well with results from standard purge and trap methods. The correlation between the measurement of hydrocarbon levels in soils by the field headspace method and by OA-1 was not as good. Whether the differences arose from heterogeneous samples or differences in extraction efficiency was not determined.

It should be remembered that these results were obtained using laboratory grade analytical equipment which was mobilized for field use. Some soil gas investigations are conducted using hand held instruments or portable gas chromatographs with little or no temperature control of the sample stream. Since these devices are not as reliable, caution should be used in applying these results to those approaches.

This study has shown that total hydrocarbons in soil and water samples can be reliably assessed using field analytical methods.

DISCUSSION

STEVE KNOLLMEYER: You seem to assume that the soil gas emanates from the same place you collect the soil sample, rather than from the water table or soil contamination deeper in the ground. Is that something you always see, or did you study that at all? And secondly, did you correct any of the soil gas readings for methane that may be there naturally?

RANDY GOLDING: The chromatograph was able to separate the natural methane and it wasn't included in any of these numbers. We didn't assume that the source for the soil gas vapors were in the same region of space as the sample collected. But, since we were evaluating this method as a screening tool, we simply collected the soil gas sample from the same region of space that any other contractor would have collected the soil sample. We were comparing whether or not the answers would agree.

DAVID CLIFT: What did you use for the standards?

RANDY GOLDING: This will surprise you, but we simply used a mixture of benzene, toluene, and xylene, and we averaged the response factor for those to calculate the total hydrocarbon number. That should over-estimate the hydrocarbon number. We didn't use gasoline samples as our standard.

DAVID CLIFT: That was just gasoline that you're looking at, right?

RANDY GOLDING: Well, we didn't know what we were looking at necessarily, since the tank pits all contain multiple products.

DAVID CLIFT: You couldn't determine if they were aliphatic or aromatic then?

RANDY GOLDING: Not from the FID detector. Only from retention time. We were limited by resolution problems because we were using this as a screening method, therefore speed was also a factor. If we had a water sample in later studies, the action level for water was defined by benzene levels. The action level for soil was defined by total hydrocarbons. And so at that point we would take the gas chromatograph, cool the temperature down, and try to separate benzene out from the other products. And we easily attained the 5 ppb action level for benzene. It was easy to obtain using a headspace method. We achieved a 0.02 ppb or 20 ppt detection limit for benzene, if we did a good separation. Then we tried to look to see whether or not benzene was the problem if we had groundwater in the sample.

DOUG PEERY: What was the spectral difference between your soil gas and your soil samples? How much apart were they?

RANDY GOLDING: It varied because being able to collect the soil sample in that probe wasn't as reliable as one would like. But typically I would say that it was within two feet. Sometimes we had to go down the same hole repeatedly because we didn't get enough sample. Remember we would try to collect split samples, one for the lab, one for us. And so sometimes, not always, the sample was collected by two different excursions into the same hole, and so it's possible that shavings from different depths were included in different samples. That's a disadvantage and a weakness of the study.

DOUG PEERY: If I understand correctly, you did your soil gas and sometimes you went back into the same hole and collected your soil samples?

RANDY GOLDING: Well, we would collect soil gas after the probe arrived. And then before removing the probe we would usually collect the soil sample.

DOUG PEERY: Would that not bias your results in your soil samples because you did your soil gas first, because the volatiles would be removed?

RANDY GOLDING: The partitioning ratio that you would get from the data was always at least as large as you would predict just by doing a batch study in the laboratory in a very controlled environment. There isn't any evidence in the results that this occurred. And I agree that it's a concern that should have been raised. We didn't evacuate large volumes of ground. In order to flush the probe adequately, you only had to evacuate soil gas from a sphere that had a radius of a few inches, perhaps four inches. But then we would often push well beyond that point 10 or 12 inches to collect the soil sample.

DOUG PEERY: Okay. I know in some procedures for soil gas there is a purging of the probe, and then we have found, (Dr. Spittler said of his previous work) that over a period of time there is an equilibrium that is reached.

RANDY GOLDING: Then it would recover. There is a steady state that you reach if you keep pumping, and then if you stop pumping it will recover.

DOUG PEERY: Right. But I take it that you did not go to the steady state position?

RANDY GOLDING: No, we only flushed the probe. We only tried to get a grab sample of the soil gas.

FIELD SCREENING OF BTEX IN GASOLINE-CONTAMINATED GROUNDWATER AND SOIL SAMPLES BY A MANUAL, STATIC HEADSPACE GC METHOD

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ABSTRACT

A manual, static headspace GC method has been developed and used in the field for the screening of gasoline-contaminated groundwater and soil samples. This developed, static headspace method has focused primarily on the analyses of benzene (B), toluene (T), ethylbenzene (E), and the three xylene isomers (X) (often collectively abbreviated as BTEX). However, this method also allows for the determination of methyl-t-butyl ether (MTBE), trichloroethylene (TCE) and tetrachloroethylene (PCE) in the headspace above the aqueous layer as detected by a photoionization detector (PID) of a field-portable gas chromatograph. The headspace method is performed in the same 40-mL VOA vial in which the sample is collected, hence reducing the possibility of sample loss due to volatilization. Good agreement was found between the field, static headspace method, a laboratory-based manual, static method and a laboratory-based, purge-and-trap method. The results of field screening for BTEX, MTBE, and PCE at several sites in the New England area will be presented.

INTRODUCTION

Simple field methods associated with the use of portable instruments have been reported to give dependable data while saving time and money (1,2). These methods can provide for the rapid screening of large numbers of samples in the field, thus providing for more effective and timely site assessment and evaluation of on-going remediation efforts. In addition, sample loss due to volatilization and/or bacterial alteration of the targeted compounds compounds can be effectively avoided.

Reports by Spittler, et al. (3-5) and Grob, et al. (6-7) have shown that the static headspace method can be used as a rapid and effective method for the analysis of various volatile organic pollutants in groundwater and soil samples. Wylie found that using optimized conditions and the same analytical instrumention that the static headspace method can be as sensitive and as reproducible as the dynamic, purge-and-trap method. He noted that the static method is obviously more portable and better able to be used on a variety of environmental samples, such as soils and sludges (8). Recently, we published a brief technical note that described using a manual, static headspace method for the analyses of BTEX in gasoline-contaminated groundwater and soil samples (9). Since the time of that publication, we have employed the manual, static headspace method in the field at four sites in Connecticut that have experienced contamination due to leaking underground storage tanks (LUST). A report of our findings will be described in this paper.

EXPERIMENTAL

Instrumentation. The field separations were performed on a portable gas chromatograph (HNU Systems, Model 311). A splitless injection was employed onto a narrow bore, 0.32 mm i.d., 25 m in length, capillary column having a 1.0 micron film thickness of dimethyl polysiloxane (Nordibond NB-30, HNU Systems). A column flow rate of 5.0 mL/min was used. The column's eluent was passed to a photoionization detector (PID) equipped with a 10.2-eV lamp whose output was to a built-in integrator on the Model 311. The column was set isothermally at 60°C, while the injector's and detector's temperature were set at 90°C. Manual injections of the head-

space vapors were accomplished using 50- or 100-microliter, gas-tight, fixed needle microsyringes (Scientific Glass Engineering).

For comparison work, a laboratory-based manual static headspace method was performed using the splitless injection mode onto a capillary column, gas chromatograph (Hewlett-Packard Model 5890A). A megabore capillary column, 0.55 mm i.d., 30 m in length with a 3.0 micron film of dimethyl polysiloxane (DB-1, J&W Scientific) was used. The column's eluent, at a flow rate of 8.0 mL/min, was passed through a PID (HNU Systems, Model 52-02A) equipped with a 10.2-eV lamp, followed by a flame ionization detector (FID). The output of each detector was displayed on an integrator (Hewlett-Packard, Model 3396A). The following column oven temperature program was used: initial temperature, 40°C, initial time 1 min, temperature program rate, 8 °C/min, final temperature, 190° C. For the laboratory-based, megabore columns, a 200-microliter portion of the headspace was injected using a 250-microliter, gas-tight microsyringe.

For the laboratory based purge-and-trap comparisons, an equivalent procedure to the one described for Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column GC/MS", was employed with the following equipment: a dynamic headspace concentrator (Tekmar, Model 2000) equipped with sixteen port, 5-mL glass sparge chambers on an automatic liquid sampler (Teckmar, Model 2016). A cryogenic focusing interface (Tekmar Capillary Column Interface) was used to attach the purge-and-trap system to the splitless injection systems of a Hewlett-Packard 5890A gas chromatograph. The detector system was a mass selective detector (Hewlett-Packard 5970) with an associated Hewlett-Packard 5895 Chem Station. A narrow bore, 0.32 mm i.d. capillary column, 30 m in length with a 1.8 micron film thickness of DB-624 (J&W Scientific) was used. The column's flow rate was adjusted to 2.0 mL/min.

In subsequent studies, a second purge-and-trap unit was used which consisted of a dynamic headspace concentrator (Teckmar, Model 4000) with ten port, 5-mL glass sparge chambers (Teckmar Model ALS) that was connected to a packed column, gas chromatograph (Perkin-Elmer, Model 3920B) equipped with two detectors, a PID (HNU Model 52) with a 10.2 ev lamp and a FID. The output of both detectors were sent to a 2-pen recorder (Perkin-Elmer Model 023) and to two integrators (Hewlett-Packard Model 3390A). A packed column, 8 ft. long, 0.125 in. o.d., 0.085 in. i.d. packed with 1% SP-1000 on Carbopak B 60/80 Mesh (Supelco, Inc.) was employed; a column flow rate of 40 mL/min was used. The following column oven temperature was used: a 4 min. hold at an initial column temperature of 75°C, followed by a 8 °C/min. temperature program to 220° C, with a variable final temperature hold. With these chromatographic conditions, the peak for MTBE eluted at about 16 min and excellent resolution for MTBE and the BTEX compounds were obtained.

Vials for the Static Headspace Method. The gasoline-polluted groundwater samples were direcly collected in 40-mL glass vials (Supelco, Part No. 2-3278), with hole caps (Supelco, Part No. 2-3283) and Teflon®-faced septa (Supelco, Part No. 2-3281). Prior to the field sampling, 100 microliters of a 24,000 mg/L aqueous solution of mercuric chloride were added to each vial. A final concentration of 60 mg/L of mercuric chloride in groundwater samples was proven to be an effective method of BTEX preservation against microbial degradation (9). Immediately after sampling, the capped vials were inverted to reduce the loss of volatile organics and placed in a 25.0 °C water bath if analysis were to be performed in the field or packed on ice and returned to the laboratory where they were kept refrigerated at 4° C.

Analyses of Groundwater Samples. The VOA vials containing the 40 mL sample of the groundwater were placed in a 25.0° C water bath in order to reach thermal equilibrium. Then a 1.5 in. long, 22-gauge needle was inserted through the septum to allow air to enter. Next, a similar needle attached to a 10-mL Luer-Lock syringe was used to remove 10.0 mL of the aqueous phase. The vial was kept in an inverted position and shaken thoroughly for 2 min. The vial, with the 10.0 mL of headspace, was again placed in the 25.0°C water bath and allowed to reach thermal and phase equilibrium. At the time of analysis, normally 50 microliters for the portable GC and 200 microliters for the laboratory GC were withdrawn with a gas-tight syringe and injected into the gas chromatograph.

Analyses of Soil Samples. First, an identification label needs to be placed on each clean, empty vial equipped with its individual holed-cap and septa. Then the weight of the empty vial is measured to within ± 0.010 g. Thereupon 25.0 mL of distilled water is carefully pipetted into each vial and 100 microliters of the 24,000 mg/L mercuric chloride added as a preservative. The vial with its cap and septa is then reweighed. During the field sampling, the soil sample with a range from 5 to 10 g. is carefully added to the vial which is then quickly capped. The vial and its contents are then thoroughly shaken for 2.0 min and the entire contents reweighed. The weight gain corresponded to the weight of the soil sample

taken for analysis. Depending upon whether the sample is to be analyzed in the field or in the laboratory, the vial is either placed in the 25.0° C water bath or on ice for transportation back to the laboratory.

RESULTS AND DISCUSSION

Figure 1a shows the separation obtained on the HNU-311 portable gas chromatograph for an eight component aqueous standard. The concentrations for the BTEX components in the aqueous phase were at the 880 ppb levels, while MTBE was 1820 ppb, TCE 3008 ppb and PCE 1747 ppb. Referring to Fig. 1a, it may be seen that almost complete return to baseline occured between the peak due to ethylbenzene (peak 6) and the peak due to the co-elution of m- and o-xylene (peak 7). However, it should be noted that only a very small peak (peak 1) is obtained by the static headspace method for MTBE, even at a significant concentration of 1820 ppb in the aqueous phase. This is because the Henry's Law constant for MTBE is very small. A preliminary estimate of <0.01 (in unitless terms) has been obtained in our work. This means that MTBE tends to remain in the aqueous phase and does not significantly partition into the headspace. Table 1 summarizes average Henry's Law constants for the compounds used in this paper.

On the laboratory-based, HP-5890 gas chromatograph, a series of monthly calibrations had established that for MTBE and the BTEX compounds that there were linear increases in peak areas with increases in concentration over 3- to 4-orders of magnitude for both the PID and FID detectors . Table 2 gives values for the method detection limits obtained for the static headspace method using the portable gas chromatograph (HNU Systems, Model 311) with its associated detector and integrators settings commonly employed in the BTEX analyses of groundwater samples.

Table 3 presents data that compares the results of analyses of the same gasoline contaminated groundwater sample performed in the laboratory by the manual, static headspace method to an automated, purge-and-trap GC/MS method, equivalent to EPA Method 524.2. It may be seen that for most of the comparison of the results by the two very different analysis methods that there is in general very good agreement. As expected the purge-and-trap method reported concentrations in the lower ppb range that were not detected using the headspace method. For the more contaminated samples, the headspace method tended to give higher concentrations. Upon examining the chromatograms, it appeared that more peaks coeluted with the peaks due to MTBE, benzene and/or toluene in the short, about 20 min. analysis time, in comparison to the longer, about 40 min. elution time employed by the purge-and-trap. Also, significant column overload of the narrow-bore, capillary column of the portable GC was observed. As may be seen in Fig. 1b, the integrator's plot of the portable GC remained above scale for a significant portion of the chromatogram, and reported values of 0.00 ppb for both MTBE and benzene, whereas the laboratory-based GC reported values of 54,600 and 1260 ppm levels, respectively for the same groundwater sample (not listed in Table 3).

In July of 1990, the opportunity arose to perform field analyses on groundwater samples from nineteen monitoring wells at a State Lust site in Westbrook, CT. The site is located in the middle of the small town at a busy intersection of coastal Route #1 (Boston Post Rd.). This is a complex site where it was believed that gasoline-contamination may have been caused from two leaking underground storage tank (LUST) locations. In January of 1989, in response to a report of gasoline fumes in an nearby commercial building, the State Dept. of Environmental Protection authorized a private engineering firm to perform investigatory and remedial action. After conducting geographical studies and historical record searching, soil gas probings and volatile organic analyses of groundwater and soil samples were performed. It was surmised that a plume of underground gasoline-contamination eminated from at least one of the underground storage tanks (UST) and travelled in a general NNWest direction towards and around the northside of the commercial building, in a line generally delineated by monitoring wells (MW1, MW2 and MW7, Table 4). A total of six, underground storage tanks were removed from the site during the spring of 1989. Holes were found in several tanks, and a film of free product noted on the water in the excavation pits. At approximately the location where the underground tanks were removed, a recovery shed housing groundwater pumps and a stripping tower were installed. Table 4 summarizes the analyses for MTBE and BTEX performed in the field on the HNU-311 at the Westbrook, CT site.

In the two days of intensive sampling at the Westbrook Site, the HNU-311 portable GC was able to rapidly and effectively screen for MTBE and the BTEX compounds in the many groundwater samples. It should be noted that analyses of MW 4,5,9 and 17 located at a distance and to the southwest of the expected plume were found to have only significant levels of MTBE. Fig. 1c shows the chromatogram of the headspace for MW5, showing only a single peak for MTBE. In an interesting article, Garrett, et al., have suggested that MTBE provides an excellent indicator for the outer limits of a gasoline

plume because it spreads further and faster than gasoline (10). Also, it is expected that MTBE is not readily degraded by the subsurface bacteria.

In August of 1990, the opportunity presented itself to use the HNU-311 portable GC at a site known to be contaminated with tetrachloroethylene (PCE). In a small shopping center in Weston, CT, a dry cleaning shop had been in operation for a number of year. In recent months, levels of PCE in the 10-100 ppb range had been found in drinking water wells of homes downgradient from the shopping center. In one day of field work, in conjunction with State regulatory officers, samples from about five home drinking water wells, groundwater monitoring wells and soil samples were all analyzed on-site. A shallow hole was manually dug almost at the back-door of the dry cleaning shop. Soil samples were taken at various depths. The results of the field analyses on these soil samples by the manual, static headspace method using both the HNU-311 and a Photovac 10S50 (operated by a State regulatory personnel) and later in the laboratory by purge-and-trap, packed column GC with PID and FID detectors are presented in Table 5. These results indicated that the manual, static headspace method was an excellent, field screening method for the determination of PCE and other such unsaturated, branched chlorinated solvents in soil and water samples. It was found that less loss of TCE occured if the samples were analyzed in the field.

CONCLUSION

A manual static headspace method has been used in the field on groundwater and soil samples at several sites found to have a wide variation in organic contamination. The method works well for BTEX, TCE and PCE as they are readily detected in the low ppb levels by the PID detector. The method has been found to be especially valuable in that it is portable and may be relatively easily performed. But, above all, the analytical results are available almost immediately to aid in evaluating any on-going site characterization and/or remediation efforts.

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DISCUSSION

MATT STINCHFIELD: Have you looked at using other disinfectants such as an organomercury compound, which is much more toxic and might allow you to use much lower concentrations.

JAMES STUART: No.

THOMAS SPITTLER: We have, with things like acids. And I believe in our Cincinnati lab they did quite a bit in biodegradation studies. Herb Brass in particular. He'll tell you a lot of the different things that he tried. Mercuric chloride just seemed to be the simplest. It didn't change the pH, was easy to use, and it worked.

Table 1. Certain aqueous properties of the compounds studied, at 25 °C

Compound	Henry's Law Constant[1,2] (dimensionless)	Solubility[1] (mg/l)
benzene	0.22	1800
toluene	0.27	510
ethylbenzene	0.35	160
m-xylene	0.29	160
p-xylene	0.29	180
o-xylene	0.20	190
1,1,1-trichloroethylene (TCE)	0.42	1000
tetrachloroethylene (PCE)	0.70	400
MTBE[3,4]	<0.01	43000

[1] Calculated from the data of Mackay, D., Shiu, W.Y., "Critical review of Henry's Law constants for chemicals of environmental interest", J. Phys. Chem. Ref. Data, 10, No. 4, 1981, 1175-1199.

[2] Calculated from the data of Ashworth, R.A., Howe, G.B., Mullins, M.E. and Rogers, T.N., "Air-water partitioning coefficients of organics in dilute aqueous solutions", J. Hazardous Materials, 18, 1988, 25-36.

[3] Approximate Henry's Law constant for MTBE from our studies.

[4] Garrett, P., et al. (10).

Table 2. Method detection limits[1] in ppb for the manual, static headspace method, obtained on the portable gas chromatograph (HNU Systems, Model 311).

On the headspace of a 8.8-30 ppb aqueous standard using the photoionization detector.

Benzene	Toluene	Ethylbenzene	m-and p-xylene	o-xylene
3.2	3.7	7.3	7.9	15.3

MTBE	TCE	PCE
5.0	6.9	7.4

[1] Method Detection Limits measured according to: Appendix B, Part 136, Federal Register, 40 CFR Ch.1 (7-1-88 Edition), pp. 510-512.

Table 3. Comparison of results, in ppb, between the static headspace method to an automated purge-and-trap GC/MS method.

Sample	Method	MTBE	Benzene	Toluene	Ethylbenz.	m-and p-xylene	o-xylene
TMW-1	headspace	ND	ND	ND	ND	ND	ND
TMW-1	purge&trap	<2	ND	ND	ND	ND	ND
TMW-6	headspace	ND	ND	ND	13	ND	ND
TMW-6	purge&trap	8.7	ND	ND	ND	ND	ND
MMW-1	headspace	72	ND	ND	861	1830	426
MMW-1	purge&trap	130	ND	ND	411	1220	276
MMW-4	headspace	483	17.3	61.8	28.5	690	399
MMW-4	purge&trap	390	12.7	40.6	15.3	315	322
MMW-6	headspace	ND	1144	4320	1500	6940	2030
MMW-6	purge&trap	11	709	2170	1420	4170	1980
MMW-7	headspace	co-elut	496	3180	489	4260	2080
MMW-7	purge&trap	165	330	2800	379	4430	2120
MMW-9	headspace	ND	84.5	ND	365	664	33.5
MMW-9	purge&trap	<50	ND	ND	361	944	ND
MMW-10	headspace	ND	10.5	ND	23.3	74.8	ND
MMW-10	purge&trap	1.3	8.1	ND	13.5	70.2	ND
MMW-11	headspace	ND	21.2	ND	ND	ND	ND
MMW-11	purge&trap	2.2	18.0	ND	ND	1.4	ND

Table 4. Results of field analyses of MTBE and BTEX at the Westbrook Site, July 1990, in ppb.

MW Location	MTBE	Benzene	Toluene	Ethylbenx.	m-and p.-xylene	o-xylene
MW1	Not accessible used for groundwater air stripping					
MW2	ND	5950	27100	2180	6220	4690
MW3	Abandoned					
MW4	117	ND	0.3	ND	ND	ND
MW5	453	ND	ND	ND	ND	ND
MW6	ND	ND	ND	ND	ND	ND
MW7	52100	NI	12400	1490	4530	4400
MW8	ND	ND	ND	ND	ND	ND
MW9	1570	16.2	ND	ND	ND	ND
MW10	5.8	0.6	ND	ND	ND	ND
MW11	ND	ND	ND	ND	ND	ND
MW12-MW14	Used for soil vapor extractions					
MW15	1730	818	790	791	778	832
MW16	Abandoned					
MW17	469	ND	3.8	1.1	1.6	1.9
MW18	ND	ND	1.6	2.6	3.0	3.8
MW19	0.4	ND	ND	ND	ND	ND
MW20	ND	1.1	4.1	9.5	10.2	8.8
B-1	ND	ND	ND	ND	ND	ND
B-2	not sampled, had septic leachate					
B-3	4210	262	512	94	375	146
B-4	ND	ND	ND	ND	ND	ND
B-5	ND	ND	ND	ND	ND	ND
B-6	813000*	33500*	123000*	5610	17500*	10800*

ND = Not Detected, NI = Not Integrated, * = Integration count exceed limit

Table 5. Comparison of the analyses for PCE in soil samples, Weston, Ct. during August of 1990, expressed as mg of PCE per kg of soil.

Soil Depth	Method & Instrument	PCE Conc.	Soil Depth	Method & Instrument	PCE Conc.
1 ft.	headspace, HNU-311	0.395	2 ft.	headspace, HNU-311	36.8
	headspace, Photovac 10S50	0.19		headspace, Photovac 10S50	12.8[2]
	purge&trap, Perkin-Elmer[1]	0.135		purge&trap, Perkin-Elmer[1]	1.52
3 ft.	headspace, HNU-311	3.71	3.5ft.	headspace, HNU-311	1.08
	headspace, Photovac 10S50	3.70		headspace, Photovac 10S50	0.61
	purge&trap, Perkin-Elmer[1]	0.17		purge&trap, Perkin-Elmer[1]	ND

1 Lab analyses performed 7 and 8 days after sampling. Soil samples improperly stored in polyethylene bags with a significant headspace.

2 Integrator reported over-ranged.

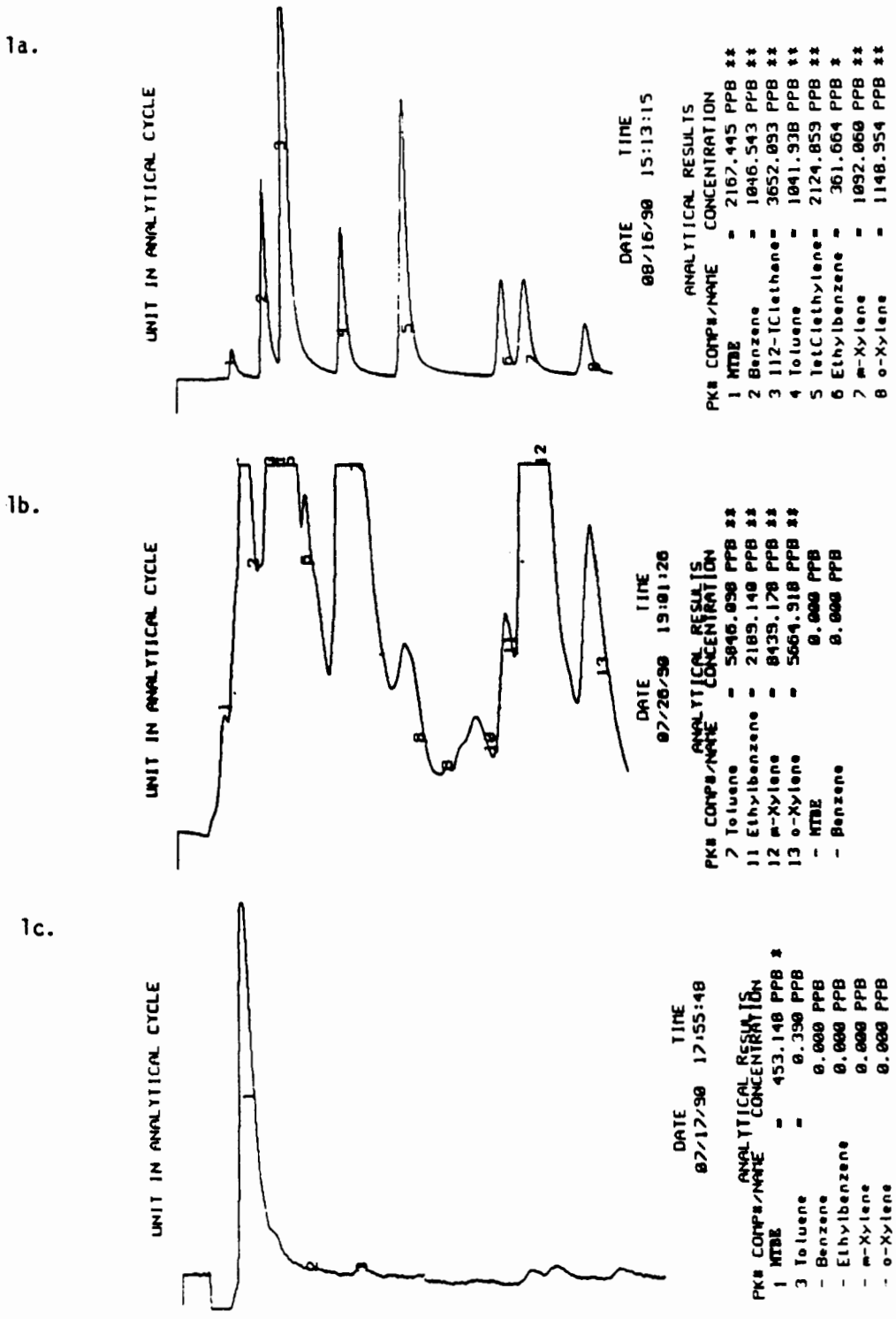

Fig. 1a. Separation of an eight component mixture by injecting the headspace of an aqueous standard solution onto the HNU-311 portable gas chromatograph.
1b. Chromatogram showing significant column overload of a highly gasoline-contaminated groundwater sample onto the narrow-bore, capillary column of the HNU-311 portable gas chromatograph.
1c. Headspace sample of a groundwater sample found to contain only methyl-t-butyl ether (MTBE).

Comparison of Aqueous Headspace Air Standard vs SUMMA Canister Air Standard for Volatile Organic Compound Field Screening

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Abstract

This paper describes the application of SUMMA canister and aqueous headspace air standards for ambient air volatile organic compound(VOC) field screening to perform quick on-site analysis using a portable gas chromatograph(GC). Studies were conducted comparing aqueous headspace standards to SUMMA canister standards using a portable gas chromatograph. A comparison of SUMMA canister analytical results from the portable GC versus GC/MS (gas chromatograph/mass spectrometer) was provided. Research on time dependent stability and temperature dependency of SUMMA canister standards was also conducted. A Photovac 10A10 portable gas chromatograph(GC), an HP 5890/5970 gas chromatograph/mass select detector(GC/MSD) and a Tekmar 5000 thermal desorber modified for canister analysis were employed.

Introduction

Toxic volatile organic air pollution is a growing concern because of its widespread presence in the atmosphere, adversely affecting public health. There has been much interest in monitoring ambient air for these toxic compounds. The United States Environmental Protection Agency(U.S. EPA) has developed several methods for measuring toxic organic compounds in ambient air. These include collection on solid adsorbents, such as Tenax GC and spherocarb traps, as well as the collection of whole air in suitable canisters[1,2]. With the increasing interest in air analysis, field screening for ambient air is becoming more important. When performing on-site ambient air analysis for volatile organic compounds (VOCs) using portable gas chromatography, it is important to have a suitable standard to be able to identify and quantitate compounds of interest. The headspace above a

10 μg/L aqueous standard kept at a constant temperature can be used as a VOC field screening standard to perform quick on-site air analysis using a portable gas chromatograph. The headspace standard is a very simple and inexpensive technique for standard preparation. VOCs, with their relatively high vapor pressures, have a natural tendency to migrate from water into air. In a closed VOA(volatile organic analysis) vial filled three-quarters full with an aqueous VOC standard (Figure 1), VOCs will move from the water into the air above the water (headspace) until an equilibrium is reached. This air above the water is a perfect medium for an air VOC standard since it consists of air and the migrating VOCs from the water.

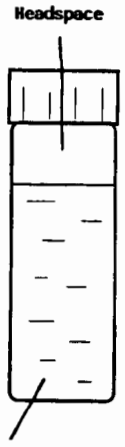


Figure 1. Aqueous Headspace

By the ideal gas equation of state:

$$PV=nRT$$

P: pressure V: volume
R: gas constant n: moles
T: absolute temperature (K)

for a single component **i** in a gas mixture:

$$p_iV=n_iRT \qquad (1)$$

p_i: Partial pressure of component **i**
n_i: Moles of component **i**

the mole fraction or the volume-concentration (ppb/v) of a component **i** in is:

$$M_i=n_i/\Sigma n_j=p_iRT/\Sigma p_jRT=p_i/P_T \qquad (2)$$

M_i: Mole fraction or volume concentration of component **i**
P_T: The total pressure of the gas mixture($=\Sigma p_j$)

Because the aqueous solution is very diluted(10 μg/L), it can be treated as a ideal solution. According to Henry's law:

$$p_i=k_i(T)X_i \qquad (3)$$

$k_i(T)$: Henry's law constant;
X_i: Mole fraction of solute **i** in the water solution.

Therefore, the concentration in the headspace is shown as:

$$M_i=p_i/P=k_i(T)X_i/P_T$$

Henry's law constant k_i varies with temperature(T), therefore, the concentration in the headspace is a function of temperature(T), the total pressure above the solution(P_T) and the mole fraction in the water solution(X_i).

$$M_i=f(X_i,T,P)$$

Whether an aqueous headspace standard can be used for an air analysis standard depends upon the ability to control the concentration of VOCs in the aqueous solution, the pressure of the headspace and the temperature of the standard. The first variable X_i which reflects the concentration of a VOC in the

water solution can be simply controlled by preparing a solution with a known concentration of the VOC. The temperature(T) of the standard can be controlled and kept constant by placing the VOA vial in an ice-water bath, keeping the aqueous standard solution in the vial at approximately 0° - 1°C. The total pressure(P_T) above the solution is equal to atmospheric pressure. Relative changes in atmosphere pressure are negligible. Therefore, for this screening application, the total pressure (P_T) can be considered a constant. With the ability to control the variables above, the aqueous headspace can be used for ambient air field screening analysis as an external standard.

SUMMA canister based sampling systems have gained wide acceptance for the collection of integrated whole ambient air samples containing volatile organic compounds. Utilization of this sample collection method has increased significantly. Some recent research has used SUMMA canisters as VOA standards[4]. As an application, SUMMA canisters are able to be used as field screening standards as well. Canister standards present the true concentration of VOCs within the can and the VOCs stored in a canister exhibit relatively long term stability. In addition, the transportation of a canister standard is easy; therefore, the development of this method can be a very effective approach of SUMMA canister methodology and VOC field screening for ambient air.

The following work is on the method studies of SUMMA canister application and aqueous headspace as ambient air standards for field screening of VOCs. The comparison of aqueous headspace standards to SUMMA canister standards using a portable gas chromatograph and a comparison of SUMMA canister analytical results from the portable GC versus GC/MS were performed. Research on time dependent stability and temperature dependency of SUMMA canister standards was also conducted.

Experimental

(1) Evaluation of aqueous headspace standards:

Experimentation was performed to determine the actual concentration of selected VOCs in the headspace above a 10 μg/L aqueous standard contained in a closed 40ml VOA vial filled with 30ml of aqueous standard kept at a temperature of 0°-1°C. Analysis was performed on a Photovac 10A10 portable gas chromatograph equipped with a 4' 1/8" SE-30 column and a photoionization detector, calibrated with a Research Triangle Institute(RTI) certified mixture of VOCs traceable to NBS primary gas standards. (Table 1.) The

Table 1. RTI Certified Concentration for 18 Component Mixture Containing Volatile Toxic Organic Compound Traceable to NBS Primary Gas Standards

Cylinder No. ALL 21378

Compound	Concentration(ppb/v)
Vinyl Chloride	5.19 ± 0.5
Bromomethane	5.68 ± 0.6
Trichlorofluoromethane (Freon 11)	5.15 ± 0.7
Methylene chloride	4.48 ± 0.5
Chloroform	4.86 ± 0.5
1,2-Dichloroethane	5.02 ± 0.5
1,1,1-Trichloroethane	5.22 ± 0.4
Benzene	5.15 ± 0.3
Carbon tetrachloride	5.02 ± 0.5
1,2-Dichloropropane	5.15 ± 0.3
Trichloroethylene	5.11 ± 0.3
Toluene	5.19 ± 0.3
1,2-Dibromoethane	4.83 ± 0.5
Tetrachloroethylene	5.24 ± 0.3
Chlorobenzene	5.27 ± 0.3
Ethyl benzene	4.85 ± 0.3
o-Xylene	5.12 ± 0.5

Photovac portable GC was calibrated by running a syringe blank and a single point of the RTI certified cylinder standard. Concentrations of VOCs in the cylinder were approximately 5ppb. An aqueous standard (working standard) was prepared using 5.0 μl of commercial (Supelco) and EPA repository standard mix solution (200 μg/ml for each component) diluted to 100 ml with VOC-free water giving a final concentration of 10 μg/L for each component. Table 2 shows the component and concentration of the Supelco and EPA repository stock standards. The working standards were stored in 40ml VOA vials with zero headspace at 0° - 1℃. Before the analysis, 10 ml of water solution was

Table 2. Components and the concentration of the Stock Standard Solution (Supelco Purgeable A and B, and EPA Repository) and of the Canister Standards

Compounds	Concentration Stock Solution (μg/ml)	Canister Standards ($\mu g/m^3$)	(ppb)
Trichlorofluoromethane	200	55.6	9.9
1,1-Dichloroethylene	200	55.6	14.0
Methylene Chloride	200	55.6	16.1
t-1,2-Dichloroethylene	200	55.6	14.0
1,1-Dichloroethane	200	55.6	13.8
Chloroform	200	55.6	11.5
Bromochloromethane	200	55.6	10.6
1,1,1-Trichloroethane	200	55.6	10.2
Carbon Tetrachloride	200	55.6	12.0
Benzene	200	55.6	17.5
1,2-Dichloroethane	200	55.6	13.8
Trichloroethylene	200	55.6	10.4
1,2-Dichloropropane	200	55.6	12.1
Bromodichloromethane	200	55.6	8.3
1,3-Dichloropropene	200	55.6	12.3
Toluene	200	55.6	14.8
1,1,2-Trichloroethane	200	55.6	10.2
Tetrachloroethylene	200	55.6	8.2
Chlorobenzene	200	55.6	12.1
Ethyl Benzene	200	55.6	12.9
Bromoform	200	55.6	5.4
m-Xylene	200	55.6	12.9
o-Xylene	200	55.6	12.9
1,1,2,2-Tetrachloroethane	200	55.6	8.1
1,3-Dichlorobenzene	200	55.6	9.3

withdrawn from the vial, leaving 30 ml of the standard water solution and 10 ml headspace in the vial. The vial was then placed into an ice-water bath to equilibrate for about 30 minutes at 0° - 1℃. After equilibration, the headspace was analyzed on a portable GC. Four trials of analysis were conducted separately. The data in Table 3 presents the analytical results from the portable GC of selected VOC concentrations in the headspace.

(2). Preparation and GC/MS Calibration of SUMMA canister standards:

Duplicate standards were prepared in 6L pre-vacuumed Anderson made SUMMA passivated canisters. The canisters were cleaned by vacuum and heating. Canisters were vacuumed to <5 mmHg at about 100℃ for 4 hours. 5.0 μl of the stock standard solution (Supelco purgeable A and B, and EPA VOC repository) was injected into the each canister. The canisters were then pressurized to 30

Table 3. Concentration of Selected VOCs in Aqueous Headspace(*)

Compound	Concentration (ppb/v) Trial 1	Trial 2	Trial 3	Trial 4	Average	RSD%
Benzene	146	161	161	135	151	7.3
Trichloroethylene	163	129	141	134	142	9.2
Toluene	166	153	191	127	159	14.5
Tetrachloroethylene	212	229	177	187	201	10.2
Ethyl benzene	128	154	134	115	133	10.6
o-Xylene	98	122	95	47	91	30.1

(*): Above a 10 μg/L water solution at 0°-1°C.

psi with 25% relative humidity. The concentrations of each VOC in the canister was 55.6 ng/l. Table 2 shows the VOC concentration of the canister standards. Following a 24 hours equilibration period at room temperature, the canisters were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a 60 m megabore capillary column and 5970 Mass Selective Detector. A Tekmar 5000 thermal desorber modified for canister analysis was used for desorbing. The calibration results are shown in Table 4. The canister cleaning and analysis were performed according to EPA Method TO-14 and EPA Region I draft SOP for ambient air VOC analysis.

Table 4. GC/MS Certified Concentration of Standard Canisters

Compound	Calc.(*)	Concentration (ppb/v) GC/MS Can A	GC/MS Can B
Trichlorofluoromethane (Freon 11)	9.9	10.7 ± 1.3	11.4 ± 2.6
Methylene chloride	16.0	12.2 ± 2.0	13.6 ± 2.9
Chloroform	11.4	9.7 ± 0.6	10.9 ± 1.3
1,2-Dichloroethane	13.7	12.0 ± 0.9	13.0 ± 1.7
1,1,1-Trichloroethane	10.2	9.3 ± 1.1	10.7 ± 1.7
Benzene	17.4	15.7 ± 2.6	17.4 ± 2.6
Carbon tetrachloride	11.9	10.0 ± 1.0	11.2 ± 2.9
1,2-Dichloropropane	12.0	11.3 ± 1.2	12.2 ± 1.9
Trichloroethylene	10.3	9.1 ± 0.9	10.4 ± 1.3
Toluene	14.8	13.6 ± 0.7	14.8 ± 1.6
Tetrachloroethylene	8.2	7.3 ± 0.6	8.1 ± 1.0
Chlorobenzene	12.1	10.7 ± 0.7	11.5 ± 1.6
Ethyl benzene	12.8	12.5 ± 1.6	13.2 ± 1.5
o-Xylene	12.8	11.4 ± 0.9	11.7 ± 1.5

(*): Calculated according to dilution.

(3). Portable GC analytical results of canister standards:

The GC/MS certified canister standards were analyzed on a Photovac 10A10 portable GC which was calibrated with the aqueous headspace working standard of VOCs. Table 5 shows the analytical results of benzene, trichloroethylene, toluene, tetrachloroethylene, ethyl benzene and o-xylene.

Table 5. Comparison of GC/MS results versus portable GC on Canister Standards

Compound	Concentration (ppb/v)				
		Can A		Can B	
	CALC.	GC/MS	PGC	GC/MS	PGC
Benzene	17.4	15.7	12.0	17.4	11.6
Trichloroethylene	10.3	9.1	8.7	10.4	8.7
Toluene	14.8	13.6	14.0	14.8	14.1
Tetrachloroethylene	8.2	7.3	9.9	8.1	10.1
Chlorobenzene	12.1	10.7	10.5	11.5	9.0
Ethyl benzene	12.8	12.5	12.0	13.2	12.0
o-Xylene	12.8	11.4	10.0	11.7	13.0

(4).Comparison of aqueous headspace standards versus canister standards:

The certified canister standards and aqueous headspace standards were used for calibrating the portable GC to analyze prepared air samples. Four air samples of different concentrations were prepared in SUMMA canisters and were certified on GC/MS. The samples were then analyzed on the portable GC. Table 6 shows the analytical results. Based on different calibration standards, two groups

Table 6. Comparison of Aqueous Headspace Standards vs Canister Standards on Portable GC Analysis

Compound	Sample:	Concentration (ppb/v)											
		#1			#2			#3			#4		
		(MS)*	AH	Can	(MS)	AH	CAN	(MS)	AH	CAN	(MS)	AH	CAN
Benzene		(27)	22	32	(14)	12	18	(6.8)	6.1	8.8	(2.7)	3.3	5.0
Trichloroethylene		(16)	24	29	(8.1)	8.1	9.7	(4.1)	3.5	4.2	(1.6)	1.6	2.1
Toluene		(23)	32	34	(12)	13	14	(5.8)	6.5	6.5	(2.3)	2.4	2.4
Tetrachloroethylene		(13)	17	14	(6.4)	7.6	6.0	(3.2)	5.0	4.2	(1.3)	1.3	1.6
Ethyl benzene		(20)	18	16	(10)	9.0	8.0	(5.0)	6.5	5.5	(2.0)	ND**	ND
o-Xylene		(20)	22	20	(10)	13	12	(5.0)	4.5	4.2	(2.0)	ND	ND

(*): Results of GC/MS analysis
(**): Non-detected

of data were obtained. The data in the columns under "AH"(Aqueous Headspace) are the results from the portable GC calibrated by the aqueous headspace standard and those in the columns under "CAN"(CANister) are the results from the portable GC using the canister calibration. Comparisons between the two data groups on benzene, toluene, trichloroethylene, tetra-chloroethylene, ethyl benzene and o-xylene were performed.

(5).Stability of canister standards and temperature dependency:

The study of time dependent stability of different manufactures' SUMMA canisters has been reported[3]. The study in this paper focused on the time dependent stability of benzene, toluene, trichloroethylene, tetrachloroethylene, ethyl benzene and xylenes. Two canister standards were analyzed on a periodic basis using HP 5890/5970 GC/MSD. With seven months of analytical results, there were no significant variation of VOC concentrations in the canisters. Figure 2 shows the time dependent

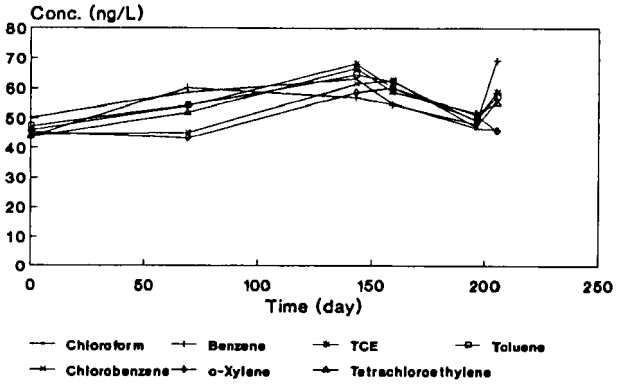
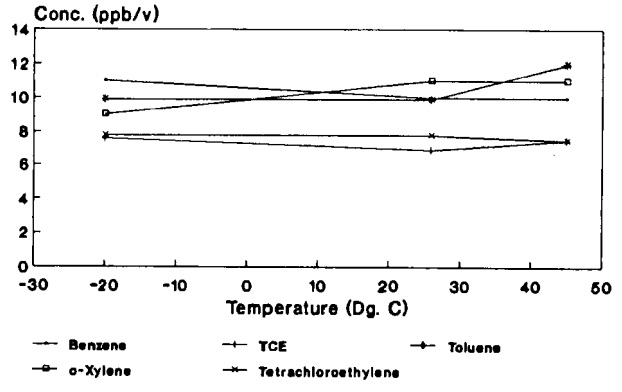


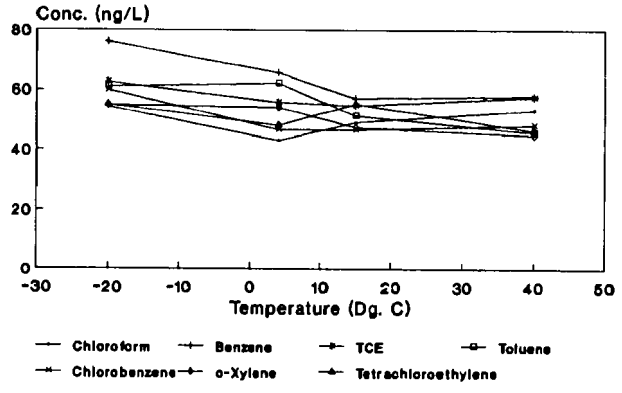
Figure 2. Time dependent Stability of Canister Standards

stability for several selected compounds.

As a standard for field screening, the temperature variation is an important factor for the canisters. The temperature dependency study was performed at various temperatures ranging from -20℃ to 45℃. A canister standard and a duplicate were stored at each temperature environment for at least three hours, then analyzed on GC/MSD



(a). Portable GC Analysis



(b). GC/MS Analysis

Figure 3. Temperature Dependency of Canister Standards

and on the portable GC. Figure 3 shows the temperature dependency result of canisters. The data shows those standards were very stable over the temperature range of -20℃ to 40℃.

Conclusions

According to both the theoretical and experimental results, the aqueous headspace standard is a suitable VOC standard for ambient air field screening analysis. The field screening headspace standard is easy to prepare with materials that are readily available in any environmental laboratory. It takes very little time to prepare and the cost to prepare this type standard is minimal.

Canister standards possess high accuracy for most of the VOCs and reflect real concentrations of the VOCs inside. Canisters are easy to store and transport, and are reusable. The temperature dependency study on canister standards showed that VOC concentration in canisters remain stable over the normal field condition ambient temperature range of -20℃ to 40℃. The time dependent canister stability tests showed that canister VOC standards have long term stability. Over a seven month time period, VOC concentrations in canister standards remained stable.

Compared with aqueous headspace standards, canister standards are relatively expensive. Because of all the necessary accessary equipment needed for standard preparation, this method is only recommended to those laboratories which have a canister analysis set up.

Acknowledgment

The authors wish to thank the Regional Laboratory of the U. S. EPA Region I, in which all of the experiments were conducted.

Reference

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DISCUSSION

THOMAS SPITTLER: I have to say that I saw this data just about two or three days before I left for this meeting, and I was literally astounded at how well that the simple, inexpensive, standard preparation correlated with the incredibly expensive, complicated GC/MS canister technology in our lab. We didn't show you half the slides he had of all the equipment required to prepare and analyze the canister standard.

RALPH SULLIVAN: When you remove about ten cc's of liquid, did you back fill with air, or make any provision to clean up that air as it went in, if you did that?

HUI WANG: No, that's just the same procedure as we prepared the headspace standard for soil and water screening. We just pull the air out and just use it. We have a mobile lab that's relatively clean. Is your question about the cross-contamination from the air getting into the headspace?

RALPH SULLIVAN: Yes.

HUI WANG: The mobile lab is relatively clean. It has probably very, very low levels of those target compounds. It's never going to affect our standard.

THOMAS SPITTLER: We've actually looked at the lab air in our building and it's as clean as the outside air. And that means about 1 ppb of benzene and toluene and nothing else. We've never seen much need to put a big charcoal scrubber in for that make-up air.

RALPH SULLIVAN: But you do put another hypodermic syringe in there to dissolve the air?

THOMAS SPITTLER: Yes, the needle is just stuck in there. Room air just goes in to replace the drawn water.

RALPH SULLIVAN: The next question has to do with the canisters. I saw nothing in the diagram that indicated that you put any water into the canister. Did you put water into the canister with a syringe?

HUI WANG: Yes, in many canisters there's about 25% relative humidity. I calculated the amount of water we need and injected more water to the canister directly.

RALPH SULLIVAN: Do you have mixtures of standards or single component standards in the vials and in the canisters?

HUI WANG: Yes, composed of multi-components not only single components.

RALPH SULLIVAN: So, you added various quantities of say, neat compounds into the vials and also into the canisters?

HUI WANG: Yes. Actually, I used the same stock solution. We use the same stock solution for canister and headspace standards.

Quantitative Soil Gas Sampler Implant for Monitoring Dump Site Subsurface Hazardous Fluids

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ABSTRACT

In conjunction with a triservice (Army, Navy, and Air Force) program to develop a cone penetrometer with associated sensors and detectors, a prototype soil gas sampling system has been fabricated and functionally tested. The system, referred to as TerraTrog, quantitatively samples hazardous soil gases and vapors. TerraTrog can be deployed by a cone penetrometer to depths of 100 ft far less expensively than drilling monitoring wells. The device may be permanently implanted or may be retrieved and deployed at multiple locations using the cone penetrometer.

TerraTrog comprises two modules: an implant of small dimensions containing a gas-permeable membrane of high diffusion impedance (located at subsurface levels) and a sampling and calibration interface with a pneumatic manifold (located at ground level). Unlike conventional non-quantitative soil gas sampling techniques requiring vacuum to operate, TerraTrog relies only on soil gas diffusion for subsurface soil gas collection and a carrier gas stream flowing at a slight positive pressure for lifting the sample to the surface. Because the sampling is diffusion-limited by a membrane of known impedance, the sampling rate and sample size are independent of soil permeability. Sampling does not deplete the local soil gas or vapor, guaranteeing the accuracy of measurements made with the device even after long periods of continuous sampling. The system has a 15 min. maximum time-rate-of-response.

Functional and performance testing has been performed with trichloroethylene in soil, water, and air, using a Photovac 10S70 portable gas chromatograph. The implant has been demonstrated to operate as designed, i.e., is diffusion-limited with implant response directly proportional to external soil gas partial pressure.

INTRODUCTION

A major problem in the cleanup process or assessment of sites contaminated by hazardous waste and toxic chemicals stems from the paucity of information regarding site subsurface characteristics, composition, and aerial and volumetric extent. Performing a general prospecting or screening

survey of the site hazardous fluids and their mobility or stability is of significant value in developing preliminary overall containment and treatment plans (1). A network of relatively low-cost implanted soil gas samplers deployed throughout the site vadose and peripheral zones as well as adjacent aquifers and high permeability strata can be utilized effectively for site prospecting and characterization. The notion of an implanted sampler network is a viable concept only if waste characterization data can be provided quickly and inexpensively and if the sampler can provide samples of all hazardous soil fluids and contaminants and can interface at the dump site with a variety of analyzers or monitors and secondary samplers.

This soil gas sampler system, called TerraTrog for easy reference, is described below and addresses the above requirements satisfactorily, offering features that promote simple, low cost sampler deployment; minimal soil disturbance from deployment; minimal sample extraction during each sampling episode, providing a correspondingly more representative sample of soil gases; minimal hardware; and small dimensions. The TerraTrog implant has a 1-in. lateral dimension and can be deployed by cone penetrometers available commercially (2). In addition, sampler operation is independent of the soil permeability over a range of 0.1 to 1000 mD, and therefore, quantitative data are obtained for sandy as well as clay soil types. These operational features also render the sample obtained independent of sampling chamber volume, line length, sampling pump head, and corresponding pressure losses.

An important consequence of using implants in the initial prospecting process and then progressing to the characterization and monitoring phases is that the network of permanent implants deployed initially can be used for the life of the dump site cleanup and monitoring tasks. Thus, an implanted sampler is a very attractive concept for long-term site monitoring requirements.

THE SAMPLER IMPLANT SYSTEM

TerraTrog comprises two modules: the subsurface implant and the surface control interface. Figure 1 illustrates the system. Soil gases enter the implant at flow rates proportional to the individual gas partial pressures and the partial and vapor pressures of dissolved and pure liquids, respectively, regardless of the soil permeability. The soil gases are lifted to the surface by the carrier gas stream, which enters the surface module and flows at a controlled and measured flow rate to and through the implant and returning to the surface as shown. Soil gas analysis and monitoring is accomplished by the analyzer or monitor attached to the carrier gas stream return line at the interface. The

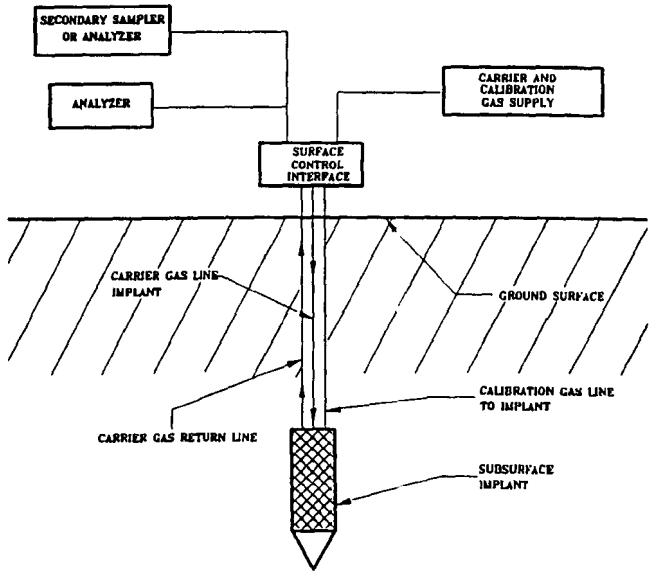

FIGURE 1 - TERRATROG SOIL GAS SAMPLER SYSTEM

analyzer/monitor and carrier gas used are compatible with all aspects of TerraTrog and the data quality requirements of the application. In situ calibration of the implant is performed with an innocuous or surrogate gas, which is carried to the implant by the calibration gas line. During one calibration episode, it is anticipated that less than 1000 μl of calibration gas is injected directly into the soil surrounding the implant.

In addition, a secondary sampling device (grab bag, bubbler, etc.) may be attached to the interface, and soil gas may be collected in batches for subsequent laboratory analysis. With a sufficiently large carrier gas stream flow rate, one or more analyzers/monitors and/or one or more secondary samplers can be attached to the carrier gas outlet of the interface and can be operated concurrently.

Implant

The cross-sectional illustration of the implant (Figure 2) depicts a cylindrical array of eight metal rods approximately 6 in. long, contained within a 1-in. diameter envelope. These are surrounded externally by a 1-in. diameter, 0.002-in. thick Teflon tubular membrane. The rods provide mechanical support for the tubular membrane.

Both ends of the tube are sealed from the surrounding soil by O-rings and a top and bottom header. A sealing cap compresses the tube and O-ring into a groove on the bottom header. A nut and the cone tip maintain the sealing cap in place as shown. Carrier gas is introduced to the tube interior and returned to the surface through the top header, which also serves as a gas manifold. There is no pneumatic communication between the calibration gas and the implant interior or the carrier gas. Calibration gas enters the header and flows directly to the periphery of the calibration gas diffuser cap where it is injected into the region external and adjacent to the tubular membrane. The calibration gas diffuser cap also serves as the sealing cap in an identical fashion as the bottom sealing cap. It is maintained in place by a metal gasket and nut. The thread sealing gasket ensures that calibration gas does not leak through the threads shown.

Surface Control Interface

The surface control interface module comprises a panel attached to a metal stake embedded in the soil. A pneumatic gas control network is mounted to the panel back side. Gas connections are made through fittings that lead to the carrier and calibration gas supplies and the respective pneumatic lines to the implant. The carrier gas return line connects to a manifold for an analyzer/monitor and/or for secondary sampling devices.

All gas connections are made at the panel face. All pneumatic lines contain inline filters. The carrier gas flow rate is controlled by a precision pressure regulator and flow adjustment valve. A 0 to 60 psig pressure gauge measures the regulated pressure, and a rotameter measures the carrier gas flow rate. Calibration gas flow rate is controlled by the gas supply pressure regulator and a flow-limiting orifice in the surface module network. Each gas line contains inline pressure relief and shutoff valves downstream to prevent overpressurization of the implant and to assist in the startup and checkout process.

When not in use, the sample ports are capped or plugged. Note that no electrical power is required to either maintain or operate the interface or the implant as described. All power requirements are associated

with the analyzer or monitor.

PRINCIPLE OF OPERATION

Implant operation is based on a flow of soil gases by diffusion through the semi-permeable tubular membrane of Figure 2 (3-7). In addition, the soil gas flow rate is diffusion limited by the membrane and consequently independent of the soil permeability. As carrier gas flows through the implant, the concentration of the soil gas species at the surface is a ratio of the two gas flow rates:

$$[G] = (Q_s/Q_c)\ 10^9 \qquad (1)$$

where

[G] = soil gas species concentration in the carrier gas stream at the interface module, parts per billion (ppb, v/v);

Q_s = soil gas species flow rate into the implant, std ml/min; and

Q_c = carrier gas flow rate, std ml/min.

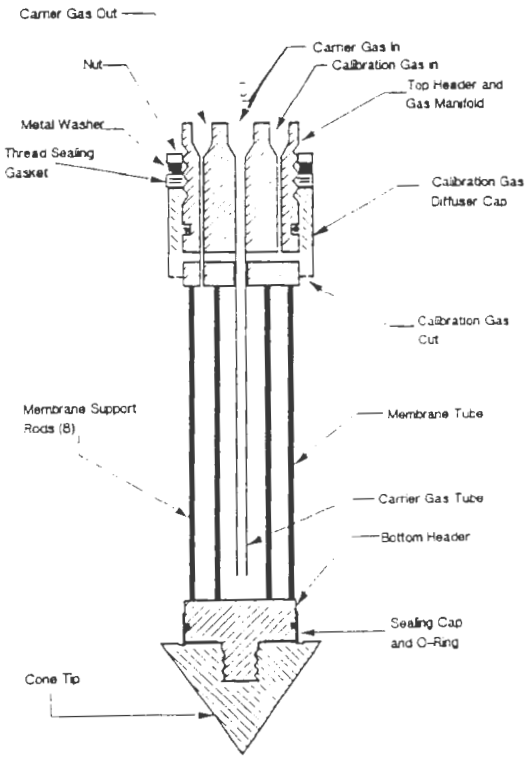

Figure 2 - Sampler Implant

The carrier gas flow rate is measured at the surface interface module. The soil gas species flow rate is the product of the soil gas species membrane conductance and partial pressure in the surrounding soil. By lumping the membrane and carrier gas parameters into the term, y, the soil gas partial pressure is related to [G] as follows (6,7):

$$P_{sg} = y\ [G] \qquad (2)$$

where

P_{sg} = soil gas species partial pressure in the soil, torr.

The system response time is the sum of the time to saturate the tubular membrane with soil gas to an equilibrium concentration, the carrier gas lag time in the pneumatic lines, and the time required from startup to establish carrier flow through the interior gas volume of the implant to the condition where equilibrium concentration is established.

For an implant with a 1.000-in. Teflon tubular membrane, 0.002-in. thick, and a soil gas diffusion coefficient of 10^{-6} cm^2/s (8), the time to saturate the tubular membrane is approximately 128 s. The lag time will depend on the inside diameter of the carrier gas pneumatic lines, the depth of the implant, and the carrier gas flow rate. For TerraTrog operating with a 50-std ml/min carrier gas flow rate stream, 0.0625-in. inside diameter pneumatic lines, and an implant 50 ft. below the surface, the lag time of the system is 73 s. Approximately 7.7 min are required to exchange five implant gas

volumes at a 50-ml/min carrier gas flow rate. It is certain that the tubular membrane will saturate shortly after deployment of the implant and long before carrier gas is flowing and thus contributes insignificantly to the system response. Thus, the time required to obtain an equilibrium reading at the ground surface from startup is approximately 10 to 11 min for the conditions listed above.

Equations 1 and 2 describe the soil gas species concentration at the surface interface for TerraTrog operating in the dynamic sampling mode, i.e., the operating mode in which the carrier gas flows continuously through the implant. The implant can also be used in the static sampling mode, i.e., the operating mode in which the carrier gas does not flow ($Q_c = 0$) for a prescribed period of time preceding dynamic sampling but flows only after the equilibrium condition described below is attained. Note that soil gas flow into the implant will continue, regardless, until the soil gas partial pressure difference across the tubular membrane is 0. At this point, the net flow of soil gas into the implant is 0, and an equilibrium soil gas concentration internally and externally of the tubular membrane is obtained. After this equilibrium is attained, the carrier is used to lift the soil gas accumulated in the implant.

For the initial condition, where the soil gas partial pressure, P_{sg}, measured at the surface interface is 0 (P_{ig}, the sampler implant intergral soil gas partial pressure is 0), the time required to obtain the static equilibrium condition with the soil gas pressure, i.e., $P_{sg} = P_{ig}$, is 7.22 days (6,7) for the implant dimensions listed above and a soil gas permeability coefficient of 2×10^{-9} std ml/min-cm^2-torr/cm (9).

P_{ig} will be less than P_{sg} at equilibrium because of mixing and subsequent dilution of the soil gas accumulated in the implant by the carrier gas stream. It is estimated that five implant chamber volume exchanges with carrier gas will be required to remove the soil gas accumulated in the implant and transport it to the surface. Assuming homogeneous mixing, the average soil gas concentration or partial pressure measured at the surface will be one-fifth the soil gas partial pressure during the five volume gas exchanges; at a carrier gas flow rate of 50 std ml/min, the time period is approximately 7.7 min.

In situ calibration of the implant is performed with calibration gas supplied to the external surface of the tubular membrane. A calibration gas stream enters the calibration gas inlet, flows through the top header and gas manifold to the calibration gas diffuser cap and through the holes in the cap to the external surface of the tubular membrane. The implant operates on the calibration gas as it does on soil gas.

DESIGN AND OPERATIONAL CONSIDERATIONS

Aside from fundamental system analytical and monitoring performance requirements, the system design constraints are established by reliability and service life requirements and deployment flexibility. TerraTrog reliability corresponds generally and most importantly with the exigencies of maintaining the relationship of soil gas species partial pressure, P_{sg}, and the measured soil gas species concentration, [G], described by equation 2. Adherence to this relationship is predicated on the design

and operational integrity of the tubular membrane and the pneumatic lines leading to the surface. It is essential that the soil gas flow into the implant by a diffusion process only, and therefore, the tubular membrane must be free of tears, punctures, and pin holes and other pneumatic leaks. Thus, pre- and post-assembly inspection of the tubular membrane as well as an implant leak check is required. The tubular membrane must not be damaged during the deployment and operational processes.

Relatively inert implant fabrication materials, e.g., stainless steel and Teflon, are used, because after deployment, every external and perhaps some internal component or surface will be exposed to chemical and physical attack. It is of prime importance that the tubular membrane material be chemically and physically inactive with the soil and with benign as well as hazardous soil fluids to ensure that the tubular membrane material diffusion conductance (3-5) remains unchanged during the life of the implant. Teflon of any form is regarded as the most suitable material for the tubular membrane. The membranes currently in use are fabricated of 2 mil (0.002 in.) thick Teflon film.

The maximum typical soil gas sample flow rate into the implant is approximately 0.01 std uL/min for arbitrary but realistic conditions. In a relative sense, it is a very small sample, yet large enough to produce a [G] for many soil gas species within the response range of many gas phase analyzers/monitors that may be attached to the interface.

There are three important aspects to the relatively small sample size or flow rate: First, the disturbance to the soil is minimized; consequently, a more representative sample is obtained independent of soil fluid conditions. Second, for soil strata in and around dump sites, the soil gas flow rate into the implant is diffusion limited by the tubular membrane and is independent of the gas permeability of the surrounding soil. Thirdly and most importantly, these conditions lead to a quantitative measurement of the soil gas partial pressure.

The soil gas flow rate is proportional to the soil gas species pressure only, without regard to the form of the sample, i.e., gas phase, liquid phase, or dissolved gas/liquid phase. For example, the implant can obtain information regarding dissolved trichloroethylene (TCE) in water or TCE saturated in water, and insoluble gases contained in the water. Furthermore, the implant also functions as described immersed completely in an aquifer or other body of water or liquid.

SOIL GAS ANALYSIS AND MONITORING

In a relative sense, the actual soil gas monitoring and analysis of the transport gas output stream from the interface panel is the most simple and direct procedure of the entire system. A variety of analyzers, monitors, and secondary sampling devices can be used singularly or simultaneously. The user, however, must establish preliminary requirements for the target species and the lower detection limits of the analytical devices contemplated, i.e., it is essential to consider the analyzer/monitor performance specifications to specify and adjust the operating conditions of TerraTrog.

TERRATROG PERFORMANCE

TerraTrog response to trichloroethylene (TCE) in soil, water and air has been characterized in the

laboratory. The test equipment was arranged in a configuration identical to Figure 1, with the implant suspended in a specially built test vessel. In separate tests, soil, water and air with measured concentrations of TCE were contained in the vessel to simulate implant field deployment conditions. The vessel was pneumatically sealed to prevent loss of TCE vapors except by diffusion through the implant gas permeable membrane and subsequent removal on the implant carrier gas stream.

The response characteristics of the implant were determined by monitoring the concentration of TCE within the test vessel external to the implant and by monitoring the carrier gas entering and exiting the implant in dynamic sampling mode, and by direct analysis of the implant contents in static sampling mode. In all tests, it was verified that the concentration and therefore partial pressure of TCE in the soil, water or air external to the implant remained stable and constant during the period of the test. All concentration measurements were made on a Photovac 10S70 portable gas chromatograph with a 10-m CPSIL5CB capillary column and a photoionization detector. The gas chromatograph was calibrated using air standards prepared from aqueous solutions of TCE of known concentration (9).

Representative data for the TerraTrog time-rate-of-response in static sampling mode to dissolved phase TCE in water is shown in Figure 3. The internal concentration reaches equilibrium with the external TCE concentration in 7 days (168 hr.). This is in excellent agreement with the calculated equilibrium response time, 7.22 days (6,7).

Representative dynamic sampling mode data for the

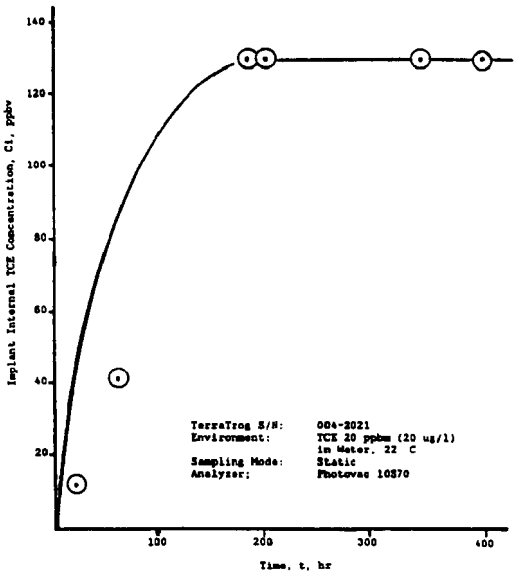

Figure 3 Implant Time-Rate-of-Response to TCE in Water

implant response, [G], to TCE as a function of inverse carrier flow rate, $1/Q_c$, is shown in Figure 4. A multipoint calibration curve, Figure 5, shows the relationship between implant response, [G], and external dissolved phase TCE concentration in water. Figure 4 show the implant response is linear regardless of whether the implant is deployed in soil, water, or air. Additionally, the flow rate of TCE into the implant, Q_s, is constant when the implant is sampled in dynamic mode in an environment of constant external TCE concentration. The sample flow rate, Q_s, is relatively small, ranging from 9.2×10^{-5} std. μl/min for dissolved phase TCE at 100 ppbm external concentration in water, to 3.7×10^{-3} std. ul/min for gas phase TCE at 227 ppmv external concentration in air. Figure 5 shows that the implant response, and hence Q_s, varies linearly with the external TCE concentration and therefore with the external TCE partial

pressure. The data demonstrate that Q_s is dependent only on the permeability, P_m, of the implant gas permeable membrane, and the external TCE partial pressure, or concentration (6,7). Therefore, the implant operation is diffusion-limited by the implant gas permeable membrane and the implant response is directly proportional to the external TCE partial pressure in soil, water, or air, exactly as

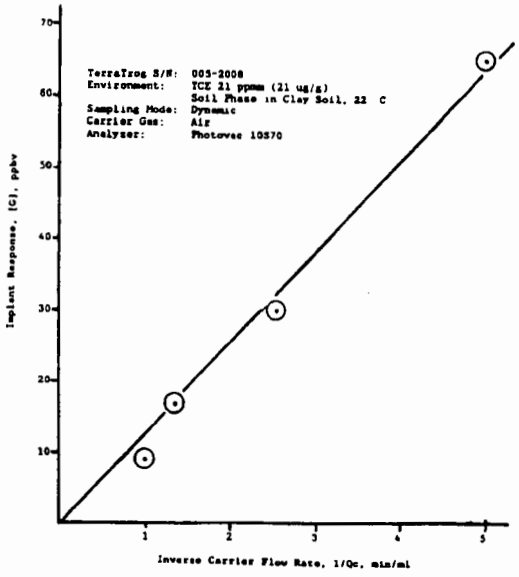

Figure 4 Implant Response to TCE in Soil

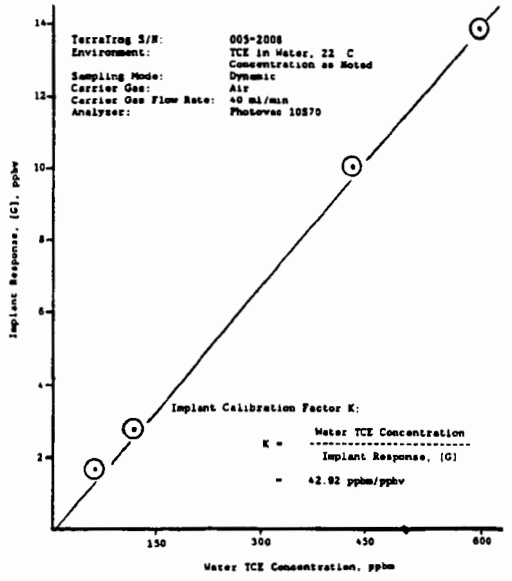

Figure 5 Calibration Curve for Implant Response to TCE in Water versus TCE Concentration

described by equations 1 and 2.

The multipoint calibration curve, Figure 5, can be used with the implant to directly measure the TCE concentration in contaminated groundwater in the field. For example, a user would deploy the implant to the desired depth in a monitoring well or other body of water and establish a carrier flow rate of 40 ml/min. The implant response would be measured using a conventional gas-phase TCE analyzer, such as the Photovac 10S70. The implant response would then be located on the vertical axis of the calibration curve, and the corresponding TCE concentration in the groundwater read off the horizontal axis of the curve.

Since the implant response is shown to be linear in the multipoint calibration curve of Figure 5, it may be replaced with a single point calibration which yields a linear calibration factor, K:

$$K = [C_e]/[G]$$

where

K = implant linear calibration factor, ppbm/ppbv

$[C_e]$ = external TCE concentration, ppbm

[G] = implant response, ppbv

The linear calibration factor may be used exactly as the multipoint calibration curve to make direct field measurements.

TEST PLANS

Laboratory and Controlled Field Testing

Further laboratory and field testing is in progress at the National Institute for Petroleum and Energy Research (NIPER). Laboratory testing is planned to demonstrate the quantitative TerraTrog sampling characteristics over a range of controlled soil

permeability from 0.1 to 1500 mD.

TerraTrog will be deployed in soil by a cone penetrometer to depths approaching 50 ft to develop deployment procedures and techniques, optimize the pneumatic line dimensions and configuration, and determine the effects of the surrounding subsoil mass on the implant operational integrity. Optimum deployment procedures will be developed regarding the mechanical aspects, the pneumatic tubing, and grouting and sealing the bore hole. In addition, the in situ calibration scheme described above will be implemented to develop optimum calibration procedures. This work will determine the utility and validity of the in situ calibration. The TerraTrog performance after calibration will be assessed with calibration gas injections.

CONCLUSION

The development of the TerraTrog is viewed as having real potential for future use in the evaluation of hazardous waste sites. The potential utility of the device includes not only initial site assessment, but possibly of more importance, its use in the routine monitoring that is essential to the long term assessment of a site before, during and after remedial activities are accomplished. Although initially designed to be used in a cone penetrometer, the utility of the device for routine groundwater monitoring is also recognized due to its small diameter and ability to descend down standard well casings.

ACKNOWLEDGEMENTS

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DISCUSSION

ROBERT LUGAR: With the TerraTrog probe, have you considered how to avoid cross-contamination between holes or carrying it to a lower depth if you're doing a depth profile?

KEN LANG: We've considered that a potential problem, but since we don't have any experience with actually pushing it into the ground yet, we're not sure whether or not it is going to be a problem, and as such we're not going to try to engineer that problem out until we see whether or not it does happen. I really don't think it's going to be a problem because, as was presented in the Navy's work, on some sites that have fairly high contamination, the device seemed to be rather self-cleansing as it was pushed down in through the soil. They made that determination based on the sapphire window, and the fact that their readings of contamination dropped off rather rapidly. And we're hopeful that that's going to happen with this device. The membrane does not come in direct contact with the soil, so I'm hoping that that will not turn out to be a problem.

SKIP WEISBERG: When you inject the carrier gas in to drive the soil gas out, do you then feed that directly into the GC, or do you add an additional supplemental carrier?

KEN LANG: The testing that we've done so far involves feeding that carrier gas directly into the gas chromatograph. We may find out later on, especially if our aim is toward reducing detection limits, that there may be other things that we have to do. Calculations suggest that in order to cleanse the chamber, the interior of the membrane, you would want to get at least five volume changes. I think we calculated that the internal volume of that is somewhere around 80 cc's. So, we already believe that for some instrumentation we're going to have to preconcentrate that material before it's actually introduced into the analytical instrument.

SKIP WEISBERG: I was wondering if you would suffer a dilution in loss of sensitivity due to the injection of a carrier gas down into the soil?

STEVE KNOLLMEYER: I was wondering if the teflon membrane acts to cause certain molecules to diffuse more through the membrane and retain some of them outside just because of their molecular size?

DANIEL LUCERO: Yes, the conductance of the membrane varies with the analyte. For example, benzene has a higher permeability coefficient than does TCE. And of course what that means is that the system has to be calibrated if you want accurate results. The variations are not great for organic molecules. But if you want more accurate results, then you do have to calibrate. And if you implant the device and start seeing a gas that you haven't calibrated against, then that was the reason for the inside calibration ports that you have in there. There are no holes in the membrane; it's not a porous membrane. It works by solution/dissolution. And as such there is a difference in impedance from analyte to analyte.

THOMAS SPITTLER: Have you ever tried to push the cone penetrometer through glacial till very far?

KEN LANG: No, we haven't pushed the penetrometer at all. That's the next step.

THOMAS SPITTLER: I don't like to be rough about it, but I think you're in for a shock.

KEN LANG: We have not pushed the penetrometer with the TerraTrog on it. We have made lots of pushes of the penetrometer with other devices on it, but not in glacial till. There are obviously some limitations. One that would come to mind right off would be once you hit bedrock that's as far as you go. Chert is also a problem, and we have tried to push through chert materials and it doesn't work there, either. So, there are some limitations of the cone penetrometer that we're already aware of.

TUNABLE CO_2 LASER-BASED PHOTO-OPTICAL SYSTEMS FOR SURVEILLANCE OF INDOOR WORKPLACE POLLUTANTS

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Disclaimer: Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

Abstract

This paper describes research work recently conducted at the National Institute for Occupational Safety and Health (NIOSH) on the use of CO_2 laser lidar for surveillance of indoor workplace pollutants. Long-term goals of this program included an ability to real-time map the spatial distributions of a variety of pollutants in a workplace atmosphere. In pursuit of this goal, a rapidly-tunable, Q-switched, low pressure laser was developed for time-of-flight aerosol backscatter differential absorption measurements. This enabled effective atmospheric freezing as well as the evaluation of possible methods for suppressing the severe multi-reflection scatter problems common in work environments. Experiments were performed to determine the practicality of utilizing aerosol backscatter methods in the desired lidar system. The results of the experiments indicated that present practical technology did not support such a methodology. Other special hardware requirements of a field-deployable lidar system were explored, including high-speed, high-sensitivity detector systems, and miniature detector cryocoolers.

Introduction

During discussions held at the National Institute for Occupational Safety and Health (NIOSH) on research needs for gas and vapor monitoring, industrial hygienists and instrumentation specialists alike voiced a need for portable surveillance equipment to map concentration distributions of selected vapor phase chemical pollutants in the workplace atmosphere, on a real time basis. It was suggested that this should be some type of optical instrument, requiring only line of sight from it to the areas to be monitored. Investigating possible approaches to this task, a number of recommendations regarding the desirable characteristics of a gas and vapor surveillance system were gathered. These recommendations indicated that an ideal system should: (a) be portable (movable into various workplace settings for surveys etc.), (b) be single-ended (no use of retro-reflector arrays or transmitters and receivers separated by large distances), (c) give real-time mapping of the spatial distribution, concentration and identity of a variety of airborne pollutants commonly found in the workplace, (d), not present any hazard to the people in the workplace (from laser radiation, chemicals, liquid nitrogen, etc.), (e) require minimal maintenance (some routine service perhaps every several months), (f) have a sensitivity on the order of 10-100 parts per billion (over sampling distances of five meters) for some pollutants, (g) have a range up to a few hundred meters, (h) be automated and programmable for unattended data gathering, (i) have a spatial resolution of at least five meters full-width-half-maximum (using a point source), and (j)

survey the workplace at least every five minutes. In reviewing previous research in this field, two principle methodologies were identified: Fourier transform infrared (FTIR) spectroscopy, and laser-based light detection and ranging (lidar) systems.

Fourier-Transformed Infra-red (FTIR) Systems

Open-beam, long-path FTIR systems appear to be gaining much attention, and showing at least a limited potential for qualitative assessments of atmospheric gas and vapor contents for toxic waste site monitoring, as well as fence-line monitoring. Such a system has been used by Herget for various outdoor studies[1,2] as well as an workroom study in an aluminum refinery potroom.[3]

Other investigators have used FTIR equipment similar to that used in analytical laboratories, for a "real time" analysis of gaseous pollutants in the workplace by use of a multi-port sampling apparatus with sample lines running from work locations to a central FTIR system.[4,5]

FTIR has several advantages over alternate methodologies including: (a) high sensitivity, (b) high specificity, (c) a large variety of chemicals detectable and identifiable, (d) technology is well tested, based on similar laboratory use, (e) proven field ruggedness and dependability, (f) no support requirements other than electricity (if detector cooling is not used), (g) commercial availability, (h) an inherent self-calibration of certain parameters of the equipment, (i) "real time" analysis capability, and (j) portability of the apparatus, making its use for temporary applications feasible. Possible problems associated with this approach include: (a) a lack of an adequate gas phase high resolution spectral library when peak identification methods are used to identify unknown compounds, (b) likely problems with chemical interferences in the analysis, (c) a lack of adequate spatial resolution for some applications, such as measuring breathing zone chemical concentrations, (d) a requirement for either a two-ended system or one using retro-reflectors, (e) a lack of adequate scan speeds to achieve "atmospheric freezing" and, (f) a reduction in the systems sensitivity due to atmospheric water vapor.

Currently, a Nicolet Instrument Co., Madison, Wisconsin, custom portable open beam path FTIR system is being evaluated for industrial hygiene applications by the University of Michigan School of Public Health (S. Levine) and the University of California, Berkeley (R. Spear).[6] This work is being supported by a NIOSH grant #1-\R01-OH02666-01. The Bomem Inc., Quebec, Canada, Model DA2 open beam path FTIR system is currently being used for a variety of atmospheric pollution studies by M. Spartz at the Kansas State University.[7]

Laser Remote Detection Systems

Laser systems have been quite useful in making remote measurements of chemical contents of the atmosphere for a variety of purposes and using several methods. Most remote photo-optical pollution detection work has been accomplished using light detection and ranging (lidar) methods where laser produced radiation was transmitted into the atmosphere to be measured and the return radiation (either aerosol scattered or terrain or retroreflector reflected) is analyzed to obtain the desired information about the chemical contents of the atmosphere. This has been accomplished by a variety of methods[8] including:

a. The analysis of Raman scattered radiation: In this method, Raman scattered short pulses of laser radiation (usually at ultraviolet (UV) and blue wavelengths) are analyzed for their photon intensity vs wavelength distributions as a function of the time from the emission of the radiation pulse from the laser. This results in the identification and quantification of the pollutant of interest as a

function of distance from the transmitter. The return signal is relatively weak due to the small Raman scattering coefficient. This limits the range of this technique to a few hundred meters, even using very powerful lasers. Its time-of-flight (the time between a transmitted laser pulse and the return signal pulse, indicating by the time differential what the distance was between the transmitter and a particular scattering or reflecting location) position resolution (ranging) can be on the order of 10 meters. This approach has been used in many investigations, usually to measure pollutants in exhaust plumes from factories or power plants. Raman lidar has the advantage of being applicable to a large variety of pollutants. However, the spectral resolution and bandwidth of the Raman signal is relatively broad leading to significant interferences in complex mixtures of pollutants. Interference often results from sunlight or other bright lighting. Principle limitations are a severe lack in sensitivity of the technique (a very weak Raman return signal) requiring the use of very powerful laser systems which are typically not "eye safe" and would be very difficult to make "eye safe" while preserving the system performance. Also, spatial resolution has been poor due to the poor data statistics of the return signal, and the near field interferences in time of flight measurements.

b. Resonance Absorption Methods: These methods depend on transmitting a laser beam having a wavelength very close to that of a resonance absorption line of a chemical species being measured, and measuring a return signal reflected off of an object or from aerosols in the laser beam's path. It is generally a much more sensitive method then that of Raman scattering due to the much higher scattering coefficient for Mie scattering. This increased scattering coefficient could result in an extended range, the use of lower powered lasers, the use of less sensitive detectors, better range resolution, and faster measurements than Raman lidar. It has the disadvantage of being able to measure only one pollutant at a time when only one laser wavelength is used. Unresolved interferences can result when only one transmitted wavelength is used. One version of such a system uses differential absorption lidar (DIAL) whereby the laser radiation wavelength is shifted between two (or more) wavelengths, one of which is very near to the resonance absorption line of the pollutant being measured and another line which is not. The ratio of these measurements is used to normalize the measurement system calibration with regard to the scattering characteristics of the atmosphere being studied. By measuring the return signal intensity for successive locations along the beam path, subtraction yields the signal loss due to the incremental decrease in the observed signal associated with a range increment ΔR, and arising from the attenuation of the specific molecular constituent for which the laser is tuned. This is described by the following equation:[8]

$$\Delta E_{o*} = [E(\lambda_o,R) - E(\lambda_o,R + \Delta R)] - [E(\lambda_w,R) - E(\lambda_w,R + \Delta R)]$$

where:

ΔE_{o*} = the incremental decrease in the differential signal $E(\lambda o,R)$ = the return signal energy at range R and wavelength λ_o, representing a maximum absorption by the chemical of interest.

$E(\lambda_w,R)$ = the return signal energy at range R and wavelength λ_w, representing an absorption off the resonance line of the chemical of interest.

Using conventional timing methods, DIAL systems can have ranges of several km, and spatial resolutions of as small as 10 m.

Ranging Methods

Principal methods used for position determination (ranging), include: (a) time-of-flight, (b) triangulation ranging (such as methods used by the U.S. Bureau of Mines for measurement of methane gas concentrations at coal seams in mines[9]), and (c) the use of variable focal distance optical systems. Variable focal distance optical systems have been used successfully in laser doppler wind velocity measuring apparatus using CO_2 lasers and heterodyned detection methods, and have produced spatial resolutions of approximately 10 m at a range of approximately 100 m, with maximum useful ranges of up to 1 km. However, this method requires a coherent detection system.[10] Practical problems have been encountered with these systems due to their instabilities and engineering difficulties, including frequency instability, harmonic generation, phase shifted echoes and loss of wavefront parallelism. In addition, there are significant problems associated with the application of coherent detection systems with rapid wavelength shifting, when the parallel retuning of both the transmitting laser and a local oscillator laser must occur or when optoacoustic wavelength shifting of part of the transmitter signals is used as the local oscillator. In addition, coherent detection is probably not practical for short distance time-of-flight measurements (believed to be necessary for our application) due the heterodyne frequencies required to achieve a 30 ns timing resolution. This is especially significant when considering optoacoustic wavelength shifting.

Laser Types

Many laser systems exist for lidar applications, from extremely short-pulse-length, high-energy/pulse systems to continuous-emission, low-power devices covering wavelengths from the far ultraviolet to the far infrared. If a very rugged, low maintenance, compact system is needed, tunable over a range of wavelengths, the number of available lasers becomes quite small. Possible candidates include dye lasers, solid state diode lasers and CO_2 lasers. The dye lasers suffer from rather narrow tuning ranges for a specific dye, moderate to high maintenance requirements and moderate to large sizes. They operate mostly in the near ultraviolet to near infrared region. Operation at those wavelengths may make design provisions for personnel eye protection more difficult due to lower allowable limits of radiation exposure.[11]

Tunable diode lasers are available at less than 1 W outputs covering wavelength ranges from approximately 2 - 30 μm. Significant problems associated with these devices are: (a) a very narrow tuning range, requiring an array of such devices in order to cover a wide wavelength range, (b) high cost, (c) low power output, and (d) large size and weight when a cooling apparatus is included.

Many gases and vapors of interest for monitoring purposes have rich absorption spectra in the near to far infrared, associated with their rotational-vibrational molecular transitions. The CO_2 laser emits radiation in any of about 80 lines in the region 9-11 μm. The number of available wavelengths can be expanded through the use of isotopes of carbon or oxygen in the CO_2. One of these lines can often be closely matched to a rotation-vibration absorption line of a pollutant of interest so that it is feasible to monitor a large variety of compounds (though not necessarily simultaneously). A wide variety of chemicals have been identified as being detectable using a CO_2 laser based lidar system (see Table I for a partial list of gases which can be detected using CO_2 lines[12]). Using rapid tuning, a single laser could presumably be used for differential absorption monitoring of more than a single substance, and under many circumstances, without interference by other vapors or aerosols in the atmosphere. Humidity would be expected to produce little interference in monitoring pollutants in the 9-11 μm region from direct absorption alone. However, in cases where the two differential absorption lines are separated by more than 2×10^{-2} μm, moisture effects on the scattering and absorption properties of certain aerosols may become a concern.[13] Other advantages of the CO_2 laser include the potential for a durable, compact and modest costing laser, lacking extensive utility and

maintenance requirements, a more liberal allowable irradiance level for laser radiation at long wavelengths vs the UV and visible[11] (this may prove to be an advantage, depending on other system performance factors), and that wavelengths produced by the CO_2 laser are transmitted well through normal atmosphere.

Table I. Partial list of CO_2 laser detectable gases[12]

Name	Wavelength (μm)	Differential Absorption coefficient (atm^{-1} cm^{-1})	Sensitivity (1% diff ab) (ppm-m)
Ammonia	9.2	56	0.9
Benzene	9.6	1.0	50
Chloroprene	10.3	8	6.3
Ethylene	10.5	28	1.8
Freon 11	9.2	11	4.5
Freon 12	9.2	7.6	6.6
Hydrazine	10.8	4.3	12
Methanol	9.7	19	2.6
Monomethylhydrazine	10.3	2.6	19
Ozone	9.6	5.5	9.1
Perchlorethylene	10.7	3.0	17
Trichloroethylene	10.5	3.1	16
Triethylamine	9.6	0.5	100
Asymmetrical dimethyl hydrazine	10.7	0.5	100
Vinyl chloride	10.6	6.5	7.7

A difficulty arises with using infrared radiation rather than visible or ultraviolet in a laser surveillance system using aerosol backscatter signals, because of the lower aerosol backscatter efficiency. As the wavelength is increased, the efficiency of light scattering from aerosol decreases quickly, approximately as λ^{-4}. Therefore, many remote sensing systems designed to provide ranging information have relied on radiation sources other than CO_2 lasers.

In an aerosol backscatter lidar workplace application, the maximum range of interest is on the order of 100 m, compared to the 1-2 orders of magnitude larger in many outdoor applications. As a result, the return light spreading radially from the points of scatter has a short distance for the intensity to drop (falling as $1/r^2$ with distance r). Thus, the limited range needed in the workplace may allow the use of infrared radiation for remote sensing applications.

A literature search revealed no information on the volume backscatter coefficient ($\beta(\lambda,R_o)$) (the parameter characterizing the backscatter efficiency) pertaining specifically to infrared radiation and workplace aerosols. Since the aerosol environment varies considerably from one workplace to another, the backscatter coefficient also will vary.[14,15]

Past Uses of Lidar Systems for Workplace Monitoring

There have been a few attempts in the past to use laser based photo-optical technology for workplace monitoring. In 1981, Britain's Imperial Chemical Industries and G.P. Elliot Electronic Systems, Ltd. made a brief report on a system they were working on using a CO_2 laser-based lidar system for scanning a workplace.[16] To our knowledge this device never was implemented. MDA Scientific, Norcross, Georgia, (formerly Tecan Remote and Environmental Laser Systems), claims to have obtained an exclusive license to use that technology for their applications.

In 1983, Egan of Bethlehem Steel's Homer Research Laboratories reported on the trial of an Er:YAG laser based differential absorption aerosol backscatter lidar for methane detection in mines.[17] In 1985, Litton of the U.S. Bureau of Mines reported on their work in developing a methane monitor using a laser diode operating at 3.3 μm, and a triangulation system for ranging. This resulted from problems with sensitivity and explosion proofing of the equipment, as well as a desire for tunability. Results are not yet available.[9]

In 1985, Persson, at Chalmers University, Sweden reported on a dual CO_2 laser differential absorption detection system for use in a workplace.[18] It used a continuous wave (CW) laser with retro-reflectors placed at the end of the laser beam path. The device measured total column content of the pollutant chemical, thus yielding an average concentration along the path.

Tecan Remote produced a commercial differential absorption CO_2 laser based system for workplace pollutant monitoring.[19] They used a total column content method and retro-reflectors. They have installed systems at some major chemical manufacturers facilities for monitoring around process equipment of special concern. Wavelength changing to monitor different chemicals monitored was possible by a manual retuning of both lasers.

Other photo-optical methods were considered including non-coherent pulsed ultraviolet, visible and infrared sources with sensitive spectroradiometric

detection systems. The method seems to be limited by the need for both very intense and very short light pulses when applied to aerosol scattering methods. Generally, adequate high intensity broadband sources having pulse lengths under 10 μs are not yet commercially available. This tends to force the use of long-path measurement methods making use of retro-reflectors, and the acceptance of much poorer spatial resolution. The system's spectral resolution could cause problems in the presence of chemical interferences.

Problems in Applying CO_2 Laser DIAL Lidar Technology to Workplace Monitoring

Based on the above information, it appeared that a CO_2 laser DIAL system had significant potential for leading to a working system that would satisfy most of the system characteristics stated earlier. FTIR methods were also considered promising; however, at least two other research groups were investigating that methodology. Many uncertainties remained in the application of current technology to producing a lidar system satisfying the recommended objectives. These included:

(a) problems in producing a system that can scan a workplace atmosphere while keeping transmitter and receiver beam path alignments precisely co-ordinated,

(b) problems in achieving overall system sensitivities using components that did not require frequent servicing or supplies of materials such as liquid nitrogen, cooling water, etc.,

(c) developing methods for unfolding the identities and quantities of unknown contaminants in complex mixtures, using multiple wavelength measurements,

(d) developing techniques for dealing with data errors due to the effects of rapidly changing aerosol concentrations with time and position. These could contribute to differences in sequential measurements on and off resonance lines,

(e) designing a system that was field portable (that was moveable into a workplace as one or several modules that can be handled by two people). This could place severe restrictions on the equipment selected for use,

(f) designing a system that could operate continuously in an industrial environment without contamination of optical components or without typical temperature and humidity extremes posing a problem,

(g) a significant probability that non-aerosol scattering (scattering from objects and walls in the workplace) could produce a sizeable interfering signal in the detection system, leading to erroneous results or a greatly reduced system sensitivity.

There were significant problems associated with large magnitude non-aerosol scattered return signals from objects in the workplace causing erroneous responses in the receiver. Scatter rejection could be the most severe technical difficulty to overcome. This effect could be reduced by using a coincidence of time-of-flight ranging and triangulation ranging, as well a possible use of both transmitter and receiver polarization for the rejection of multiple scattered return signals (see Figure 1). The triangulation ranging uses a stationary alignment between the transmitted beam and a linear array of receiver detector elements. This fixed transmitter-receiver relationship could also help avoid the difficulty in achieving adequate tracking between a scanning receiver and a stationary or scanning laser beam. In addition, this approach could help to eliminate another potential problem associated with short-range lidar signals, which is a lack of adequate dynamic range in the receiver for return signals arriving from both near and distant scatter sources. By having given detectors look only at a narrow distance range of return signals, acceptable dynamic ranges should result. It was anticipated that combining the narrow field-of-view with time-of-flight ranging would allow a 5m FWHM spatial resolution. It was felt that HgCdTe detectors cooled to liquid nitrogen temperatures might be required here due to the low allowable laser power levels for eye safe conditions, as well as many other demands of the system design.

Calculations for a specific system were performed, using values for variables

suited to the desired system performance. The choice of values for these variables resulted from a review of the specifications of available components and subassemblies (including a consideration of their costs). An example can be seen in Appendix I. The calculations show that we would need a single pulse energy of 2.75×10^{-3} J for the system to function under the conditions defined. The stability of the system's electronics and optical equipment may limit reliable differential measurements to 1 to 2 percent;[12,20] consequently, signal to noise ratio (SNR) values greater then 500 to 1000 may not be useful.

The results of these calculations indicated that if the assumptions used were correct, it would be possible to produce a lidar system having the required sensitivity, beam irradience, pulse energy, etc. However, these calculations: (a) assumed a hypothetical value for the volume backscatter coefficient ($\beta(\lambda_o,R_o)$) which may not represent workplace conditions well, (b) did not address large scattering signals from surrounding objects, (c) assumed perfect performance of optical and electronic components, (d) did not address interfering chemical species, (e) did not address pulsed electrical noise from the laser and Q-switch being introduced into the detector signal, degrading the systems SNR, and (f) assumed that the limited information on detector D^* values were valid for the fast signals necessary for the time-of-flight measurements required.

Equipment and Methods

Laboratory Test System

Based on the review conducted, and the potential benefit of a workplace pollutant monitoring system based on a DIAL system, a laboratory evaluation was conducted of certain aspects of a CO_2 laser workplace DIAL system using time-of-flight and triangulation ranging. In order to make measurements of certain un-evaluated parameters relative to the performance of the lidar system, to verify the practicability of certain design concepts, and to provide for experimental development of a working system, a laboratory test system was assembled. The goals in designing this system were to construct a laboratory apparatus having a maximum flexibility to evaluate various methods of assembling a workable lidar system. It also needed to be capable of measuring many of the system parameters necessary for the development of future designs of a field useable system.

The laboratory test system consisted of the following subassemblies:

Laser

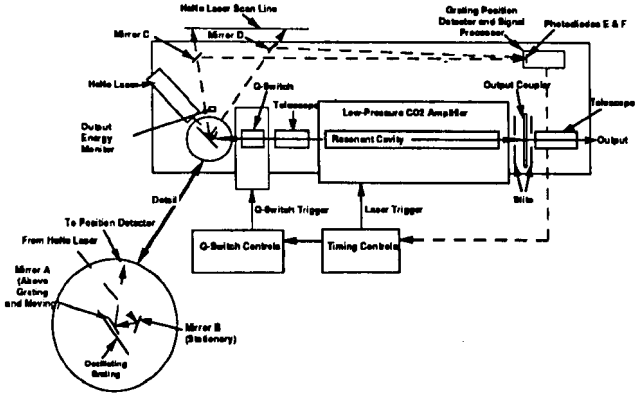
System performance goals necessitated the use of a recently developed low pressure pulsed CO_2 laser in combination with a high performance intercavity Q-switch for producing near-Gaussian (no tailing as is associated with TEA CO_2 lasers), short, high-intensity pulses. In differential absorption lidar systems, it is important that differential absorption measurements in an atmosphere take place on and off of the resonance line of the chemical compound of interest, with a very short time interval between the two measurements. In the past, this has been accomplished by using multiple lasers tuned to different wavelengths, fired sequentially with a short time interval between pulses[20]. It was considered desirable that the two pulses of the pair be produced by the same laser, lowering equipment size, weight, costs and alignment problems.

Rapid wavelength changing of a single laser could allow for a rapid change of chemicals monitored, thus allowing a more frequent monitoring of pollutants of interest. This has not proved to be practical in the TEA lasers typically used, due to both power supply constraints as well as the mechanical behavior of the lasing medium. It was also desirable that the laser be compact, require a minimum of cooling, have an extremely long lifetime (greater that 5×10^7 shots), and use low radio frequency interference (RFI) components.

A laser was constructed using a modified Pulse Systems, Los Alamos, NM, model LP30 low pressure CO_2 amplifier section, due to the long upper lasing level lifetime (greater than 60 ms) of low-pressure CO_2 lasers. This lifetime permitted the Q-switching of two output pulses from a single laser amplifier electrical transverse discharge pulse, while allowing several microseconds for wavelength changing between pulses. An intracavity beam telescope was employed to use the amplifier discharge cavity

cross-section efficiently with the small CdTe Q-switch crystals available. A 1200 Hz oscillating grating with a high-resolution grating position sensor was used to change and reprogram wavelengths rapidly. Programming of wavelengths was accomplished by selecting appropriate delay times from the grating position reference signal for triggering the laser amplifier and Q-switch (see Figure 1). The resulting laser was relatively compact and had a low mass, and low power consumption. It had output pulses of approximately Gaussian shape with full-width-half-maximum values adjustable between 50 and 100 ns; an ability to produce "pulse pairs" having interpulse spacings of 5-50 μs, each pulse of the pair being independently wavelength selectable over most CO_2 laser emission lines; a repetition rate for the "pulse pair" up to 10 Hz;, a pulse energy of approximately 5-10 mJ; and pulse pair wavelengths reprogrammable between pulse pairs. The output of the laser was emitted through a beam expanding telescope such that the irradience was well below maximum permissible occular exposure limits[11] for the pulse widths and repetition rates used. Most of the basic performance goals of the device were achieved in the laboratory prototype. A full description of this laser is presented in a paper soon to be published.[21]

FIGURE 1. Q-SWITCHED DOUBLE-PULSE CO_2 LASER



Beam Power/Energy Monitor

Provision was made for extracting a fixed percentage of the output beam to a beam power and energy monitor. The beam power/energy monitor was used for continuously monitoring the beam pulse-to-pulse energy differences to normalize the results of differential absorption measurements to constant beam pulse energy conditions. This monitor consisted of a fast (<1 ns rise and fall time) room-temperature HgCdTe detector (Boston Electronics Corp., Boston, MA, model R004-0) and a Comlinear Corp., Loveland, CO, model CLC100 low noise amplifier. The monitor had a short term (1 h) reproducibility better then $\pm$1.0 percent and an absolute long term accuracy better then $\pm$5 percent (2σ). This detector monitored the laser output radiation intensity and waveform via radiation reflected from the tuning grating.

Receiving Telescope

The receiving telescope was a Newtonian type having a mirror diameter of 8 inches and an effective aperture of approximately f/4.5. It was used for gathering the return signal laser radiation and projecting a line image of the aerosol scattered laser beam onto HgCdTe detectors.

Detectors

Several types of detectors were available for sensing radiation in the 9-11 μm wavelength band; however, only the HgCdTe detectors had sufficiently high detectivities (as indicated by D^*) for use in this application. HgCdTe detectors are manufactured in a variety of forms, varying in surface area, wavelength sensitivity, frequency response, etc., depending on their applications. Unfortunately, the manufacturers' data on their products were often sketchy, and their testing methods often did not include actual measurements of fast pulses of radiation. Thus, one was often left to speculate on their actual performance in a particular application. Competing performance parameters, frequency response and detectivity, were both critical to the function of the lidar concepts to be evaluated. The detectors evaluated in the receiver system were cooled HgCdTe detectors of photovoltaic (77 K) and photoconductive (77 K and 200 K) types, and were selected as representative of devices commercially available at the time. The photoconductive detectors were specified to have approximately 10 degree fields of view, 1.3 x 1.3 mm size, D^* values of approximately 1 x 10^{11} cm $Hz^{1/2}$ W^{-1} at 10 kHz, and a high frequency roll-off at approximately 10 MHz. The elements were useable as single elements or as a linear array with 5 elements. Element six was a photovoltaic detector 1

mm diameter, had a 10° field-of-view, a D^* rating of 2 x 10^{10} cm $Hz^{1/2}$ W^{-1} at 100 kHz, and a high frequency roll-off at approximately 50 MHz. The detector array was manufactured by InfraRed Associates,Inc., Cranbury, NJ, as their model #89-251R. For very high-speed measurements (<10 ns rise and fall times) a Judsen model J15TE4:10-MC31G-S01M thermoelectric cooled (200K) HgCdTe photoconductive detector with a model TC-4 controller (both manufactured by EG&G Judson, Montgomery, PA) was used. It had a 1 mm diameter detector element, a D* rating of 3 x 10^8 cm $Hz^{1/2}$ W^{-1} at 10 kHz, and a high frequency roll-off at approximately 100 MHz. Generally, the HgCdTe detectors designed for higher operating temperatures exhibited much better frequency responses, but this is accompanied by a significantly lower D^* value. Due to the photovoltaic detectors large capacitances and consequential long time constants, a Comlinear model AJP401 transimpedance preamplifier was used to help reduce the effective time constant. Comlinear Model CLC100 video voltage preamplifiers were used with the photoconductive detectors.

Detector Cooling

The detectors used for detecting return signals were cooled by two methods. The linear array detector was kept at its operating temperature (45-77 K) by a closed cycle miniature refrigeration system (a Philips/Magnavox Model MX 7043, Magnavox Electro-optical Systems, Mahwah, NJ). This consisted of a split Stirling cycle, linear motor device using no bearings or lubricants, and having clearance seals. The overall device was hermetically sealed. Mean times between failures for this device are guaranteed to exceed 2500 operating hours, with test data implying lifetimes >10,000 h. Heat power capacity at 77 K was approximately 1 W, allowing reasonably large assemblies of detectors to be cooled. Total power consumption at those operating conditions was approximately 50 W. The vibration produced by the mechanical refrigerators can cause unwanted motion in the detector, which may degrade system performance by modulating the detector's position relative to the focused photon beam to be detected. The satisfactory performance of such a closed-cycle cooler could provide a considerable advantage to the performance of a field-deployable workplace lidar, allowing the utilization of high sensitivity detector systems without the difficulty of supplying liquid nitrogen for it. The single element photoconductive detector (see identified in "Detector" section) was cooled to 200 K by a four-stage thermoelectric cooler. Such coolers had extremely long expected lifetimes, produced no vibration and required little power (8 W for the one used). The lower temperature limit of such coolers resulted in a less than optimum D^* value for the detector, when detection sensitivity at very high frequencies was not critical.

Transient Waveform Analyzer

A high speed waveform analyzer was needed both for general system diagnostics as well as for analyzing lidar return signal time of flight information. This consisted of two LeCroy Corp., Spring Valley, NY, Model TR8828 Transient Waveform Recorders, capable of capturing two fast waveforms simultaneously and recording them in temporary memory. These recorders digitized the waveform information in 5 ns increments, with an 8-bit accuracy, and stored the information in file lengths up to 32k. These recorders were interfaced via a CAMAC IEEE-488 interface to a data processing system for display and data reduction. ASYST waveform analysis software (Asyst Software Technologies, Inc., Rochester, NY) was used to display and treat lidar return signal data. A specialized fast-Fourier-transform filtration method utilizing a Blackman attenuation function[22] was used to remove unwanted high frequency components of the data, allowing a better extraction of return signal information. After using a wide range of cutoff frequencies with the data, a 30 ns cutoff was selected which, considering the slope of Blackman filter function, appeared to have an effective frequency cutoff of approximately 100 MHz. Some data were recorded using a model 54021A oscilloscope manufactured by Hewlett Packard Co., Palo Alto, CA.

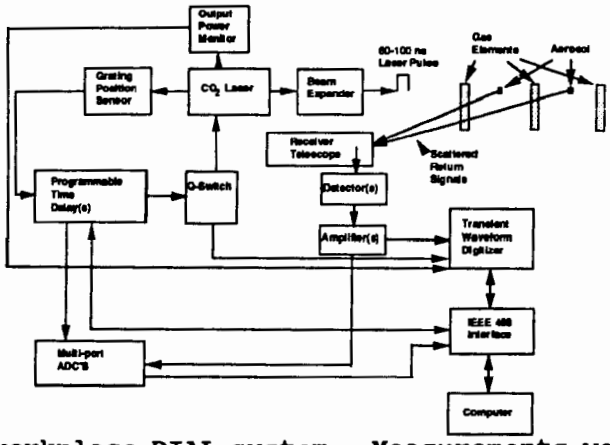
Data Logger

A data logger consisting of at least 12 parallel channels of fast sample and hold amplifiers coupled to 10 bit ADC's, was interfaced to the data processing system via a CAMAC IEEE-488 interface. The sample and hold amplifiers had gate times as small as 10 ns. This enabled the setting of individual time of flight range windows for individual detectors in

a linear array, and a rapid shift of signals from one set of input channels to another between short-interval pulse-pairs.

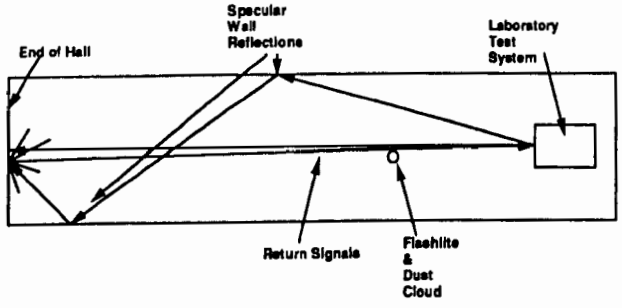
With the assembled laboratory test system (see Figure 2), a series of experiments was performed to help to understand better the potential for using aerosol backscatter as a signal source for a

FIGURE 2. LABORATORY TEST SYSTEM.



workplace DIAL system. Measurements were carried out in a corridor having dimensions of 1.85 x 2.75 x 79 m. Major components of the laboratory test system were mounted on a movable bench positioned at one end of the corridor. The transmitted laser beam was then projected along the major axes of the corridor under several conditions (see Figure 3) including: (a) co-axial with the corridor and intercepted by the end of the corridor;, (b) as in (a), except with an object (a light source mounted on a tripod), and separately, a generated aerosol (wood dust, and bleached flour) in the beam path located 28m from the source; (c) with the laser beam projected to reflect off the walls of the corridor, as well as the end of the corridor. Return signal measurements were made using both the thermoelectric-cooled and

Figure 3. Corridor Measurements Using Laboratory Test System.



Stirling-cycle-cooled detector systems, located at the focal point of the receiver telescope for particular distance intervals along the transmitted laser beams path. The profile of the transmitted laser beam was mapped at a position approximately 28 m from the transmitter, using the thermoelectric-cooled HgCdTe detector operated above its normal operating temperature of 200 K, to reduce its efficiency. The detector was scanned in 2.5 cm intervals from -15 to +15 cm along both the x and y axes on a plane orthoganal to the beam axes. Measurements were made at 10.6 μm wavelength (10P20 line), with a laser output of approximately 2 mJ/pulse. Measurement of the overlap of the receiver acceptance angle and solid angle of the transmitted beam at a given focal distance were made by scanning the detector element across the focal plane for a point reflector backscatter source located at the extremes of the beam cross section. This was accomplished at distances from the transmitter/receiver of 15 and 28 m.

Data and Discussion

Table II shows the transmitted beam cross section relative irradiance profile.

Table II. Mapping of the Relative Irradiance of the Laser Beam Cross Section at 30 m.

Relative Irradiance (W cm^{-2})

Y-axes (cm)	-12.5	-10	-7.5	-5.0	-2.5	0	2.5	5.0	7.5	10	12.5
-12.5					0	0	0				
-10				0	15	50	25	0			
-7.5			0	15	60	100	70	25	0		
-5.0		0	25	175	270	300	250	50	0		
-2.5			0	100	200	250	210	25	0		
0	0	0	50	125	250	275	175	25	25	0	
2.5			0	50	175	300	225	15	0		
5.0				0	50	150	75	20	0		
7.5				0	15	50	25	0			
10					0	0	0				
112.5											

From the slight bipolar shape, it appears that there are probably two cavity resonance modes present. Figure 4 shows the output from the laser as measured by the 200 K detector. The approximately 6 μs interval between two sequential pulses on the 10P16 and 10P20 lines respectively can be seen. Figures 5a-5c show the return pulse (diffusely reflected from an object at 10 m) as monitored by a photoconductive detector element (77 K), a photovoltaic detector element (77 K), and a photoconductive (200 K) thermoelectrically cooled detector respectively. It should be noted that the polarity of the pulses shown in Figure 5 varies with the detector and amplifier used. The output of the 77 K

Figure 4. Dual-pulse Laser Output.

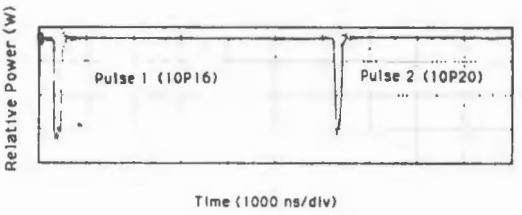
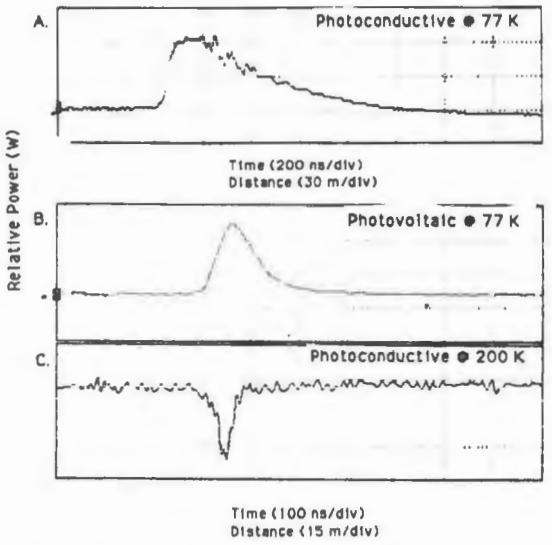


Figure 5. Frequency Response Characteristics of Three Types of HgCdTe Detectors.

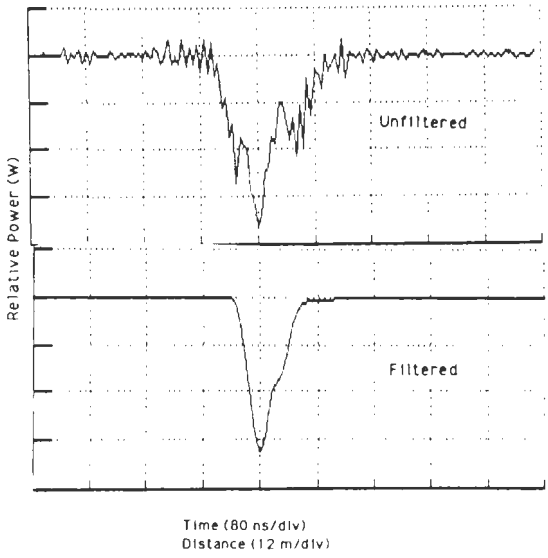


photoconductor and photovoltaic detectors is positive-going, and the 200 K photoconductive detector is negative-going. It is clear that the frequency response of the photoresistive detector is quite poor, with a 1/e time constant of approximately 500 ns. The 77 K photovoltaic detector frequency response was much better, with a 1/e time constant of approximately 80 ns. The frequency response of both of these detectors was somewhat poorer than anticipated. Manufacturer D* specifications for their detectors are often based on low frequency measurements (1 - 10 kHz) and extrapolated to higher frequencies, with possibilities for substantial errors. Pulse shape distortions by the detectors for fast rise and fall time pulses were often not specified by the manufacturer. The time constant of the 200 K photoconductive detector was small enough (specified as <10 ns by the manufacturer) that the laser pulse shape detected by it was not easily distinguishable from that displayed from the high-speed room-temperature HgCdTe detector. Examining the time resolution required for a 10 m time-of-flight (round-trip for the desired 5 m spatial resolution, approximately 33 ns), it seems apparent that, based on frequency response alone, the 77 K photovoltaic detector would be quite marginal, since tailing in its output pulse excessively extended over neighboring spaces, and only the 200K and room temperature photoconductive detectors would be fully adequate. Considering that 60 ns FWHM is probably a lower limit for the transmitted laser pulse width, any further degradation of that pulse width would be unacceptable. It should be noted that it would be difficult to achieve a 5 m spatial resolution from a continuous aerosol backscatter source using time-of-flight methods and a 60 ns FWHM transmitted pulse. We anticipated that the combination of triangulation and time-of-flight could make this possible). Examining the D^* ratings of these detectors, it is clear that substantial system design compromises would be necessary to utilize either one, with the room-temperature device being particularly poor. Considering the above findings, it appears that the earlier use of a D^* value of 1×10^{11} cm $Hz^{1/2}W^{-1}$ in the example calculations was overly optimistic, and that in practice a value of 10^8 cm $Hz^{1/2}$ W^{-1} may be more realistic. This is a result of both the pulse shape distortion resulting from some detectors, as well as an inaccurate extrapolation of D* values to higher frequencies. It is possible that this could be improved by the use of lower capacitance photovoltaic detectors, detectors with a much smaller surface area, or the use of coherent detection methods. The use of much smaller surface area detectors would demand a much more sophisticated optical assembly to achieve a sufficiently stable focus of the return photons on the appropriate detector element. Some practical improvements could probably be achieved with this; however, their magnitude would be difficult to estimate. Additional system sensitivity improvements could be achieved by increasing the receiving telescope

diameter (a 30 cm diameter would increase A_o by a factor of 2), and by increasing laser power (narrowing safety margins to 400% should allow an increase by approximately a factor of 10) to approximately 25 mJ/pulse. Both the closed-cycle Stirling cooler and the thermoelectric cooler worked well during the several hundred hours of operation they were used.

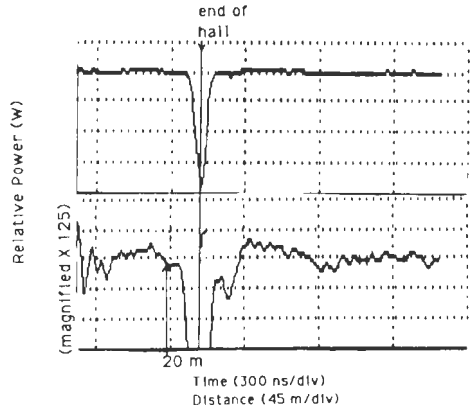
The curves in Figure 6 show the effect of filtration on a single return pulse. Figure 7 shows the overlap of an end-of-corridor return signal with a space separated from it by 20 meters, using the high-speed 200 K HgCdTe detector, and an approximately 90 ns FWHM transmitted pulse. The ratio of the end-of-corridor signal to the adjacent space along the beam path (assumed to be an insignificant signal for the aerosol backscatter component) is approximately 300. Sources of this unwanted signal may include stray light, aberrations in the receiver optics, inadequate collimation of the detector, and the shape and width of the transmitted pulse.

Figure 6. Example of Filtration of Single-pulse Waveform.



If the ratio of the aerosol scattered signal to that from a diffusely reflective surface is approximately 10^{-4}, it appears that the return signal from a space adjacent to such a strong signal would have to be isolated from that signal source by a ratio of at least 10^5, in order for aerosol backscatter from the space to be detectable and useful. Depending on the aerosol concentration

Figure 7. Effect of Large Signal Source on Detection of Neighboring Small Signal Source.



and its reflective properties the aerosol scattered signal could vary over several orders of magnitude. It appears from the data in Figure 7 that the "tails" of the very strong specular or diffuse reflections from walls or other solid objects cause overlaps of signal in neighboring spaces such that the resulting SNR ratings for the adjacent space along the beam path would be inappropriate for detection of aerosol backscatter signals.

Figure 8 shows an example of an aerosol backscatter signal produced by a fine mahogany wood dust aerosol along an approximately 3 m pathlength of the laser beam, at a distance of approximately 28 m from the transmitter/receiver. The waveform was the result of the subtraction of a return signal without added aerosol from one with the added aerosol. The limiting background noise in the signal appeared to be the result of electrical noise from the Q-switch induced into the detector signal path, rather than amplifier and detector noise. This aerosol was poorly characterized; however, it very likely represented wood dust levels in excess of OSHA allowable limits (a visible cloud). This experiment was used to produce an example of an upper practical limit of the amount of backscatter signal that could be obtained. Normal aerosol concentrations in the air-conditioned laboratory space were insufficient to observe aerosol backscatter with the receiver efficiency and transmitted laser power of the present system.

An examination of the difficulties in using aerosol backscatter as a signal source for a workplace DIAL system prompted an examination of alternatives. The above data suggest that the scatter from workplace objects and walls could provide a strong signal source for a "column content" system. Time-of-flight return signals, such as in Figure 9, could be cross-correlated with the transmitted signal to enhance the separation of return pulses having differing time-of-flight values, thus enabling a determination if only one significant scattering of the transmitted

Figure 8. Backscatter From Wood Dust Aerosol.

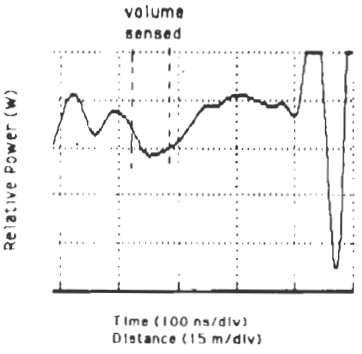
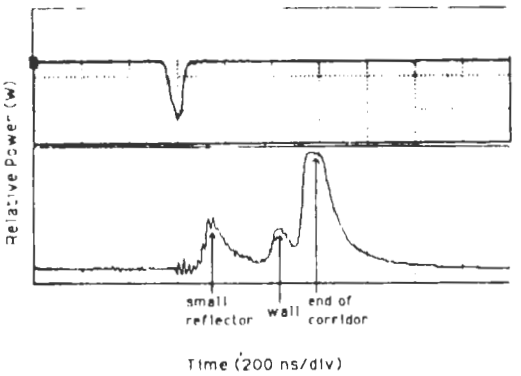
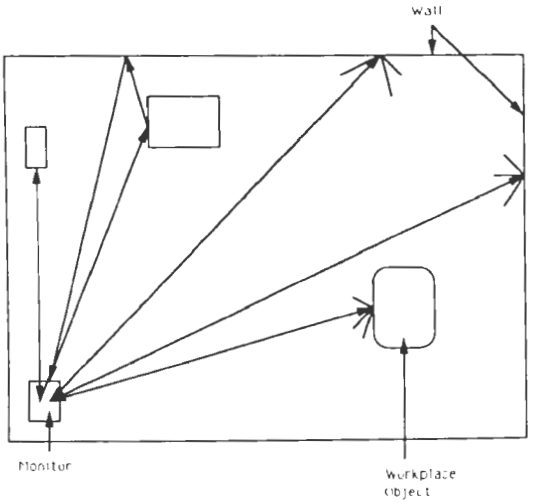


Figure 9. Multiple-scattered Return Signal.



signal had taken place, as well as to determine the round-trip path length of the transmitted pulse to the receiver (see Figure 10). The continuous radial scanning of a workplace utilizing this methodology may provide a useful means of generating an angular mapping of average beam-path concentrations in the workplace. The use of more than one transmitter/receiver system, having overlapping monitoring fields, could allow construction of a workplace pollutant concentration map. It is also possible that an aerosol backscatter signal could be used if the reflective surfaces the beam could intercept were treated to reduce their refectivities (perhaps by a few orders of magnitude), or in outdoor workplaces where no significant non-aerosol backscatter sources were in the field-of-view. Outdoor settings should also provide a substantially larger backscatter coefficient.

Figure 10 Radial-scanning Workplace Monitor.



Conclusions

This study identified several substantial limits to the use of an aerosol-backscatter DIAL system for workplace monitoring. These were (a) the limitations of currently available detectors, when applied to a high spatial resolution time-of-flight lidar, (b) the difficulty in providing very high optical isolation ratios for adjacent spaces along the laser beam, (c) the probable low aerosol concentrations for air conditioned workplaces (compared to outdoor concentrations),[14] and (d) the difficulty in eliminating induced signals from the laser Q-switch into the receiver electronics. Of these, (b) is probably the most difficult problem to correct. A consideration of these basic problems identified in the use of aerosol backscatter as a means of providing a continuous source of return signal leads the author to conclude that present practical technology precludes such a methodology. Outdoor workplaces without

non-aerosol backscatter sources in the field-of-view could be a suitable setting for using aerosol backscatter methods. As an alternative, it appears that the use of backscatter from workplace objects may provide a useful means of generating an angular mapping of average beam-path concentrations in workplace. Further work is needed to indicate the viability of this approach.

Acknowledgment

The author wishes to acknowledge the efforts of Gregory J. Deye, physicist, for his work in the difficult task of adapting the Asyst software to the requirements of the data output of the laboratory test system, and David Bartley, research physicist, for his initiation of the concept for this project. Both are employees of the Division of Physical Sciences and Engineering, the National Institute for Occupational Safety and Health, Cincinnati, Ohio.

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APPENDIX I

From Measures[8]

$$E^{min} = \frac{2R^2 \ (SNR)^{min}}{\beta(\lambda_o,R)\ \xi(R)\ A_o\ \xi(\lambda_o)\ \Delta R\ D^*\left(\frac{4B}{A_d}\right)^{1/2}} e^{2\int_o^R k(\lambda_o,R)dR}$$

where:

E^{min} = minimum laser energy pulse required to observe a return signal at range R (J)

R = range to ΔR being sensed (cm)

ΔR = range interval being sensed (cm)

SNR^{min} = signal to noise ratio

$\beta(\lambda_o,R)$ = volume backscatter coefficient cm^{-1} sr^{-1}

$\xi(R)$ = overlap factor of laser and receiver beam (geometric form factor)

λ_o = wavelength of resonance line at which laser is operating (cm)

A_o = area of objective lens (cm^2)

$\xi(\lambda_o)$ = receiver spectral transmission factor

τ_d = detection time interval (s)

D^* = specific detectivity (cm $Hz^{1/2}$ W^{-1})

$k(\lambda_o,R)$ = normalized attenuation coefficient for pollutant in atmosphere (STP) (ppm cm)$^{-1}$

C = concentration of pollutant (STP) (ppm)

B = detection bandwidth (sec^{-1}) ($=1/2\tau_d$)

A_d = detector area (cm^2).

Using the following values for variables in the previous equation:

R = 10,000 cm

ΔR = 500 cm

SNR = 1.5

$\beta(\lambda_o,R)$ = 10^{-8} cm^{-1} sr^{-1} (this value may be much higher in an industrial atmosphere or lower an air conditioned atmosphere)

$\xi(R)$ = 1.0

λ_o = 9.639 μm

A_o = 314 cm^2

$\xi(\lambda_o)$ = 1.0

τ_d = 5 x 10^{-8} s

D^* = 10^{12} cm $Hz^{1/2}$ W^{-1} (10^o acceptance angle) (practical values for this variable using non-coherent detection are probably on the order of 10^{11})

$k(\lambda_o)$ = 2.4 x 10^{-6} ppm^{-1} cm^{-1} (Benzene at 1ppm cm^{-1}) (other compounds may have values up to 10^2 times that for benzene)

C = 1 ppm

A_d = 1.7 x 10^{-2} cm^2 (0.05" on side).

Then,

E_L^{min} = 4.13 x 10^{-6} J

If 10 sequential shots are accumulated, then:

$\tau_d = 5 \times 10^{-7}$ s

and

$E_L^{min} = 1.3 \times 10^{-6}$ J per shot

$$N_i^{min} = \frac{1}{2\,\sigma^A(\lambda)\,\Delta R}\ \ln\left(1 + \frac{1}{(SNR)^{min}}\right)$$

$$C_i^{min} = \frac{N_i^{min} \times 10^6}{N_{atm}}$$

$$C_i^{min} = \frac{1}{2\sigma^A(\lambda_o) N_{atm}\,\Delta R}\ \ln\left(1+\frac{1}{(SNR)^{min}}\right) \times 10^6.$$

The attenuation coefficient $k_A^i(\lambda_o)$ (cm^{-1}) of component i under atmospheric condition of interest is given by:

$$k_A^i(\lambda_o) = \sigma^A(\lambda_o)\ N_{atm}$$

Therefore,

$$C_i^{min} = \frac{1}{2k_A^i(\lambda_o)\,\Delta R}\ \ln\left(1+\frac{1}{(SNR)^{min}}\right) \times 10^6$$

Where

$\sigma^A(\lambda_o)$ = absorption cross section of the molecular constituent of interest at wavelength λ_o (cm^2)

C_i^{min} = threshold concentration that can be detected (ppm)

N_i^{min} = threshold number density of species i that can be detected (molecules cm^{-3})

N_{atm} = total number density of molecules in atmosphere under atmospheric conditions of interest (molecules cm^{-3})

For

SNR = 1.5,

$k_i^A(\lambda) = 2.42\ cm^{-1}\ Atm^{-1}$ (for benzene STP)

$\Delta R = 500$ cm

$N_{atm} = 2.55 \times 10^{19}$,

then

$$C_{benzene}^{min} = \frac{1 \times 10^6}{4(2.42)(500)} = 207 \text{ ppm},$$

and we would need a single pulse energy of 6.1×10^{-6} J.

If

SNR = 1000,

then,

$C_{benzene}^{min} = 0.41$ ppm,

and we would need a single pulse energy of 2.75×10^{-3} J.

DISCUSSION

CHUCK FLYNN: I'm curious about the decision, or finding, that it was not useful because of the near scattering effects. If you could do away with this scatter, would it be desirable?

HARLEY PILTINGSRUD: One of the things I mentioned in the paper, and didn't have time to mention here, was that there possibly are some options in some workplace situations where you could attenuate the backscatter from objects in the workplace by some treatment. But it would be a little difficult because you'd have to reduce it by a couple orders of magnitude and that's not real easy to do.

CHUCK FLYNN: And if you took away the desire to do your ranging, could you then do it easier?

HARLEY PILTINGSRUD: As I mentioned the second approach is one where you lose some ranging. You know the direction the beam is pointed but the measurement is a total column content one, so you don't know how the concentration varies along the beam path. By using two such systems at different angles of view, you could achieve some two-dimentionsal spatial resolution.

Immuno-based Personal Exposure Monitors

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Abstract

The feasibility of direct air monitoring using immuno-based collection systems is being investigated with the goal of developing personal exposure monitors that take advantage of the high specificity and sensitivity of immunochemical systems. A system is under development which will lead to compact, diffusion-based personal exposure monitors for specific target analytes. The interface problem of the aqueous based antibody system and the air medium has been overcome using semipermeable membrane tubes with a very high surface to volume ratio. An immuno-based collection and analysis system using a monoclonal antibody developed specifically for pentachlorophenol has been investigated. Similar systems are being developed for aldicarb and various nitroaromatics.

Introduction

The goal of this research is to develop personal exposure monitors (PEMs) that use either a polyclonal or a monoclonal antibody immobilized onto a silica support for collection and detection of a specific target analyte or compound class. Selectivity is based on the inherent characteristics of the antibody system used in the PEM device. The device should be applicable to short- and long-term monitoring and should allow the analysis to be performed immediately after sampling and in the field.

PEMs, both dynamic and passive, have long been used for assessing occupational exposure to hazardous materials. Recently, passive (diffusive) sample collection systems have become popular as PEMs, especially those that use sorbents. The well characterized diffusion rates, high sample capacity, and compact size of many of these sorbent-based diffusion samplers make them ideal for non-intrusive monitoring. Sorbents such as charcoal or Tenax which allow the PEM to collect an array of organic compounds are most commonly used. These compounds are then extracted and analyzed by gas chromatography or gas chromatography/mass spectrometry in a laboratory setting. This is an excellent approach when several components are of interest and the vapor is not characterized. However, this method is not particularly cost effective when only one or two compounds are to be monitored during a specific exposure scenario, such as a pesticide application or bag and drum operation. Only a limited number of compound-specific PEMs are currently available for this type of monitoring (i.e., formaldehyde and NO_x).

Immuno-based collection and detection systems have many attributes which enhance their appeal as PEMs. The antibodies are generally selective for a single compound or closely related class of compounds. This selectivity is an advantage for the isolation of target compounds. Also,

antibodies generally exhibit high binding constants for the target analytes, which means that their collection efficiencies are high. Finally, the antibodies can be easily regenerated to the appropriate labeled or active form and reused.

The antibody-based detection systems available exhibit good sensitivity, with detection limits often in the 10 pg to 100 pg range. Recent applications of amplification methods such as enzyme linked immunosorbent assays (ELISA) have led to these increases in sensitivity. The radioimmunoassay (RIA) procedures, previously used in many immunoassays, have been replaced with colorimetric methods which allow for rapid analysis of multiple samples using inexpensive colorimetric readers (or even visual comparison to standards in some cases). Most immunoassay formats are also relatively simple to use and are readily adaptable to field laboratories.

The limitation in using immunochemical techniques for air sampling is that antibodies are designed to work in aqueous systems. The few attempts to use "dry" antibodies have not been very successful. Studies have been carried out using antibodies immobilized to substrates such as polyethylene, Tenax, and indium [1,2]. The immobilized antibodies were then exposed directly to vapors without a wetting solution. Success was limited to those systems which developed a response in an aqueous solution after exposure. This limited success was most likely the result of the target analyte binding non-specifically to the protein covered surface and then binding specifically with the antibody after wetting. We have overcome this limitation by using a vapor permeable membrane as an interface.

The system we are investigating consists of a vapor-permeable membrane and a cavity that encapsulates the aqueous medium and the immobilized antibody. The membrane acts as the air-to-liquid interface, allowing vaporous analytes to diffuse into the aqueous medium. The ideal membrane should allow the molecules to pass freely and should not interact with the analyte and cause losses by nonselectively retaining the analyte. It should also provide a high surface-area-to-interstitial-volume ratio to keep the PEM small and the mass transport process rapid. Figure 1 shows a diagram of the PEM device. The analyte in vapor form diffuses through the porous membrane of a microdialysis tube. Once inside the tube, the analyte is captured by the antibody immobilized to the packing inside the tube. The capture results in the release of a labeled compound or an enzyme product (depending on the type of detection system) to the aqueous medium. At the end of the sampling period, the tube fittings are attached to a syringe or pump, the packing rinsed with solvent to remove the labeled compound or the enzyme product, and the rinsate analyzed to determine the concentration of the target analyte that diffused into the microdialysis tubing.

Information on the diffusion rates of selected compounds across the membranes is presented in this paper. Preliminary data on an antibody-based collection system for pentachlorophenol (PCP) are also presented.

Experimental

The membranes under evaluation are regenerated cellulose microdialysis tubing (Spectrum Medical). Typical tube dimensions are 50 μm in external diameter, 35 μm internal diameter, and 20 cm in length. Tubes are collected in bundles of 22 or 88 with pore sizes rated at 6,000 or 9,000 molecular weight cutoff (MWCO).

The vapor chamber (Figure 2) consists of a 10 L stainless steel vessel with air sampling ports and a stirrer to ensure even vapor distribution within the chamber. Previous evaluations have indicated that the distribution is even throughout the chamber using this propeller mixer. The saturated vapor is created by placing the material (e.g., radiolabeled PCP) in the bottom of the chamber and allowing it to equilibrate until saturation is reached as determined by collecting periodic air samples on solid sorbents and analyzing them by gas chromatography (GC) or liquid scintillation counting (LSC).

PCP, 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT) were obtained from Aldrich Scientific at 98% purity or better. The C^{14} radiolabeled materials were obtained from New England Nuclear. The radiochemical purity of each material was greater than 95%. The monoclonal PCP antibody was developed by WBAS, Inc. of Rockville, Maryland, and obtained through the U.S. Environmental Protection

Agency, Environmental Monitoring Systems Laboratory - Las Vegas. All other reagents were obtained from Sigma Chemical.

GC analysis of DNT and TNT was performed on a Varian 3700 equipped with an electron capture detector and a DB-5 30m, 0.25mm ID fused-silica open-tubular column. LSC was performed using a Packard 4170 Scintillation Counter.

The procedure used for the PCP vapor/liquid diffusion study is as follows. A 9-inch, 22-fiber bundle was masked off with Teflon tape to allow only 1.5 in. of fiber to be exposed to the atmosphere. The bundle was rinsed with ethanol and phosphate-buffered saline (PBS) to wash out the plasticizer according to the manufacturer's instructions. The bundle was filled with PBS, fitted into the cell holder, and placed into the ^{14}C-PCP vapor chamber. At 5-min intervals for 1 hr, 2 mL of fresh PBS were drawn through the bundle. The 2 mL of fluid, which contained the PCP samples during the interval, were transferred to a LSC vial. At the end of the 1-hr exposure time, the bundle was removed from the chamber and hooked up to a peristaltic pump and fraction collector. PBS was pumped through the bundle at a rate of 0.25 mL/min for 5 hr and the effluent collected in LSC vials. This post exposure study was performed to help identify and quantitate any hysteresis effect from PCP adsorbed to the tubing but not yet migrated into the filling solution. Quadruplicate vapor samples were taken from the exposure chamber while the bundles were being exposed and analyzed for PCP.

Preliminary experiments for nitroaromatics used water-filled dialysis tubing as the analyte collector in the chamber. These evaluations were performed in deionized water because it was unknown at this time what buffer system would be used. This allowed the determination of the analyte diffusion rates into the internal filling solution of the tubing. The bundles were not masked with Teflon tape as they were for PCP. This results in a larger sampling surface area for these evaluations than for the subsequent PCP evaluations. The microtubes were filled with deionized water after the manufacturer's extensive solvent rinsing procedure was performed. The filled tubes were placed into the chamber containing ^{14}C labeled DNT or TNT for 0, 5, 10, 20 and 60 minute periods, then removed, and the labeled analyte amounts contained in both the filling solution and the tubing material was determined by LSC.

The procedure for the diffusion studies using an antibody filling solution is as follows. The PCP antibody was suspended in a PBS-Tween 20 solution and injected into the microtubes. The tubes were then suspended for 15 minutes in the chamber containing the radiolabeled PCP vapor at 3 μg/L. Control tubes were also placed into the chamber, including one filled with PBS-Tween and another with Bovine Serum Albumin (BSA) protein suspended in PBS-Tween. The antibody-filled tubes were then dialyzed against deionized water for 4 hours to remove any unbound PCP and then analyzed.

Results

Table 1 lists the approximate equilibrium vapor concentration determined for the three analytes using solid sorbents to sample the vapor chamber. Repetitive samples were collected until the chamber concentration reached equilibrium. These values are not corrected for recovery efficiencies from the collection sorbents because previous work at MRI has indicated recoveries of better than 90% for these particular analytes.

Table 1. Chamber Vapor Concentrations

Analyte	Estimated Vapor Concentration (μg/L) from Solid Sorbent Collection	Confirmation Method
DNT	3	GC
TNT	100	GC
PCP	3	LSC

Figure 3 contains the results from an evaluation of the diffusion of DNT and TNT through the 6000 MWCO and 9000 MWCO dialysis microtubes.

The results for TNT and DNT are similar. The lower apparent diffusion rates for TNT are expected because TNT has a much lower equilibrium vapor concentration than DNT. The

plotted values are the average of two determinations at each time interval and have been corrected for surface area differences. Future work will couple this collection system with antibody-based detection systems.

The larger pore tubing (9000 MWCO) does exhibit faster diffusion than the smaller pore tubing (6000 MWCO). However, the magnitude of the difference is not large enough to justify the use of the larger pore tubing, which is more likely to lose water by evaporation over extended sampling periods.

The results from the diffusion rate studies of PCP are shown in Tables 2, 3, and Figure 4. Duplicate assays of each bundle type were performed. The results of assaying the PBS effluent while the bundles were in the exposure chamber are presented in Table 2, and representative plots of each bundle type are presented in Figure 4. Linear regression analysis was performed on the cumulative PCP passed through the membrane and into the PBS buffer as a function of time. The data indicate an average mass sampling rate of 14.3 ng/min for the 6000 MWCO bundle and 19.2 ng/min for the 9000 MWCO bundle. The effective sampling rate, calculated by division of the mass sampling rate by the PCP vapor concentration, averages 0.27 L/min for the 6000 MWCO bundle and 0.30 L/min for the 9000 MWCO bundle.

The correlation coefficients (Table 2) indicate good linearity for both bundle types with the MWCO 6000 bundles being greater than 0.970 and the 9000 being greater than 0.995. The x-intercept indicates the approximate delay time in which the vapor permeates into the bundles and into the PBS. These times are 6.7 min for the MWCO 6000 bundle and 2.9 min for the MWCO 9000 bundle.

The total amount of PCP that permeated the membrane during and after exposure is presented in Table 3. In the 5 hr after the bundles were removed from the chamber, 1049 and 709 ng of PCP continued to migrate through the MWCO 6000 bundle. Likewise, these values are 507 ng and 438 ng for the 9000 MWCO bundle. These results indicate a large fraction (46 percent for the 6000 bundle and 30 percent for the 9000 bundle) of the PCP takes a considerable amount of time to permeate through the membrane and into the buffer. However, this should not affect the usage since a waiting time of 1 hour can be inserted into the analysis scheme.

Representative plots of the postexposure permeation results for each bundle type are presented in Figure 5. These results indicate a very rapid PCP passthrough during the first 30 min, followed by a very slow accumulation during the next 4.5 hr. The slow permeation phase may be reaching an asymptotic limit, but it is impossible to estimate the limit from these data. A reasonable explanation for this phenomenon is that the fast permeation phase is the PCP diffusing through the aqueous portion of the open pores of the membranes, while the slow phase is the PCP diffusing through the regenerated cellulose portion of the membrane. The membrane may also become saturated with PCP at this vapor concentration.
To provide a mass balance, another type of exposure experiment was conducted in which the bundle was exposed while being completely static. A 9000 MWCO bundle was filled with PBS buffer and placed in the PCP exposure chamber. After 1 hr, the bundle was removed from the chamber and 10 mL of PBS buffer immediately washed through the bundle and assayed. Next, the buffer was pumped through the bundle and collected for 5 hr. At the end of the experiment, the bundle was sacrificed and assayed for PCP. This experiment detected 1400 ng PCP in the first of 10 mL of effluent, 376 ng in the postexposure effluent, and 61.5 ng in the bundles. The fraction of PCP permeating through the bundle was 20 percent of the total PCP sampled by the membrane. Only 3 percent of the PCP remained in the membrane indicating a low degree of permanent nonspecific adsorption. Therefore, while diffusion may be slow, very little of the analyte becomes permanently affixed to the tubing.

Table 4 contains the results from the preliminary evaluations of PCP-antibody loaded tubes. The tubes were exposed to the radiolabeled PCP vapor at 3 μg/L for 15 minutes in the static exposure chamber previously described. Tubes filled with the PBS-Tween solution and PBS-Tween/BSA were suspended in the chamber as controls. The purpose of this experiment was to demonstrate that the antibody-based collection system would irreversibly bind the target analyte for later

analysis. Such binding is important because analyte exposure may occur in an episodic manner and the retention of the analyte is key to accurately determining the exposure.

In assessing this limited data set, it is clear that the PCP-antibody is binding the PCP diffusing into the tube. This can be inferred, in a non-quantitative way, by comparing the amount of PCP retained in the PCP-antibody loaded tubes versus that retained in the control tubes after dialysis as determined by LSC. More definitive experiments are underway to quantify the relative retentions.

Conclusions

The above data indicate a high probability of success for the application of antibody-based PEMs. Monitoring limits are of course constrained by the detection capability of the antibody-based system. However, based on the reported limit for the PCP assay (1 ng) [3] and the diffusion measurements reported in this paper, the limit of detection for the PEM device should be from 1-5 ng of PCP. Based on a vapor concentration of 5 ppb (arbitrarily chosen as a representative air concentration for PCP), this would convert to a minimum exposure time around 20 minutes for the analyte to reach a detectable quantity within the PEM device.

The data, even though preliminary, demonstrate the viability of using such PEMs. Studies carried out as part of this program have also indicated that the 6000 MWCO dialysis microtubing exhibits sufficient collection efficiency for other targetanalytes. Several antibody systems are under evaluation for use in PEM devices, and new systems will be evaluated as they become available. These early studies indicate that it will indeed be possible to apply antibodies to direct air monitoring systems through the use of microdialysis tubing as a semipermeable barrier which allows vapor diffusion without significant moisture loss.

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NOTICE: Although the research described in this paper has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE 2. RESULTS OF UTILIZING MICRODIALYSIS TUBING FOR SAMPLING PCP VAPOR

	Linear Regression Analysis				
Bundle type	Correlation coefficient (r^2)	x-Intercept (min)	Slope (ng/min)	PCP vapor concentration (ng/L)	Effective sampling rate (L/min)
MWCO 6000	0.970	6.81	19.5	71.8	0.272
	0.972	6.69	14.8	55.4	0.267
MWCO 9000	0.996	3.08	20.5	58.3	0.351
	0.995	2.86	17.9	52.8	0.340

TABLE 3. DIFFUSION OF PCP THROUGH THE HOLLOW FIBER BUNDLES

Bundle Type	Amount of PCP diffused through membrane			
	With bundle in chamber		With bundle out of chamber	
	(ng)	(%)	(ng)	(%)
MWCO 6000	1135	52.0	1049	48.0
	857	54.7	709	45.3
MWCO 9000	1162	69.6	507	30.4
	1049	70.5	438	29.4

TABLE 4. COLLECTION OF PCP BY ANTIBODY SUSPENDED IN MICRODIALYSIS TUBES (15 min exposure time)

Filling Solution	PCP Amount (ng)[a]
PBS-Tween/PCP Antibody	184
	162
PBS-Tween	18
	29
PBS-Tween/BSA	39
	57

[a] Duplicate determinations by LSC; Exposure time of 15 minutes

FIGURE 1

Personal Exposure Monitor

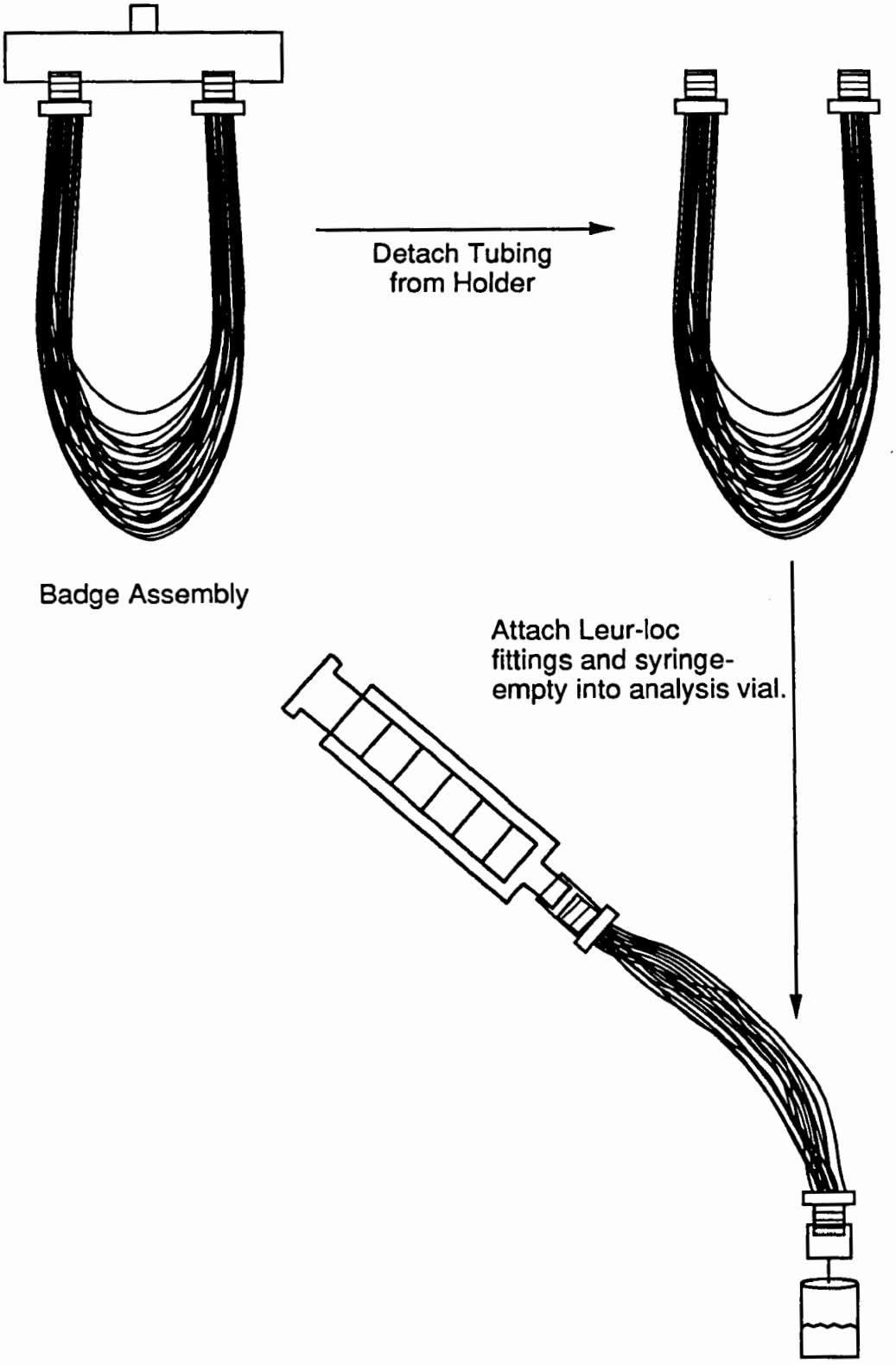


FIGURE 2

Exposure Chamber Used for Exposure Studies

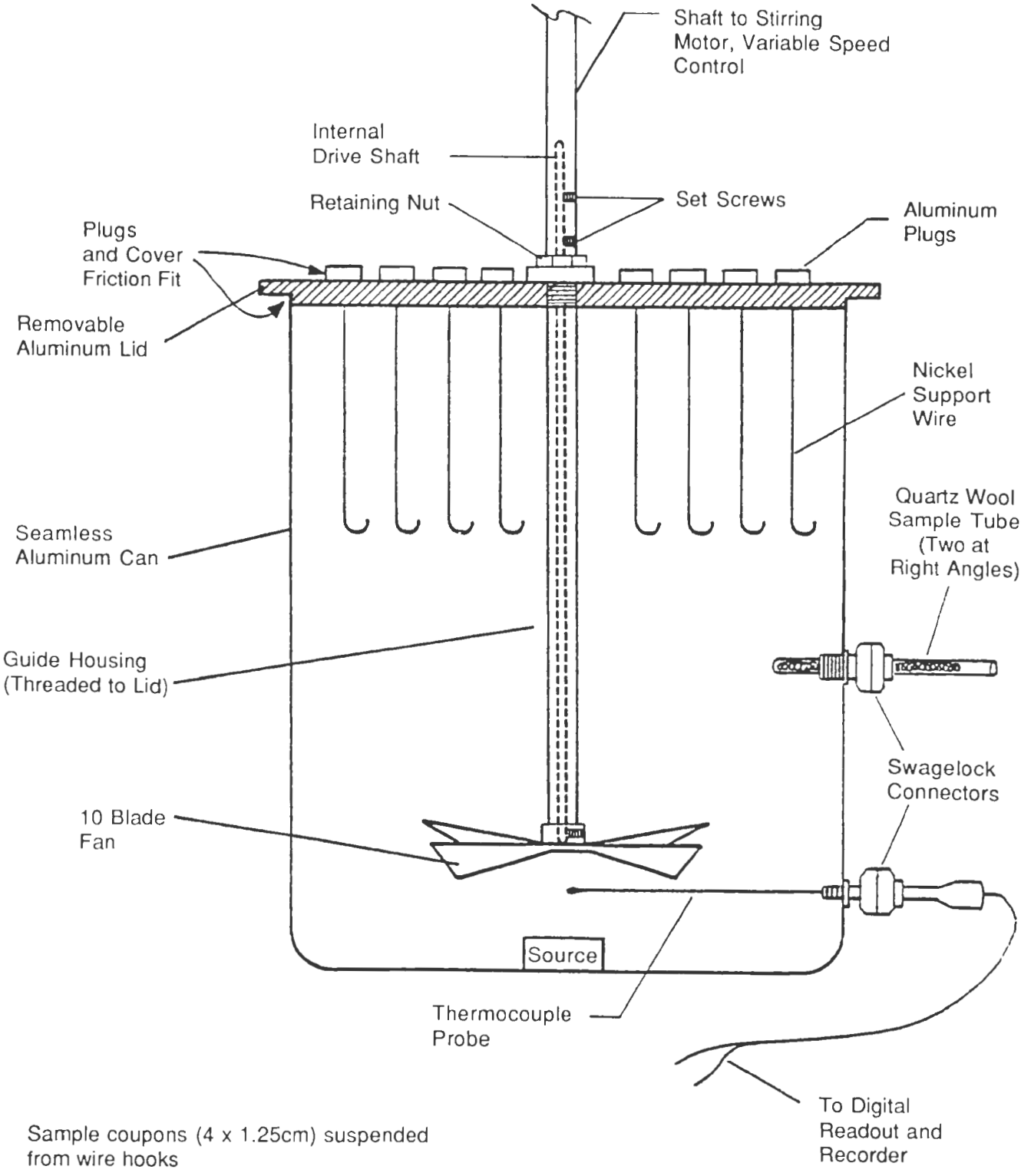


FIGURE 3

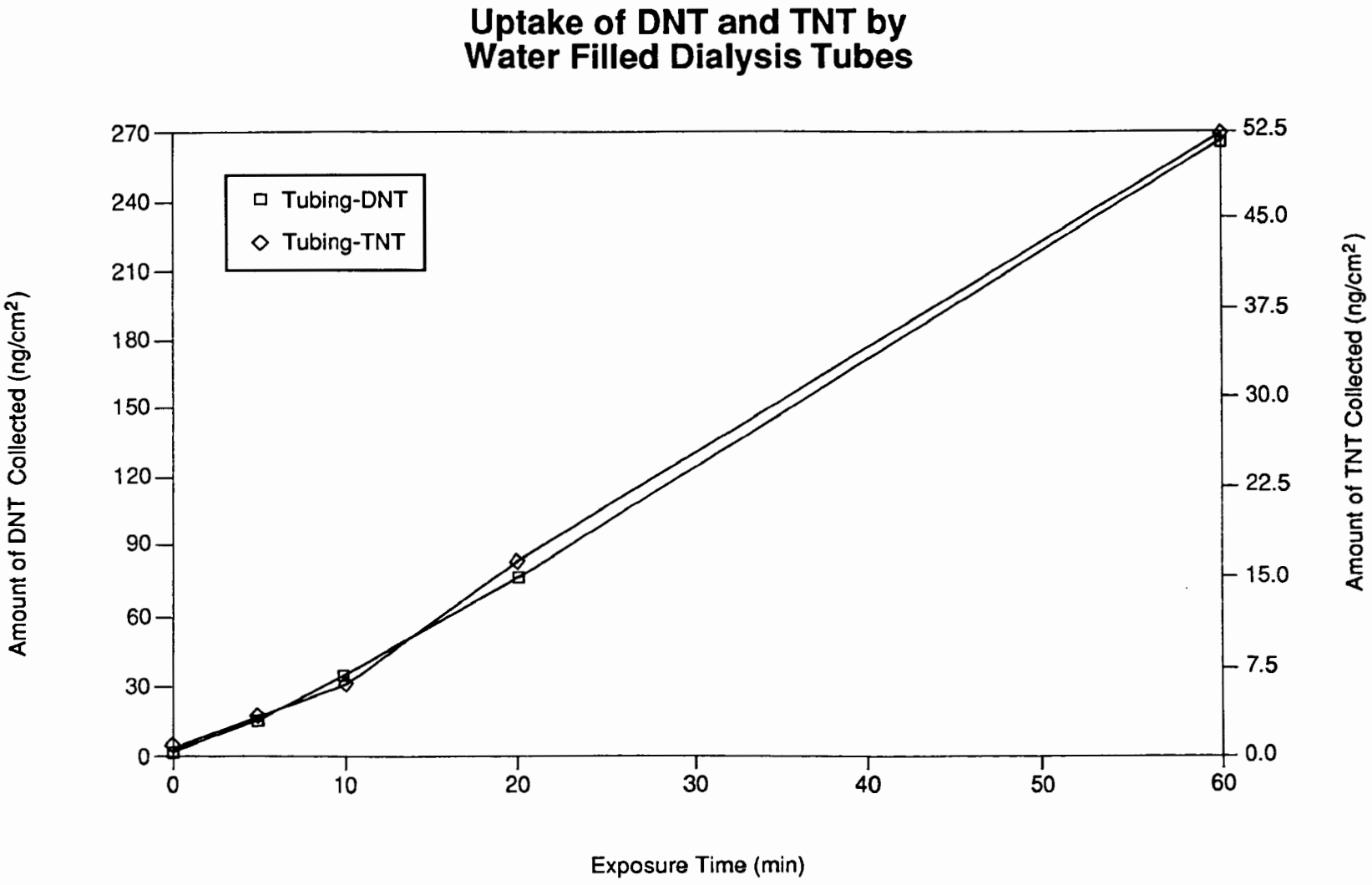

Uptake of DNT and TNT by
Water Filled Dialysis Tubes
Tubing-DNT
Tubing-TNT
Amount of DNT Collected (ng/cm²)
Amount of TNT Collected (ng/cm²)
Exposure Time (min)
270
240
210
180
150
120
90
60
30
0
52.5
45.0
37.5
30.0
22.5
15.0
7.5
0.0
0
10
20
30
40
50
60

FIGURE 4

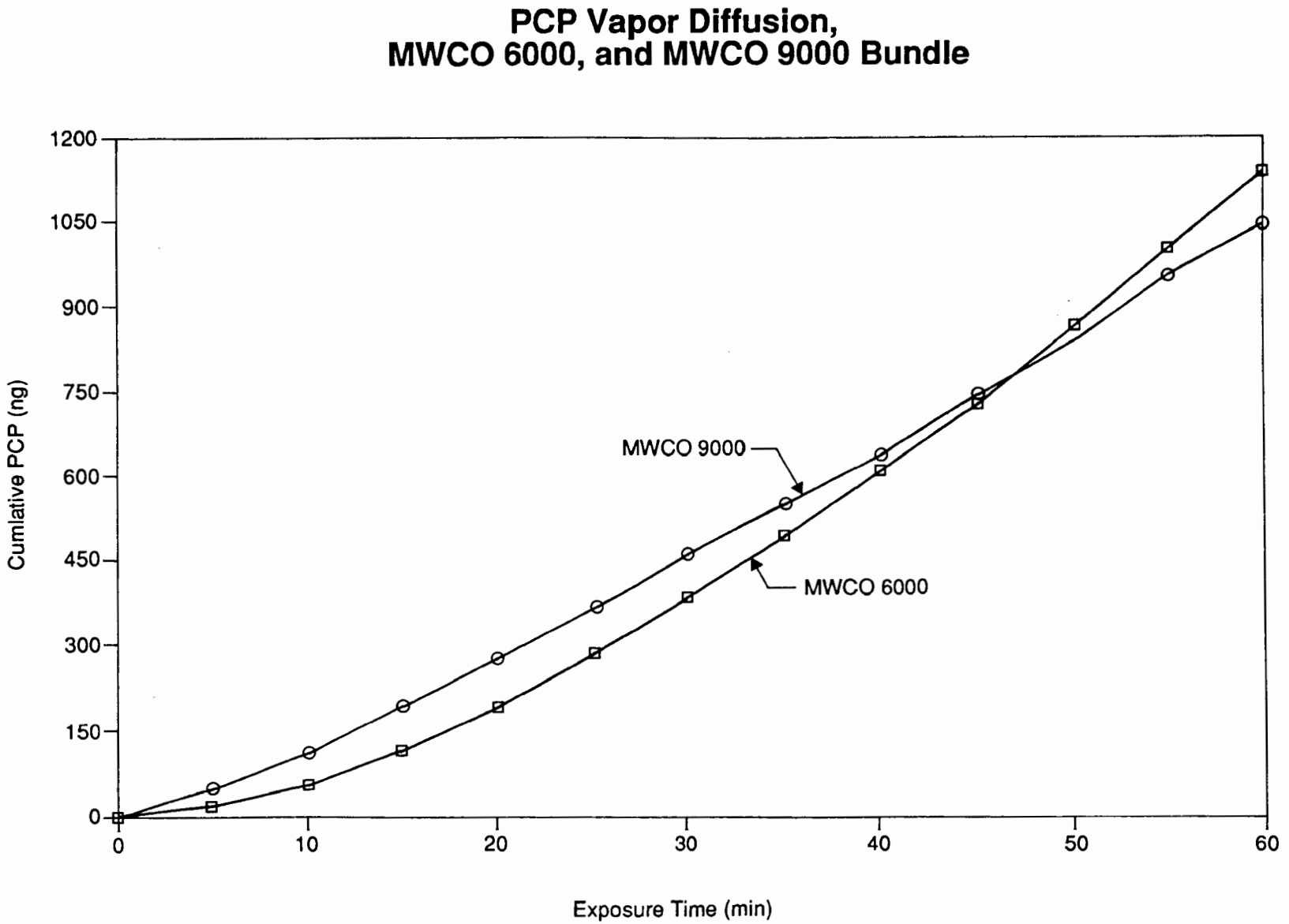
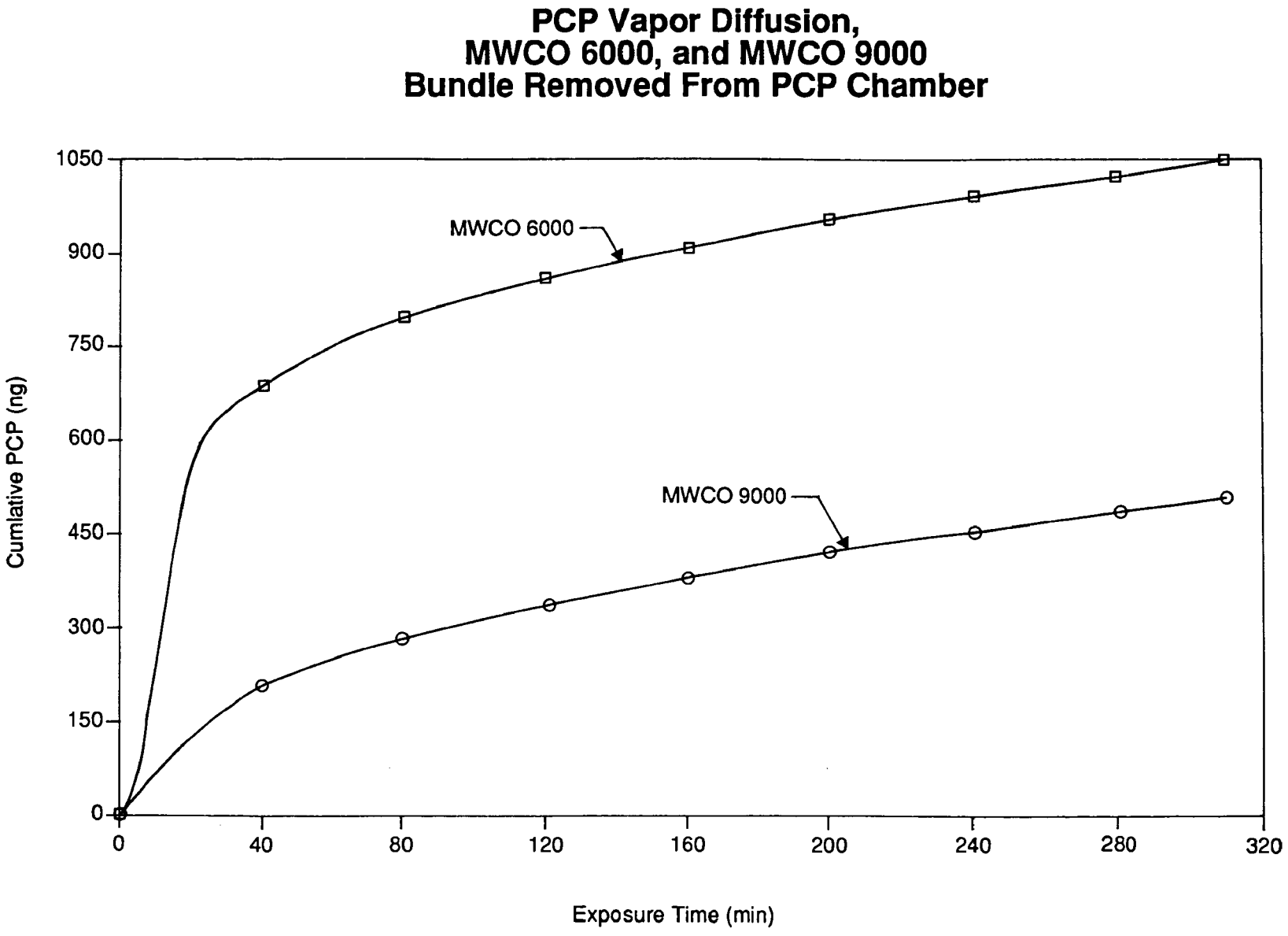

PCP Vapor Diffusion,
MWCO 6000, and MWCO 9000 Bundle
Cumlative PCP (ng)
1200
1050
900
750
600
450
300
150
0
0
10
20
30
40
50
60
Exposure Time (min)
MWCO 9000
MWCO 6000

FIGURE 5


PCP Vapor Diffusion,
MWCO 6000, and MWCO 9000
Bundle Removed From PCP Chamber
Cumlative PCP (ng)
1050
900
750
600
450
300
150
0
MWCO 6000
MWCO 9000
0
40
80
120
160
200
240
280
320
Exposure Time (min)

A REMOTE SENSING INFRARED AIR MONITORING SYSTEM FOR GASES AND VAPORS

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Abstract

A prototype transportable remote sensing instrument has been built that is capable of performing real time quantitative analysis of gas and vapor contaminants in air.

Introduction

In the early 1970's, papers appeared in the literature on the investigation of "remote sensing of emissions" (ROSE) for air monitoring (1-5). In all of those papers, the instruments were large, and the data analysis was off-line and depended on an experienced spectroscopist interpretation.

In the mid-1980's the use of FTIR without remote sensing, but instead with the use of a closed gas cell into which the sample was pumped, and using the classical least squares fit (LSF) data analysis methods of Haaland (8,9), was explored for air monitoring applications (6-14).

Recently, several groups have begun experimentation with ROSE-FTIR (15) and differential absorption laser systems for remote sensing of pollutants at hazardous waste sites, and potentially for fenceline emergency chemical-release monitoring. The first such study at a hazardous waste site, a joint effort in 1987 between the EPA-ERT and The University of Michigan, resulted in the definition of questions of instrument stability under field conditions, and aiming problems over long (km) distances (16). Other studies have been summarized (17,18). All reported systems require manual interpretation of data.

In this paper, we report on some of the design and operational bases behind this small, transportable ROSE-FTIR system.

Experimental

The light source/optical bench weighs 16 kg, and measures approximately 20 cm (h) X 48 cm (w) X 36 cm (l). The infra-red (IR) light source is an air cooled Globar operating at 1300 K. The optical bench contains a "porch-swing" interferometer capable of up to 2 cm^{-1} resolution at scan speeds as high as 2 scans/second.

The receiver/detector module consists of an 8 inch (20 cm) diameter Cassagrain telescope equipped with first-surface aluminum coated mirrors, and a 3 inch (7.6 cm) diameter convex spherical secondary mirror. The IR light detector is liquid nitrogen cooled HgCdTe (MCT), with an image area of 1 mm^2 .

The receiver/detector is mounted on an aluminum plate, and also weighs 16 kg. Dimensions of this module are 28 cm (h) X 38 cm (w) X 36 cm (l), plus a 30 cm (l) X 25 cm (d) extension on the telescope cover. The electrical requirement for the complete instrument is <10 amps of 115 V. electrical service.

Mirrors may be used to direct the IR beam around the monitoring site. These mirrors are 1 foot square (929 cm^2) first surface aluminum coated mirrors. All modules, including mirrors, but not including the computer, may be mounted on tripods.

The computer is a Dell 310 20 Mhz 80386 system with an 80387 co-processor, 150 Mb hard drive, 4 Mb of RAM, a Dell VGA-Plus color card and NEC Multisync II color monitor, a Nicolet Fourier transform co-processor board, and a Nicolet A/D controller board. Software is Nicolet PC/IR, equipped with special systems to aid in ROSE operation.

Discussion

The objective of this work was to design, build and evaluate a small, transportable remote sensing (ROSE) Fourier transform infrared (FTIR) spectrophotometer system designed specifically for use as a gas and vapor air monitor for the workplace or in emergency response situations. The system has a maximum viewing distance of 40 meters, and can yield one or more analyses every minute.

The IR beam can be placed linearly or, using mirrors, around monitoring stations that are not linear. In order to aid in the accurate aiming of the beam, the He-Ne laser beam that emerges from the instrument is co-axial with the IR light beam. The laser beam has an intensity of 260 microwatts/cm^2 at 1 meter distance from the instrument, so protective glasses are not needed.

In theory, the beam could be moved around the workplace using a digital stepper motor-controlled aiming mirror. Thus, the most important paths within an entire workplace or emergency response site could be traversed in a few minutes. The optimal choice of the beam path is a question being explored using a large exposure chamber at the University of California-Berkeley.

Evaluation of the system has shown that beam path length and detector response, under conditions of constant and uniform concentration, are directly related for paths tested up to 12 meters. Path lengths beyond that have not yet been tested.

Most important appears to be the presence of non-analyte contaminants in the "clean" background air spectrum. These non-analytes cause baseline non-linearities in the spectral regions in which analytes must be determined.

The key advance that has made the use of ROSE-FTIR and closed cell-FTIR methods possible for air monitoring applications has been the use of LSF analysis of the data. Since LSF techniques make assumptions with regard to the linear behavior of the baseline, "poorly behaved" baselines (with non-linear regions) degrade the performance of the LSF software. This, in turn, results in higher limits of detection (LOD), poorer linearity, and degraded accuracy and precision.

The effects of temperature (10-35 ^0C) and relative humidity (20-85%) have been evaluated and found to be minimal. However, when the instrument is moved between monitoring sites and the telescope optics are realigned, minor variations in the baseline may be significant with respect to the performance of the LSF method.

The solution of this problem is therefore central to the use of ROSE-FTIR methods. In initial tests in the

laboratory, this problem has been solved through the use of negative and positive least squares fitting. With an analyte vapor mixture of five components and a seven component non-analyte mixture spectrum, both at 1 ppm concentration in ambient air per component, the mean recovery of analyte was 103% with a standard deviation of 10%. Without this method, the mean recovery degraded significantly, as did the precision of the results.

The use of an iterative classical least squares fit (ILSF) approach has also been evaluated for the identification of unknown compounds in the spectra of mixtures of vapors in air (19). This method appears, in preliminary tests, to be capable of identifying unknown substances in mixtures. However, field testing of this method has not yet been performed.

Conclusions

1. A transportable remote sensing ROSE-FTIR instrument has been designed, built and tested under controlled conditions.
2. Positive and negative LSF methods can be used, under controlled conditions, to compensate for the presence of non-analytes in the background spectrum.
3. Iterative LSF methods can be used, under controlled conditions, to identify unknown components of the spectra of mixtures.
4. Further testing is needed.

Acknowledgements

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DISCUSSION

MAURY FEE: In your expert system, did you have to reduce the interference by successive subtraction, like a water vapor or CO_2, in identifying your species?

STEVE LEVINE: The iterative least squares, which is the algorithmic heart of the expert system, does that essentially by doing a least squares fit and getting an optimal fit through several successive iterations. Instead of doing a classical library search, we'll take the spectra we think are there one at a time, and look at the residual. What it does is attempts, through the windows that have been chosen in the spectra, to do that with least squares fitting. So the answer is yes, but not in the way that people used to do it.

JUDD POSNER: Have you ever considered the use of neural networks to make it an artificial spectroscopist?

STEVE LEVINE: I did not pay him to ask that question! In fact, we had just published a paper on neural nets in Analytical Chemistry. We did indeed try it. The difficulty with neural nets is that you have to train them. To train them you have to be able to see the peaks. When you're looking at the FTIR spectrum of environmental or industrial gases or vapor mixtures you can't see a lot of the peaks. And so the neural net can't be easily trained. The net failed at any concentration below about 50 ppm for anything above about three component mixtures that we tried. It was an interesting idea. We were hoping to use it as a pre-screening tool for the iterative least squares to speed up the process and reduce the algorithmic load on the system. But aside from producing an interesting publication, it did not work.

BRIAN PIERCE: My question concerns the localization of leaks throughout the plant. Could you distribute an array or retroreflectors and then direct your source at these — to enable the ability to localize such a leak?

STEVE LEVINE: That of course is what we're ultimately hoping to do. At this point we're hoping to make everything work with a single beam, manually operated. Again you have to look at the things that MDA has done with their DIAL laser system and their digitally controlled mirror for moving the beam around, and what the Army has done with their seven position moving mirror that surveys the battlefield in their XM21 FTIR. So this is something that others have done, and we want to be able to do it in the workplace. We haven't done it yet.

DON LAVERY: On the qualitative part of your study, you're doing something rather similar, I think, to what folks at the Atomic Energy Commission of Canada have done in the UV. In their library search they look first for the candidate spectrum that will explain the largest amount of variation. And then proceed through the secondary and tertiary candidates so that they pay the most attention to the most important first. Have you done anything like that?

STEVE LEVINE: We've tried three strategies. One is to take the entire spectral library in one array and see which combination of fits matches the known peaks that we have best. That turned out to be the least satisfactory and the slowest. We then tried the set building method where we go through the library one compound at a time and look for the best matches that way. And the third is the set reduction method where we start with 16 compounds in the library at a time, and match the best for each 16, and attempt to squeeze the positives down to the fewest number. The set building method which, in a way, parallels what you say the Canadians have done on the UV system, is the method that is the fastest and has given us the best results. The difficulty with me giving you a definitive answer is, again, it's not robust. We have one publication on it. It needs more work.

ADRIAMYCIN EXPOSURE STUDY AMONG HOSPITAL PERSONNEL

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ABSTRACT

Using antineoplastic drugs is one of the routine treatment regimes employed in combatting cancer. Nearly 250,000 cancer patients are treated annually with chemotherapeutic agents usually in either hospital outpatient or inpatient settings, however, some patients receive these drugs in physicians' offices or outpatient clinics.[1] The number and types of health care professionals who are potentially exposed to antineoplastic drugs includes but is not limited to 4,000 medical oncologists, 10,000 oncology nurses, 30,000 pharmacists, and even greater numbers of staff nurses and support personnel.[1,2]

A project was undertaken to utilize a visible light fluorescent method previously developed at the University of Cincinnati, to document areas of adriamycin contamination (skin and work surfaces). Specific aims of the study were to compare the degree of contamination among pharmacists or pharmacy technicians, intravenous (I.V.) therapy administration personnel, oncology nurses, patient care nurses, maintenance workers, and hospital laundry workers, and to describe the population at risk of dermal exposure to this antineoplastic agent and recommend measures to prevent exposure.

Sixty-four observations/monitoring sessions for adriamycin exposures in a hospital setting were conducted from June - August 1988, for dermal contact with adriamycin. No dermal exposures to adriamycin among the hospital staff monitored were found. In addition, no adriamycin contamination was documented on any work surfaces. There were however, several noteworthy findings. The ability to detect fluorescence of adriamycin (2 mg/ml to 0.002 mg/ml) applied to some of the disposable latex gloves, disposable gowns/smocks, toweling, front covers of the infusion pumps, and several other work surfaces typically found in the hospitals surveyed, varied according to the material/work surface and the concentration applied. Understanding of the sensitivity of the methods and potential interferences will greatly aid in the interpretation of positive results.

INTRODUCTION

Background

Antineoplastic drugs such as adriamycin, cyclophosphamide, methotrexate, mitomycin, dacarbazine, and cisplatin, are used in cancer treatment. Several of these drugs produce mutagenic, carcinogenic, and teratogenic effects in some cancer patients.[3,4,5] Clinical research has been concerned with patients and their health status following drug administration. Relatively little attention has been given to persons exposed to antineoplastic drugs occupationally, during preparation and administration of the drugs, or following treatment of the patient. However, there has been a growing number of studies in this area, some of which have shown mutagens or thioethers in the urine and sister chromatid exchanges among personnel regularly handling cytotoxic drugs.[6,7,8]

Some 25 antineoplastic drugs are commonly used in cancer therapy.[5] Thirty-two agents are commercially available for treatment, and another 80 are in clinical development.[1] Many of these modern antineoplastic drugs are highly toxic. Health care personnel who formulate, administer, and clean surfaces that have contacted these drugs may be at risk of developing a number of adverse effects, including cancer and fetal loss. The population presently estimated to be occupationally exposed to antineoplastic agents includes, but is not limited to, thousands of employees in the pharmaceutical manufacturing plants, 30,000 hospital pharmacists, 4000 medical oncologists, 10,000 oncology nurses, and even greater numbers of general staff nurses and support personnel in hospital laundry maintenance and housekeeping. Effects of chronic exposure to these drugs at very low dosages, as would be expected occupationally, cannot be predicted with presently available data. Only two studies have been published reporting any environmental sampling for antineoplastics in the hospital setting. Both of these papers reported airborne levels of antineoplastics, though neither study developed acceptable methods for generalized use in airborne exposure assessment.[9,10] In addition, no studies are available to confirm the effectiveness of engineering controls, protective apparel, or work practices, along with proper handling and disposal techniques for controlling the risk of contact with these drugs. Few if any reports have been published which examined drug contamination of hospital surfaces, staff clothing, or soiled bedclothes or methods to remove residual drugs.

Antineoplastic drugs include alkylating agents, antimetabolites, antimitotic agents, antibiotics and other drugs. The main therapeutic purpose is to destroy cancer cells by blocking various biochemical pathways. The specific site of action varies, depending on the particular class of agent. The general mechanism of action is either through direct interaction with DNA or inhibition of nucleic acid synthesis.[11] Many of these drugs have been shown to be carcinogenic, mutagenic and teratogenic in experimental systems, and therapeutic doses of antineoplastic drugs have been associated with the

development of secondary tumors in patients receiving chemotherapy. Aside from their actions on tumor cells, antineoplastic agents can interfere with normal body cells resulting in damage and, in some cases, cell death.[11]

Surgery, radiation, and chemotherapy are three types of medical treatment commonly employed to combat cancer. Chemotherapeutic agents such as adriamycin, are used because of their cytotoxicity. Adriamycin is one of the most widely used of all the anticancer agents. It is frequently used to treat tumors characteristic of leukemias, lymphomas, Hodgkins disease, and carcinomas of the breast, ovaries, bladder, stomach, lung, thyroid, and bronchus. Most of the antineoplastic agents currently in use today are supplied as powders in vials or as liquid solutions requiring reconstitution or dilution prior to administration by intravenous or parenteral injection. Often pharmacists wearing gloves and protective smocks handle these drugs in biological safety cabinets. The concentration is usually 2 mg/ml adriamycin hydrochloride in sterile saline solution and the volume is adjusted for each patient using additional sterile saline for dilution. The recommended dosage schedule (adriamycin) for adult patients is 60-75 milligrams per square meter (mg/m^2) of body surface as a single I.V. infusion. The drugs are administered in various schedules, such as once every three weeks, or on three successive days every four weeks, until a total dose of 550 mg/m^2 (adriamycin) has been given.[12] The exact regimen depends on the drugs used, type of cancer and the health status and responsiveness of the patient. Patients may receive drug therapy in a variety of settings; hospital inpatient, hospital outpatient, in the physician's office or in the home.

A variety of personnel are potentially exposed to the antineoplastic drugs including nurses, doctors, and pharmacists who prepare and administer the drugs, and maintenance and housekeeping staff, who repair, clean, and/or dispose of equipment following administration of the drugs or work in the rooms or offices where the drugs were administered. Adriamycin, like most other drugs, is often not fully utilized by the patient (the dose administered is not fully absorbed: some of the drug is excreted as is and some is excreted in metabolized forms). Therefore, vomitus and excreta may contain the drug and/or its metabolites. Housekeeping and custodial staff may be exposed during routine operations. Patient care personnel must handle bed linens contaminated with vomitus and excreta which may contain drugs. Unprotected laundry workers may unknowingly transfer drugs from the linens to their hands. In general, contaminated waste, bedlinens, vomitus and excreta may be handled by a number of persons involved in either treatment, patient care or facility maintenance and the extent to which the personnel contaminate their skin as a result of contact with drugs, waste or soiled linens has not been documented. Other ways that the antineoplastic drugs can be released into the work environment include contaminated packaging (broken vials damaged during shipping), powders and liquid sprays (aerosols) released during preparation, administration and routine cleanup operations, spills or leakage from syringes, I.V. bags, residual contamination on used syringes, gloves, linens, vials, I.V. bags, and tubing. Although volatilization is not a property of the currently available cytotoxic agents, aerosolization of the drugs can occur during preparation and administration. Routes of entry into the body

are through skin absorption (dermal), inhalation of aerosolized drug, accidental self-innoculation and ingestion. Ingestion can occur during mouth-breathing, smoking, eating, drinking, or other hand-to-mouth contamination. Direct skin contact and inhalation of aerosolized drug are often the greatest sources of exposure.

Adriamycin

Adriamycin, also known as doxorubicin, is a red crystalline solid that is soluble in water, aqueous alcohols and methanol. This cytotoxic antibiotic is isolated from cultures of Streptomyces peucetius. It is produced by three companies; one in Japan, one in Italy and by one domestic manufacturer. Spectrofluorometric methods have been used for identification and estimation of the drug in biological fluids and tissues.[12]

By knowing the excitation and emission wavelengths characteristic of a compound, one can use the fluorescence phenomenon to identify and quantitate such compounds. One of the physical characteristics of adriamycin is that it fluoresces when activated by certain wavelengths of visible and short wave ultraviolet light. In prior research studies conducted by Rice, Van Raalte, and Dimos et. al.[13] at the University of Cincinnati, a spectrophotometer was used to characterize the absorption spectrum of adriamycin hydrochloride in saline solution with lactose, as it is constituted for patient administration. They found that absorption in the visible range took place, with a peak at 470nm. Using a spectrofluorometer they examined the excitation/emission spectrum for adriamycin hydrochloride in saline solution and found a maximum intensity occurring at 580 nm. The examination of fluorescence excitation/emission was confined to the visible region since ultraviolet illumination was not considered as an option for the project.

EVALUATION METHODS

To insure the easy availability of the equipment used for this project, only readily accessible materials were considered for the various components shown in Figure I. A Kodak model AF-1 Ektagraphic slide projector was used as a light source to stimulate fluorescence; the optical system of the projector was equipped with a condensing lens and an infrared filter. The projector was equipped with a 300 watt tungsten-halogen projection lamp and a glass filter (BG-12 4084 Filter) which selectively passed short wave (blue) visible light was placed into the slide projection compartment. A 35mm single lens reflex camera with a Vivitar 55mm 1:2.8 macrolens and a Kodak Wratten number 21 gelatin filter (75mm x 75mm) was used to photograph the fluorescent emission from adriamycin. The Wratten filter absorbed the stimulating blue light emitted by the light source, allowing only the orange-red fluorescent glow of the adriamycin to be photographed. Sunglasses were worn during visual observations to filter out the interfering light emitted by the stimulating light source; ultraviolet and blue filtering sunglasses manufactured by Sun Tiger (Pasadena, CA) block transmission of light below 550 nm and were used in this research. To insure constant intensity and maximize sensitivity, attempts were made to maintain the background light levels at a minimum. All photographs were taken with the stimulating light source (projector) and camera held at 20-25cm from the fluorescent materials, and the angle between the light source and camera held to less than 45 degrees. With background light levels under 10 lux, using Ektachrome 160 tungsten film, exposure times between 1/4 and 1 second, and a maximum aperture setting of 2.8, the presence of adriamycin fluorescence on test materials was demonstrated with concentrations ranging from 2.0 to 0.002 mg/ml placed on various materials including but not limited to stainless steel, benchtop absorbent padding, a cotton lab coat cloth and latex glove material. These materials were felt to be typical of the types of materials on which antineoplastics might spill or leak in the clinical setting. Orange-red fluorescence was observed on all test materials at all concentrations except for the most dilute which was not observed to fluoresce on stainless steel or latex. Monitoring was conducted on the worksurfaces, protective clothing and exposed skin both prior to and after handling adriamycin itself or materials possibly contaminated with adriamycin.

RESULTS

Sixty-four separate monitoring sessions for adriamycin exposures in hospital environments were conducted from June - August 1988, for dermal contact with adriamycin. The various jobs monitored for adriamycin exposure included full-time pharmacists, pharmacy interns, technicians, physician assistants, nurses, laundry workers and maintenance workers. The areas and work surfaces monitored for adriamycin contamination included chemotherapy preparation areas, outpatient departments, filters in biological safety cabinets and HVAC systems, hospital laundry areas, and chemotherapy infusion equipment. No dermal exposures to adriamycin among the hospital staff monitored were found. Many of the pharmacists monitored were double gloved and wore protective smocks when they mixed adriamycin. Furthermore, all the hospital personnel surveyed followed good work practices when handling antineoplastic drugs. In addition, no adriamycin contamination was documented on any work surfaces. There were however, several noteworthy findings.

The ability to detect fluorescence of adriamycin (2 mg/ml to 0.002 mg/ml) applied to some of the disposable gloves, disposable gowns/smocks, toweling, front covers of the infusion pumps, and several other work surfaces typically found in the hospitals surveyed, varied according to the material/work surface and the concentration applied. For example, the ability to detect fluorescence on some types of latex gloves and especially orange-red colored gloves, and on stainless steel, was reduced with the more dilute concentrations of adriamycin. Allowing the eyes time for dark adaptation may play a role in increasing one's ability to detect fainter fluorescence over smaller areas. The increased illuminance of background light levels in the survey area which were more than the optimum range of 10 to 35 lux, provides for an additional interference problem. The excitation BG-12 4084 filter mounted on the projector was chosen due to its availability and because it has a transmission peak at 400nm; it passes relatively little of the fluorescence stimulating energy of 480 nm wavelength. While the filter was adequate, fluorescence intensity would likely increase with the use of a filter with peak transmission at 480nm. Lastly, some difficulties arose in conducting the field evaluation using the bulky equipment. No doubt, miniaturization of the detection system would provide greater acceptance for its use throughout the health care environment.

CONCLUSIONS

This research demonstrates that a unique fluorescent detection system can be used to reduce present uncertainties involved in occupational exposure to antineoplastic drugs. Fluorescence detection provides a simple means of measuring the contacted area. This method is quite useful in assessing the adequacy of cleanup after the drug has been spilled. The method is sensitive, minimal equipment is required, and very little training is needed to enable personnel to monitor their own work areas and skin. For less than $100.00, along with a slide projector, any work area can be monitored for adriamycin contamination on a continuing basis by visual observations. Further research is needed to define the limit of detection of visible light stimulated fluorescence detection of adriamycin and optimize the method for use in the field. The use of visible light to stimulate fluorescence may have broader applications in industrial hygiene and dermal exposure and surface contamination studies. Stimulating light sources equipped with several interchangeable filters could allow for rapid detection of a number of compounds.

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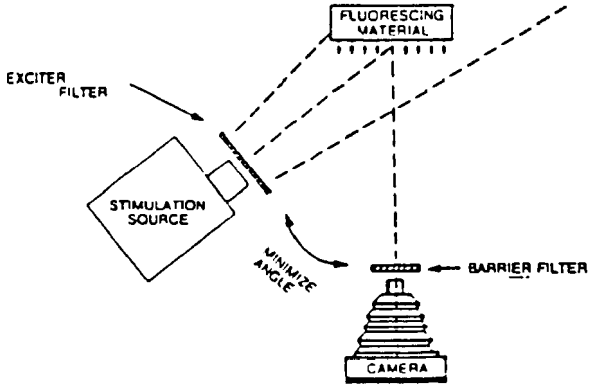

Figure I. Schematic of fluorescence detection equipment.

DISCUSSION

PHIL GREENBAUM: I wondered if you had checked to see if any studies had been done as far as birth defects related to this drug?

RICH STEPHENSON: Perhaps there's some literature that has been published on that. I can't recall them off the top of my head, though.

JUDD POSNER: It seems to me that this red drug had a capacity for being determined with probably the simplest of the spectrophotometers that involve the eye, and how much more sensitive in general was the UV than just looking around for red spots?

RICH STEPHENSON: We didn't use the UV detector because of the hazards associated with the UV light. We went with something that posed less of a hazard, the visible light source.

JUDD POSNER: How much more sensitive was the visible light measurement than the eye could see? I mean, do you have some idea about what kind of increase in sensitivity that gave you?

RICH STEPHENSON: That wasn't part of my thesis. It perhaps would be an interesting topic for additional work.

HARRY SALEM: You stated that there was no dermal contamination, yet I observed from your slide the pharmacist was wearing double gloves and short sleeves. Was the potential dermal contamination tested on the bare arms or under the gloves or protective clothing?

RICH STEPHENSON: Before the pharmacist or intern mixed or applied the drug, we looked at the hands and the arms, and any exposed skin surface. And definitely before they donned any gloves. And then we looked at it afterwards. In prior studies done by Rice and VanRaulty, they did find some contamination. But I think just knowing that we were present in the hospital environment and telling the participants what we were looking for and why we were there, there was a learning curve that happened right on the spot. So they took extreme caution to follow good work practices and not spill any on their hands or clothing.

REAL-TIME PERSONAL MONITORING IN THE WORKPLACE USING RADIO TELEMETRY

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Mention of a company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

Abstract

A system used to radio transmit data from remote locations within a workplace to a personal computer for immediate interpretation has been developed by NIOSH researchers. The system consists of several radio transmitters and a base receiver that is capable of multi-channel reception. Exposure data obtained from any direct-reading instrument with a recorder output signal can be displayed and stored at the computer. The worker being monitored carries the instrument in a backpack, along with a radio transmitter. Using telemetry, the concentration of the airborne contaminant under study can then be plotted on a video monitor for immediate assessment. If there is more than one worker under study at a time, multiple exposure curves can be displayed on the screen.

The base receiver is a commercial (frequency) scanner that has been modified to accept RS-232 serial communication. The manual keypad has been removed so that channel selection is accomplished through system software. The radio transmitter is similar to a wireless telephone; there are no wires to entangle. The radio telemetry system allows a worker unrestricted movement within its effective range. It also can be used to monitor up to five individual workers per program execution.

A case study involving a furniture refinisher's exposure to methylene chloride is described here to demonstrate the utility of radio telemetry. The worker carried a radio transmitter that was attached to a photoionization air analyzer. Qualitative methylene chloride exposures were remotely monitored on a video monitor throughout the day. Increases in exposure levels, due to job tasks, work practices, and emission sources were immediately identified so that corrective action could be taken at that time.

It is important for researchers who are developing real-time monitoring techniques to consider the procedures discussed in this report. Also, researchers conducting field studies should be cognizant of the variety of real-time monitoring techniques and use them to their advantage in evaluating worker exposure.

Introduction

In recent years, researchers at the National Institute for Occupational Safety and Health (NIOSH) have used microcomputers, data loggers or coaxial cables, and video-taping techniques during hazard control studies to help acquire real-time exposure data.[1,2,3] The data source was a portable direct-reading instrument that measures a worker's exposure to a hazardous vapor, gas or dust. Such instruments measure the concentration of airborne pollutants through detection by flame ionization, photoionization, electrochemical reactions, infrared and ultraviolet radiation, and chemiluminescence.[4] Most of these devices provide a continuous analog signal through an output connector that is proportional to the concentration detected. The signal can be routed to a strip chart recorder for a continuous record of exposure levels, or it can be routed to an electro-mechanical device (e.g., a solenoid valve) for process control. Or, the analog signal can be converted into an audio signal and transmitted over a radio channel to a distant receiver for immediate processing by a microcomputer.

The radio telemetry system, discussed herein, was developed to improve this real-time exposure monitoring by allowing: (1) the acquisition and analysis of exposure data at locations remote from non-stationary sources and (2) immediate access to exposure information that is not possible with data loggers. The radio telemetry system overcomes the distinct disadvantage of delay by continuously supplying data to a personal computer throughout a monitoring session.[A] An interface modification of a commercial (frequency) scanner allows the computer to selectively tune up to five separate frequencies through its RS-232 serial port (i.e. the system would permit monitoring of five individual workers per program execution). The operator specifies, in system software, a carrier frequency that a remote transmitter will be utilizing in operation. Each transmitter can then be connected to the output signal of any direct-reading instrument involved with the analysis of a vapor, gas, or dust concentration. Data are continuously transmitted to the scanner. Upon reception, data enters the computer. While data are being stored to disk, the information is simultaneously displayed on a video monitor in either a text or graphic format. Should a breakdown in the equipment occur (i.e., battery failure), it could be quickly discovered and corrected.

This radio telemetry system has been deployed on several field studies with encouraging results. One such study involved the generation of methylene chloride vapor during the removal (stripping) of old furniture finishes. NIOSH engineers performed an evaluation of a newly-installed ventilation system at the refinishing facility.[5] Using the radio telemetry system and a photoionization air analyzer, a worker's qualitative exposure levels were remotely monitored as they occurred. A work practice or emission source that caused an increased exposure was immediately identified so that proper corrective action could be taken at that time.

System Description

Referring to Figure 1, the microcomputer and base receiver share two-way communications through an RS-232C interface. When the computer is directed to listen to a particular carrier frequency (88-108 MHz) in accordance with system software, the computer sends a tuning instruction to the receiver. Once the receiver has tuned to the specified frequency (channel), the receiver will continuously send digitized exposure measurements from the remote transmitter that is operating on the same channel. Each transmitter is programmed to a unique carrier frequency before it is placed in operation. Every direct-reading instrument is assigned a particular channel so that its exposure measurements can be positively identified upon reception at the computer. The transmitters digitize, then modulate, the analog signals (exposure measurements)

[A] Recent changes in the Code of Federal Regulations, Part 15 have had an impact on the Federal Communications Commission's type approval of telemetering devices. As a result, the telemetry system, discussed herein, is currently under review by the authors for compliance.

for transmission over the radio channel. Using frequency-shift keying (FSK) modulation, the advantages include an error rate that is essentially independent of signal amplitude, equal per-digit error probabilities for a mark and space, and simple noncoherent detection without need to process the carrier.

The base receiver, a modified Regency Z60 Programmable Scanner, contains the FSK demodulator needed to reconvert a transmitter's audio-frequency signals (FSK tones) back to binary signals. The Z60's normal keyboard programming has been replaced with an RS-232 interface connection to the IBM AT® or compatible computer. Programs in BASIC were written during system development to evaluate performance; C-language programs are used in the field for data collection.

The input section of the remote transmitter consists of an 8-bit successive approximation analog-to-digital (A/D) converter. The A/D converter operates continuously in a free-running mode. Each frequency-synthesized transmitter can be programmed to operate on any frequency in the FM broadcast band.[6] Selection of the carrier frequency is important since reception can vary from one broadcast region to the next. Engineering firms that specialize in radio frequency (RF) design can build a transmitter to Part 15 (CFR 47) specifications. Independent RF testing laboratories can provide the certification required by the Federal Communications Commission (FCC).

Field Demonstration

The radio telemetry system's first field use was in a furniture refinishing facility where the substance under study was methylene chloride (NIOSH recommends that worker exposure to methylene chloride be controlled to the lowest feasible limit).[7] A photoionization air analyzer (Photovac TIP II™) was strapped to a rack which, in turn, was attached to a tubular-framed backpack (Figure 2). The TIP II™ comes with a receptacle that allows an electrical connection to a portable chart recorder. Instead of the chart recorder, the analog signal was split between a data logger (Rustrak® Ranger) and a radio transmitter. Two air sampling pumps also were attached to the backpack. (The data logger and pumps shown in Figure 2 were unrelated to the demonstration of the telemetry system, and will not be further discussed.) Although data collected through radio telemetry could be used to determine if exposure limits were exceeded, the data presented here are the result of a qualitative approach. Instead of parts per million (ppm), DC voltage (an analog output of the direct-reading instrument) was used to identify and minimize peak exposures to methylene chloride. For example, 0.5 VDC may represent a concentration of 50 ppm, but it is approximately one-half the exposure represented by 1.0 VDC.

During the field demonstration, the subject worker and equipment backpack provided qualitative exposure data from three separate work areas within the facility.[8] Figures 3 and 4 show where furniture finishes were removed (stripped) and rinsed off, respectively. In the absence of chemical leaks or spills, the worker was not subjected to a vapor buildup in the third work area.

A cart provided mobility for the computer, video monitor, and base receiver. The system demonstrated during test runs that data transmissions could be accurately received over 100-ft. distances within the facility.

Figure 5 shows the worker stripping the finish from a wooden chair, while wearing an air-purifying respirator. (It should be noted that NIOSH recommends the use of either a supplied-air respirator, or a self-contained breathing apparatus with a full facepiece and operated in a pressure-demand mode for any detectable concentration of methylene chloride.)[9] Each time that he completed a piece of furniture, a table or chair, the worker had to carry it into the rinse room to spray off the chemical residue. After the rinse, the furniture was usually placed outside the double doors (in the area of the cart) to air dry. The worker also sometimes left the stripping room to replenish his supply of solution before

starting another piece. Regardless of the worker's activity or location, it was important to maintain accurate records during monitoring.[8]

While the video monitor displayed the worker's exposure to methylene chloride vapors, the computer simultaneously stored the data to disk. Figures 6 through 8 are reproductions from selected data that were stored on the disk. The reproductions are similar to the original graphs that were temporarily viewed at the work site as the exposures occurred. With few exceptions, the emission sources and work practices which led to increased exposure were easily identified.

It should be noted that researchers should consider instrument response time when viewing work processes. To pinpoint the sources and practices that contribute most to the overall level of exposure, the researcher should avoid choosing instruments with a response time of more than 10 seconds (5 seconds in some applications). A delayed response may create difficulties in interpreting the relationship between instantaneous exposure levels and the work process itself.[10] If the duration of a delayed response is known, data that have been saved on disk can be offset to reflect the true time for each exposure level.

Figure 6 illustrates the worker's relative exposure to methylene chloride during the removal of a table's finish. When the worker was observed leaning directly over the table, the particular exposure level that was seen provided evidence that worker participation in the elimination, or reduction, of personal exposure is as important as engineering controls. The relationship between the exposure of a worker to solvents and the work method used is often a comparison of actions and consequences.

Dramatic improvements can be obtained in the job environment by relatively simple changes in work practices. A method called PIcture Mix EXposure (PIMEX) was developed at the National Institute of Occupational Health in Solna, Sweden that specifically addresses the problem of employee awareness.[11] The method assumes that exposure depends to some extent on the way the individual employee works at his/her workplace. Good examples of this are a spray painter's exposure to solvents, a welder's exposure to welding fumes, and many other cases in which an employee handles the source of the contaminant. Swedish field studies employing video techniques make it possible to identify problems on videotape. Through the use of a video mixer, measurements obtained by direct-reading instruments are superimposed at the edge of a monitor screen in a form similar to a bar chart. The height of the bar is proportional at all times with the level of the signal. Since the PIMEX method uses radio transmitters to route the measurements to the mixer, video mixing is performed on site so that superimposed videotapes can be available for the company debriefing. While NIOSH researchers use a videotaping system, present video techniques exclude video mixing on location.[1,2] Superimposed videotapes are not available until the exposure measurements (data) have been averaged, formatted and synchronized to the appropriate videotape.

While the local exhaust ventilation system appeared to be effective at the furniture-stripping station, another potential area of concern was discovered. Referring to Figure 7, a piece of furniture is undergoing a chemical strip approximately 80 seconds after the start of the file. The piece, dripping with solvent, was removed by the worker, and entered the water rinse booth after 800 seconds. Note the worker's qualitative exposure during the next 450 seconds.

Besides registering a sizeable peak in exposure as a result of the initial water rinse, the contamination is slow, in terms of breath cycles, to dissipate. The initial peak, followed by a gradual reduction in the relative vapor concentration, was characteristic for both types of furniture. Figure 8 shows the water rinse of another piece of furniture. The series of smaller peaks following the initial one is a response to the jet of water striking fresh solvent on unrinsed areas of the furniture.

There appeared to be a potential ventilation problem in the rinse booth that required further investigation. NIOSH researchers were alerted by the exposure levels that were being displayed on the video monitor (Figure 8). Once alerted, a smoke tube was discharged in the booth and its trail was followed. It was found that the temperature of the chemical solution was outside the chemical manufacturer's recommended range, resulting in a breakdown in a paraffin-based vapor barrier which created unnecessary fuming and product loss.[B] Through the use of radio telemetry, immediate action was taken to correct the problem.

Conclusion

The usefulness of radio telemetry, a system that instantly transmits exposure data from direct-reading instruments to a microcomputer, has been demonstrated on a field survey at a furniture-stripping operation. The system offers advantages over other methods of data collection. Using telemetry, workers under study can enjoy more natural movement than they can by being tied with coaxial cables. Unlike data loggers, radio signals produce instantaneous results. The researcher can view exposure information received from several workers and/or processes on a moment-by-moment basis, thus preserving the primary advantage (instant feedback) of direct-reading instrumentation. Immediate exposure determinations are needed in the workplace to prevent employee injury and to advise management. Such determinations allow the swift elimination of emission sources and the timely development of exposure scenarios, proper work procedures and training aids.

Video techniques used by Swedish researchers have recognized the expediency of radio telemetry. Although information that has been saved on disk can be later mixed with videotape to produce training aids, there is an advantage in video mixing at the job site. By combining the results as they occur, the need to mix hours of data files and videotape at another time and place is eliminated.

Finally, the application of radio telemetry provides more flexibility and personal involvement while monitoring in the workplace. Personnel involved in a field study are generally more productive. There is more interaction, observation, and discussion. The focal point of this activity centers around the video monitor. As exposure information is updated on the screen, comments can be made and notes taken. Researchers have the opportunity to take additional measures in response to higher-than-expected exposure readings. Follow-up investigations could become unnecessary when corrective actions are proven effective before leaving the work site.

It is important for researchers who are developing real-time monitoring techniques to consider the procedures discussed in this report. Also, researchers conducting field studies should be cognizant of the variety of real-time monitoring techniques and use them to their advantage in evaluating worker exposure.

Acknowledgment

We would like to thank Martin Abell of NIOSH and William Metzger, a NIOSH summer employee, for their assistance in the development of the radio telemetry system software.

[B] Temperature Range: 60° to 85°F per product label instructions for paint remover #2105 manufactured by Kwick Kleen Industrial Solvents, Inc., Vincennes, IN.

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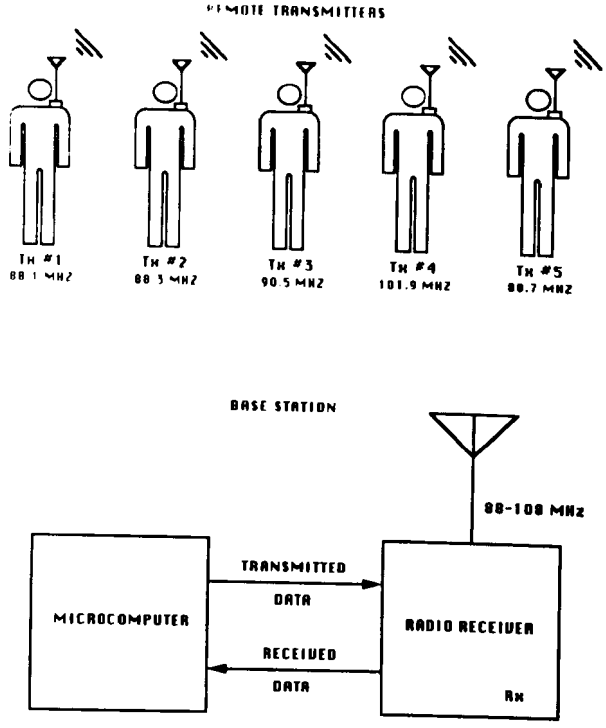

Figure 1. Radio Telemetry Block Diagram

Figure 2. Equipment Backpack

Figure 4. Rinse Room

Figure 3. Workstation

Figure 5. Stripping Furniture

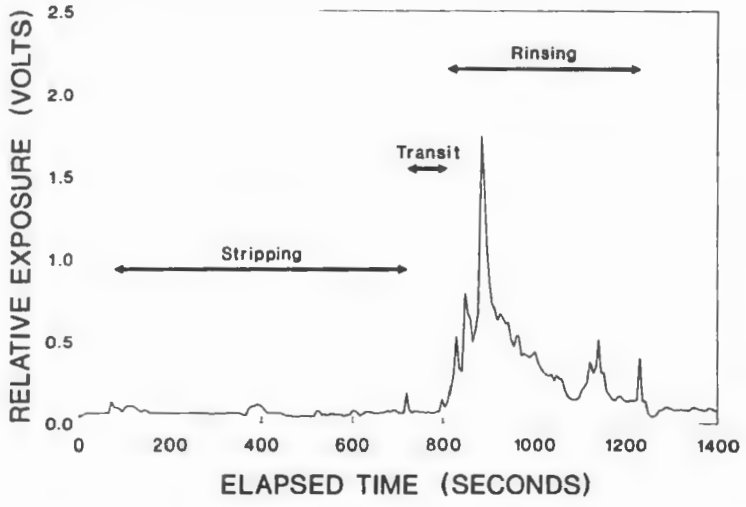

Figure 7. Chemical Stripping/Water Rinsing

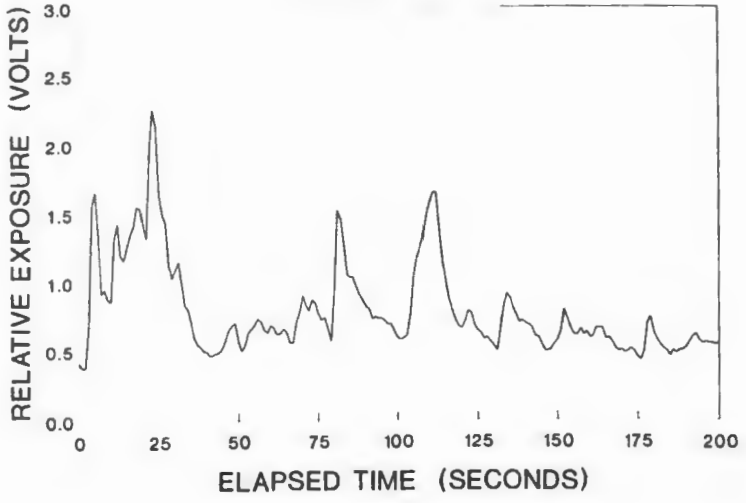

Figure 8. Peak Exposures in the Rinse Room

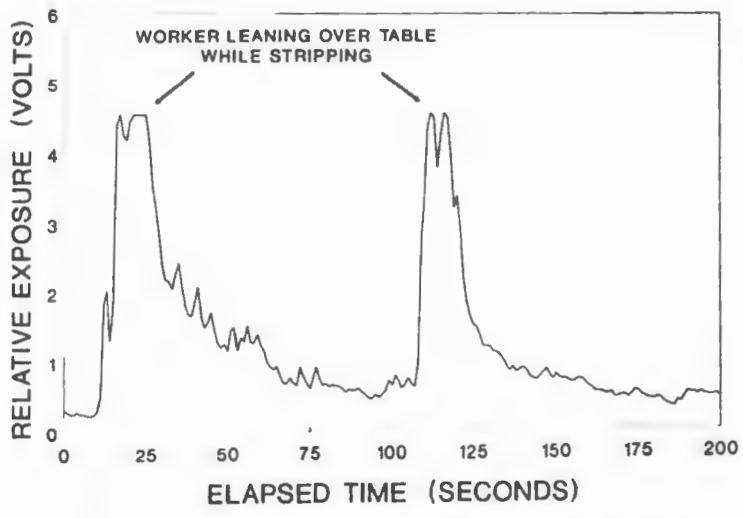

Figure 6. Personal Exposure as a Result of Poor Work Practices

DISCUSSION

MATT STINCHFIELD: Did you attempt to calibrate your relative reading to actual air concentrations, and if so, how did you do it?

RONALD KOVEIN: That's something we took for granted. We were not out to determine the exact concentration in that room. This is like a background sniff to identify the sources, practices, so on. In other words, along the y axis there may or may not be 50 ppm. But in a relative fashion we know the air quality of that room, that rinse booth, was far less superior than, say, close proximity to the ventilation system.

MATT STINCHFIELD: Yes, the work procedure and the corresponding spike that we saw was apparent. Have you considered how you might go about calibrating your field instrument?

RONALD KOVEIN: Yes, it is highly doable at this stage. In my mind it is even secondary to others because it is so doable. We've tested the hardware. For instance, the A to D in the front end of that transmitter is highly linear. We can improve system software. It's still growing. All these things can help make the system more user friendly and to allow for actual concentration readings. It is highly doable.

MATT STINCHFIELD: One final part to that. The software you were using for receiving the information through your RS-232- is that a commercially available type of data acquisition software, or was that something custom?

RONALD KOVEIN: Yes, it is. But once it's on the floppy disk it's part of the data storage and you can use just about anything you want, similar to a data logger. It is custom in that everything was built from scratch. We're not aware of anything out there commercially that does quite what we do. And in fact, we think it is quite unique, though it may be considered very basic. You'll notice it is simple. It is asynchronous, one-way communications. We have nothing sophisticated or as expensive as cyclic redundancy checking, for instance. I don't feel we need it. We have improvements down the way, and it is going to get better in range. There is so much left to do. The commercial scanner by the way, is rough. It did a great job for what we wanted it to do, but we can optimize it. We can give it better filtration making it much more sensitive and selective. And at the same time we have improvements to do on the prototype transmitters. We can increase field intensity for instance. Now with the revision of CFR 47 for a Part 15 device, it can go from about 50 microvolts per meter up to 250. So as I say, things are starting for our system in both performance and quality.

IMPROVEMENTS IN THE MONITORING OF PPM LEVEL ORGANIC VAPORS WITH FIELD PORTABLE INSTRUMENTS

Gerald Moore

GMD Systems, Inc.

An Overview of the Scope for Monitoring

In the whole field of gas detection and measurement, organic compounds represent by far the largest group of interest to users due to the wide variety of these substances that are used in different applications. Measurements are made for reasons of process control, flammability hazard or toxicity and sometimes for all of these reasons with the same substance.

Before focusing on the specific area of toxic level monitoring, it is interesting to review the number of organic compounds and the needs for monitoring.

One of the most widely used reference books, the CRC Handbook of Chemistry and Physics[1], lists a grand total of 17,746 chemical compounds, both organic and inorganic. This listing breaks down into 4,126 inorganic and 13,620 organic compounds; i.e., approximately two-thirds of all the listed compounds are organics.

However, when one looks for a more specific listing of compounds likely to be of interest for monitoring in industry, there is a vast difference in the numbers. One of the most comprehensive list of organic vapors in common use is that published by the National Fire Protection Association (NFPA) in the U.S.A.[2] This listing covers the fire hazard properties of liquids, gases and volatile solids and has been progressively updated over the years. After eliminating synonyms and inorganics, a total of approximately 1,250 substances remains, suggesting that this may be a reliable estimate of the number of organic compounds in common use for which organic vapor monitoring may be needed. Clearly this number of compounds far exceeds any other group of compounds that require monitoring in air, but represents a small fraction (less than 10%) of the total organics listing.

When one thinks of toxic hazards, TLV guidelines come to mind as the accepted numerical classification. The American Conference of Governmental Industrial Hygienists (ACGIH) recently published a guide for TLVs[3] in various countries . In this listing there are 972 compounds of which 355 are organic vapors having a defined and listed TLV. The other 617 are dusts inorganics and organics having no listed TLV (carcinogens, etc). Since this paper is concerned with monitoring toxic organic vapors, the analysis will concentrate on the 355 listed TLVs in an attempt to put an overall context on to organic vapor monitoring needs.

An Overview of the Scope for Monitoring (continued)

Figure 1 shows the results of this numerical breakdown. From a starting point of 1,250 substances in common use, those substances clearly of interest only for their flammability were next identified. This produced a surprisingly small total of 44 substances, typified by methane, ethylene and substances such as corn oil, soybean oil, etc. Taking out this group, together with the 355 listed by the ACGIH, leaves a total of 851 (68% of the total number) which the author believes to be toxic at some level even though they have no formal listing. Obvious examples are members of the same chemical family or series such as ketones or aldehydes, where one member of the family has a TLV listing and the others do not. It could be argued that only certain members of the series are in fact toxic, but the author believe that a more reasonable explanation is that the medical and epidemiological data has not yet been produced and formalized.

From a starting point of 1,250 organic vapors, one can only, therefore, subtract around 4% as being purely of interest from a flammability point of view. All the rest should be considered as having either listed or unlisted toxic properties and might, therefore, be of interest for monitoring in the atmosphere. This is quite a challenge, requiring monitors for over 1,200 different compounds at toxic levels.

The Need for Sensitivity in Monitoring

A breakdown of the ACGIH listed TLVs for organic vapors is shown in Figure 2. It will be seen that the numbers of TLV listings below 100 ppb or above 1000 ppm are very small and that the largest single groups are in the ranges 1-10 ppm and 10-100 ppm. A flexible direct reading instrument having a range from approximately 0.1-->1000 ppm would therefore be of great utility in measuring around 90% of the toxic organic vapors and 70% of the listings could be covered with a range of 0.1-->100 ppm.

Detection Principles in Common Use

The user has available a wide variety of detection techniques to bring to bear on the problem of organic vapor monitoring. Figure 3 provides a simplified overview of these techniques in relation to one another and to the spectrum of requirements.

Eliminating those techniques that are highly specific in nature, e.g., colorimetric paper tapes and those that are primarily intended for use as flammability monitors, leaves the following list of methods as suitable for <u>portable</u> direct reading monitors:

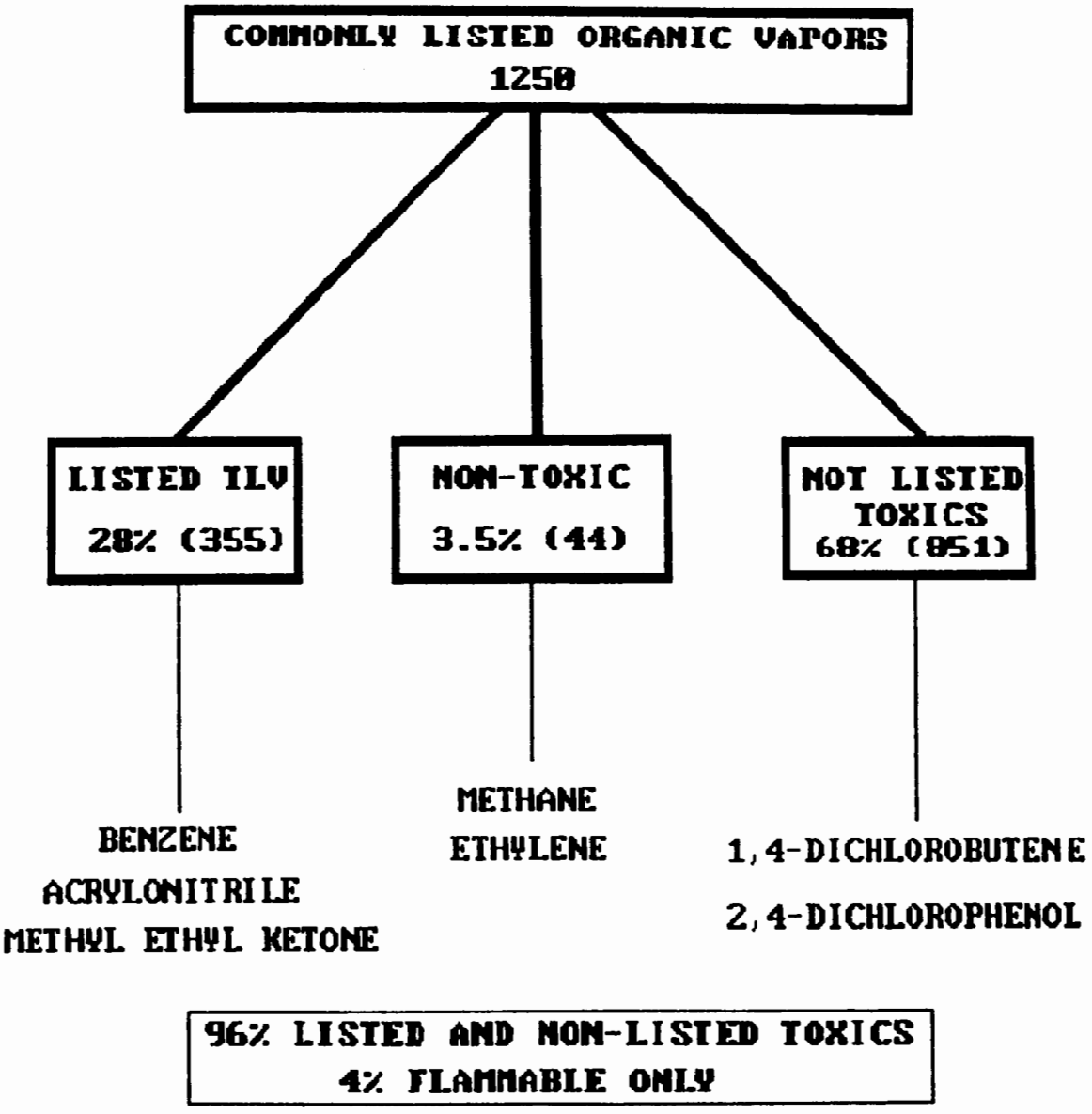
COMMONLY LISTED ORGANIC VAPORS
1250
LISTED ILV
28% (355)
NON-TOXIC
3.5% (44)
NOT LISTED TOXICS
68% (851)
BENZENE
ACRYLONITRILE
METHYL ETHYL KETONE
METHANE
ETHYLENE
1,4-DICHLOROBUTENE
2,4-DICHLOROPHENOL
96% LISTED AND NON-LISTED TOXICS
4% FLAMMABLE ONLY

Figure 1

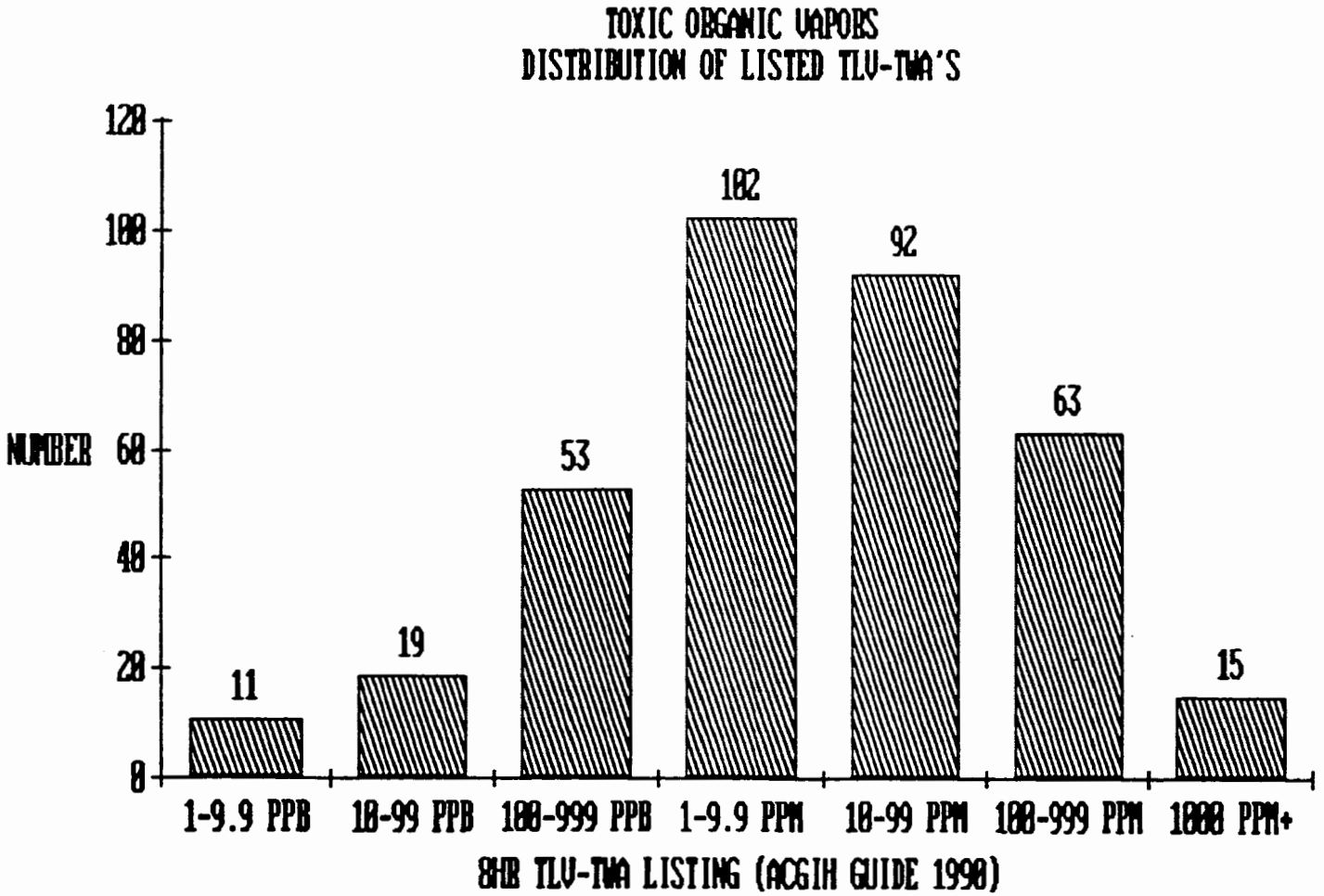
TOXIC ORGANIC VAPORS
DISTRIBUTION OF LISTED TLV-TWA'S
NUMBER
120
100
80
60
40
20
0
11
19
53
102
92
63
15
1-9.9 PPB
10-99 PPB
100-999 PPB
1-9.9 PPM
10-99 PPM
100-999 PPM
1000 PPM+
8HR TLV-TWA LISTING (ACGIH GUIDE 1990)

Figure 2

SENSITIVITY RANGES FOR ORGANIC VAPOR MONITORING INSTRUMENTS

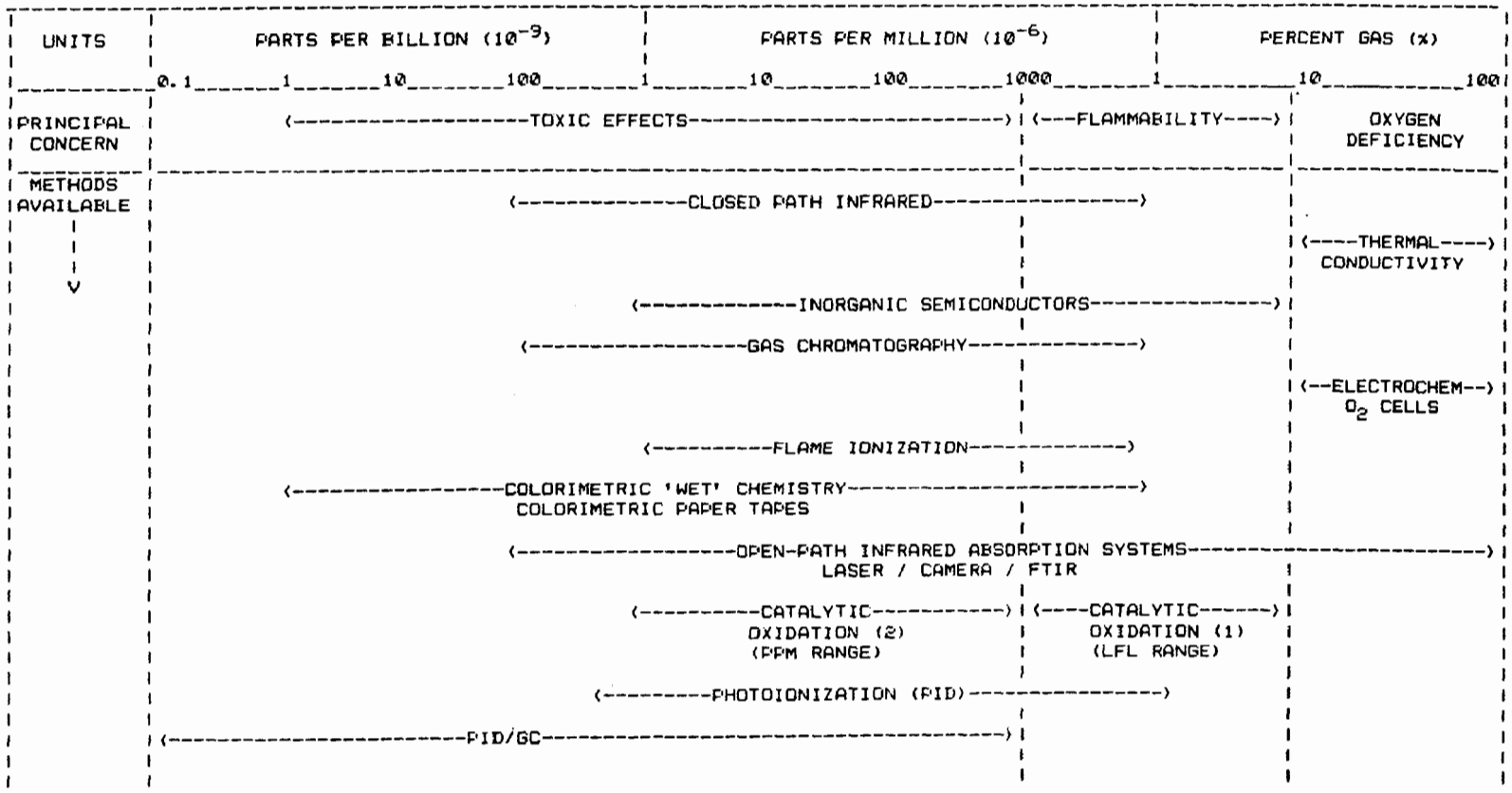

Figure 3

Detection Principles in Common Use (continued)

* Closed Path Infrared Absorption	(IR)
* Flame Ionization	(FID)
* Gas Chromatography with FID	(FID/GC)
* Catalytic Oxidation	(Catalytic)
* Photoionization	(PID)
* Gas Chromatography with PID	(PID/GC)

The last two categories have seen many improvements in the last five years, resulting in a new generation of lightweight direct-reading instruments for monitoring organic vapors. The need for specific compound identification in complex mixtures has stimulated the development of portable gas chromatographs of high sensitivity, suitable for field use.

Since the other techniques mentioned have been described frequently in other published material, this paper focuses on the particular properties of the photoionization detector and the ongoing development of truly portable instruments based on the use of this detector in conjunction with gas chromatographic technique.

General Description of PID Based Instruments

Photoionization is becoming a very popular technique for the detection of organic vapors at low ppm levels. This detection principle, especially when combined with gas chromatography can provide a powerful tool in identification and quantitation. A photoionization detector is similar to an FID except that the ionization energy is provided by an ultra-violet emitting lamp. A photon of UV radiation is absorbed by a molecule of the organic vapor causing ionization of the molecule. An ion flux is generated between two high voltage electrodes and a detectable current results. The detector usually consists of a sealed interchangeable UV lamp that emits photons of specific energy. If this energy level is high enough to ionize the organic molecule, this will be detected in the ionization chamber as an electrical signal which is electronically converted to a measured concentration. If the proper lamp is chosen, sensitivities can be as low as 0.1 ppm, but there is a trade-off between high energy emissions and lamp life. The high cost of replacement lamp (>U.S.$500) makes this trade-off of importance. These direct reading instruments are simple to use, highly portable and reasonably cheap. However, the range of relative responses is very wide as will be discussed later. Examples are the Photovac "TIP"[4] and MSA "Photon"[5] instruments.

General Description of PID Based Instruments (continued)

As mentioned earlier, if this type of detector is used in conjunction with gas chromatography, specificity improves and limits of detection can be lowered. Several instruments having this configuration have been designed and brought on to the market in recent years. A good example is the PHOTOVAC Model 10S70[8]. One of the little used advantages of a PID based GC is the possibility of using air as the carrier gas, thus eliminating all consumable supplies and the need for compressed gas cylinders. This feature will be discussed in more detail in the next section of this paper.

Special Features of PID Based Instruments

The versatility of a PID based direct reading portable instrument and its ease of use has stimulated the development of a number of commercially available instruments and encouraged their widespread use in the field. However, the particular advantages and limitations of the technique are not always well understood and this can lead to improper application.

As stated earlier, the extent to which an organic vapor is ionized depends on the energy level of the photons emitted by the UV lamp, relative to the level required to ionize the vapor (Ionization Potential). There are various published tables of ionization potentials and some of these also give the relative responses of these detectors to a variety of organic vapors.[7,9,10] UV lamps are available having energy levels ranging from 8.5 --> 11.7 eV with the higher energy lamps typically having shorter lifetimes.

Figure 4 provides a breakdown of the number of organic vapors that can be measured with each of the three most commonly used lamp types, assuming the same total number of 1,250 as used earlier. It will be seen that the use of a 9.5 eV lamp would drastically curtail the usefulness of this technique and, thereby, possibly give many "false negatives" in field use. A 10.2 eV lamp gives a far more comprehensive general purpose response, allowing around 85% of all commonly used organic vapors to be measured. It should be particularly noted, however, that many of the compounds of most interest from a toxicity point of view are halogenated organics which require higher energy lamps to achieve ionization. Therefore, the improvement in the numbers detectable with an 11.7 eV lamp is not as superficial as might at first appear, since the halogenated compounds are heavily represented in this difference number. Care should, therefore, be taken in choosing a PID that is appropriate to the <u>particular</u> compounds in a given application.

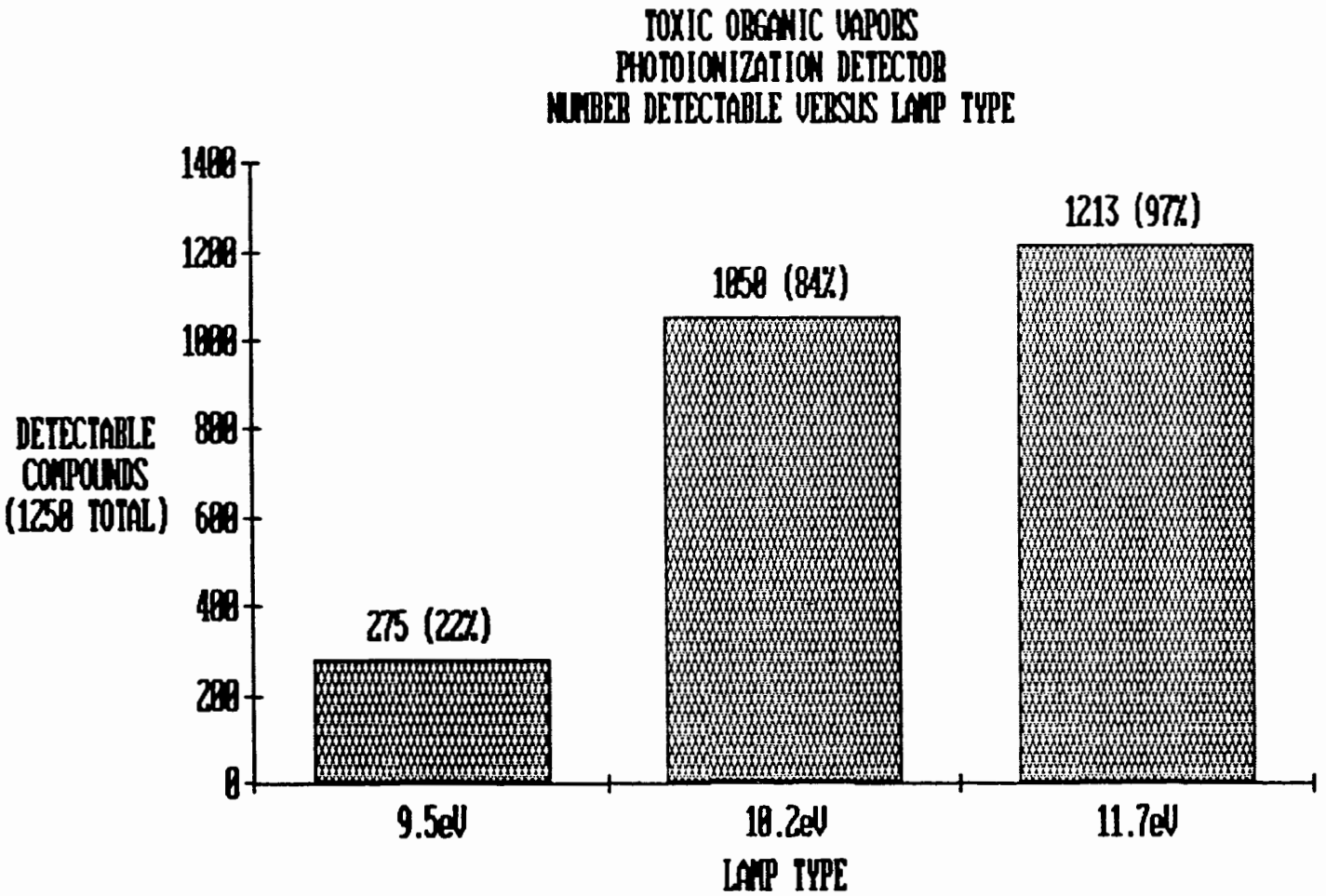
TOXIC ORGANIC VAPORS
PHOTOIONIZATION DETECTOR
NUMBER DETECTABLE VERSUS LAMP TYPE
DETECTABLE COMPOUNDS (1258 TOTAL)
1400
1200
1000
800
600
400
200
0
275 (22%)
1058 (84%)
1213 (97%)
9.5eV
10.2eV
11.7eV
LAMP TYPE

Figure 4

Special Features of PID Based Instruments (continued)

The main advantage of a PID based portable monitor is its universality of response. Subject to the careful choice of lamp as described earlier, the monitor will give reading for an extremely wide range of organic vapors. Typically such an instrument is calibrated on the substance of choice, or alternatively on a so-called "typical" substance. For other substances, there will obviously be a range of relative responses both above and below the nominal calibration.

Unfortunately, some suppliers use an aromatic compound such as benzene for their "nominal" calibration. This is undesirable since aromatics, in general, are the most easily ionized and, therefore, respond with most types of UV lamps. In addition, they tend to give high responses, meaning that most other substances will have lower relative responses, in some cases as little as 1/100th that of benzene. Clearly, a more general purpose instrument would be calibrated on a "median response" substance so that relative responses would be distributed more evenly above and below the nominal calibration (this assumes that an individual calibration for a particular substance is not available).

This approach was researched using the available references, and the result is shown in Figure 5. By listing all available relative responses and scaling them to the median value, a compound could be selected (methyl propyl ketone) and the distribution of relative responses of such a median-calibrated instrument is shown. A useful number of compounds (263 or 21% of the total) fall within relative response range of $\pm$25% which could be considered sufficiently accurate for many applications. However, it will also be noted that almost half of the total number are outside the range of $\pm$80% so some care is still necessary. Clearly, the PID technique is wide-ranging in its uses but some care is necessary if general purpose uses are being considered.

PID GC Improvements

The addition of capillary column gas chromatography to a PID-based monitor results in an extremely flexible and portable organic vapor monitor. The authors have been involved with the development of such a system during the last few years and believe that it represents a significant advance in technique. This technique was originally developed at the Swedish National Defense Research Institute (FOA) and was licensed to GMD Systems, Inc., who will be marketing it under the trade name "Autograph". The unit is presently at the advanced prototype stage and will be available on the market during 1991[6].

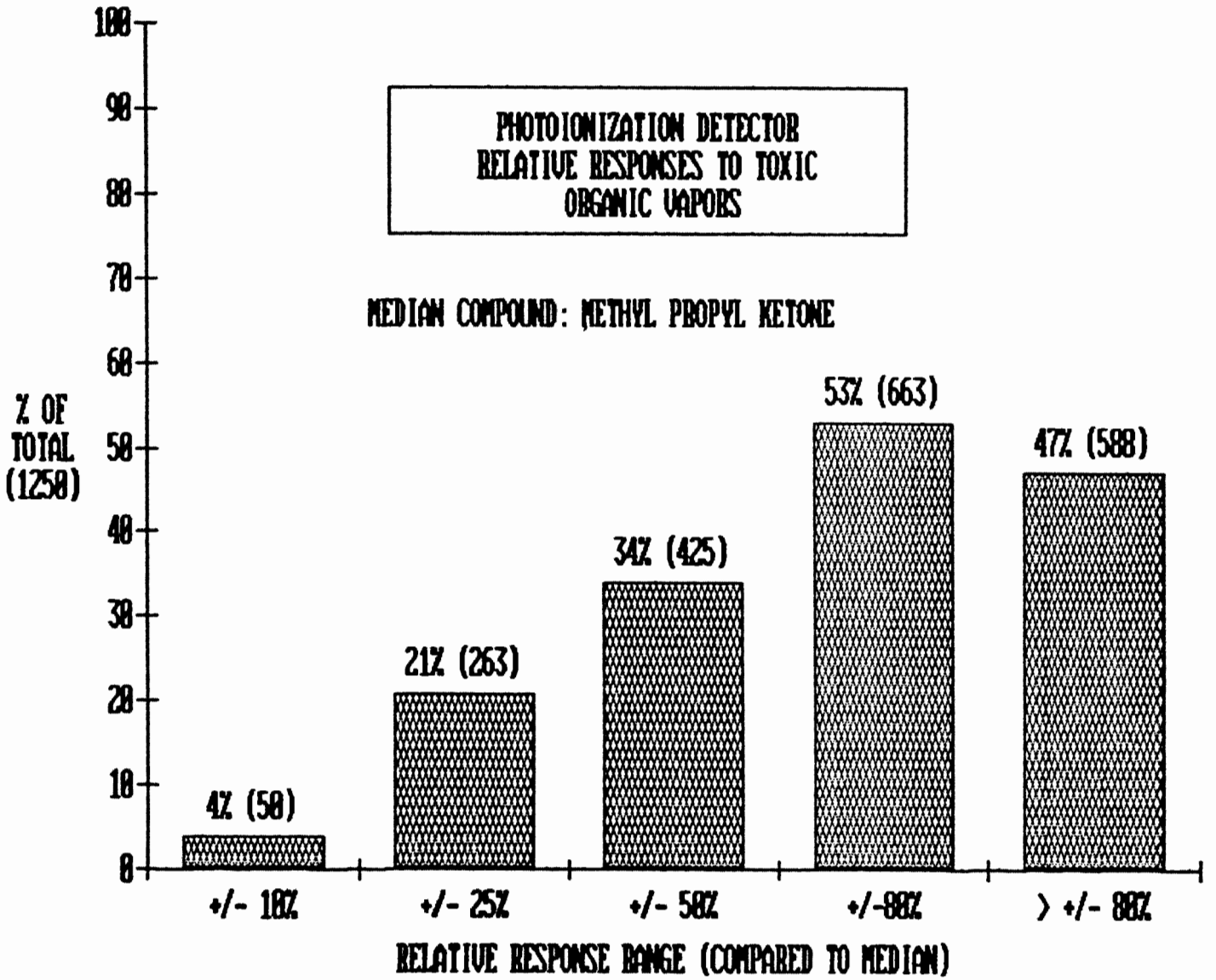
PHOTOIONIZATION DETECTOR
RELATIVE RESPONSES TO TOXIC
ORGANIC VAPORS
MEDIAN COMPOUND: METHYL PROPYL KETONE
% OF TOTAL (1250)
100
90
80
70
60
50
40
30
20
10
0
4% (50)
21% (263)
34% (425)
53% (663)
47% (588)
+/- 10%
+/- 25%
+/- 50%
+/-80%
> +/- 80%
RELATIVE RESPONSE RANGE (COMPARED TO MEDIAN)

Figure 5

PID GC Improvements (continued)

The Autograph is a fully portable PID based GC system which can be operated either in direct reading "detector" mode with the sample flowing directly to the PID; or alternatively in "GC" mode permitting selectivity and identification of compounds in mixed atmospheres.

Figure 6 shows the block diagram of the system, emphasizing the extreme simplicity of the flow path and minimum of functional components.

It should be noted that no external supply of carrier gas is needed, since outside air from the environment is used as the carrier and cleaned of organics by passing through the sorbent trap shown, which consists of a small tube containing one or more synthetic sorbent materials in granular form.

The sorbent trap thus, simultaneously serves to provide a clean air "carrier" stream and also acts as a preconcentrator for the pollutants of interest.

The sorbent tube is tightly wound with an electrical heater winding; and after a preset sampling period, the tube is electrically heated to around 250^{o} C for a few seconds, thereby desorbing the organics previously adsorbed. The desorbed substances pass on to the heated capillary column (typically 10 meter 0.3 nm I.D.) in which they are separated from each other. Each component of the mixture emerges from the column after a fixed retention time and is detected and quantified by the PID.

Since retention times are dependent on flowrate and column temperature, these two parameters are tightly controlled via the microprocessor and appropriate sensors.

This technique of preconcentrating the organic pollutants via a sorbent with subsequent rapid thermal desorption, improves the lower detection limit by about 50 - 100 times as compared to a PID alone.

The preconcentrator sorbent tube is also removable and can be used alone as a diffusion-operated personal sampler. By distributing a number of these samplers and analyzing them later, all the functions of a normal analytical laboratory can be performed in the field with a single instrument which can also be used for survey work.

The microprocessor calculates concentration data, identifies compounds against a known substance library and displays all parameters on the instrument's LCD graphics display panel. All data is also stored for each sample period.

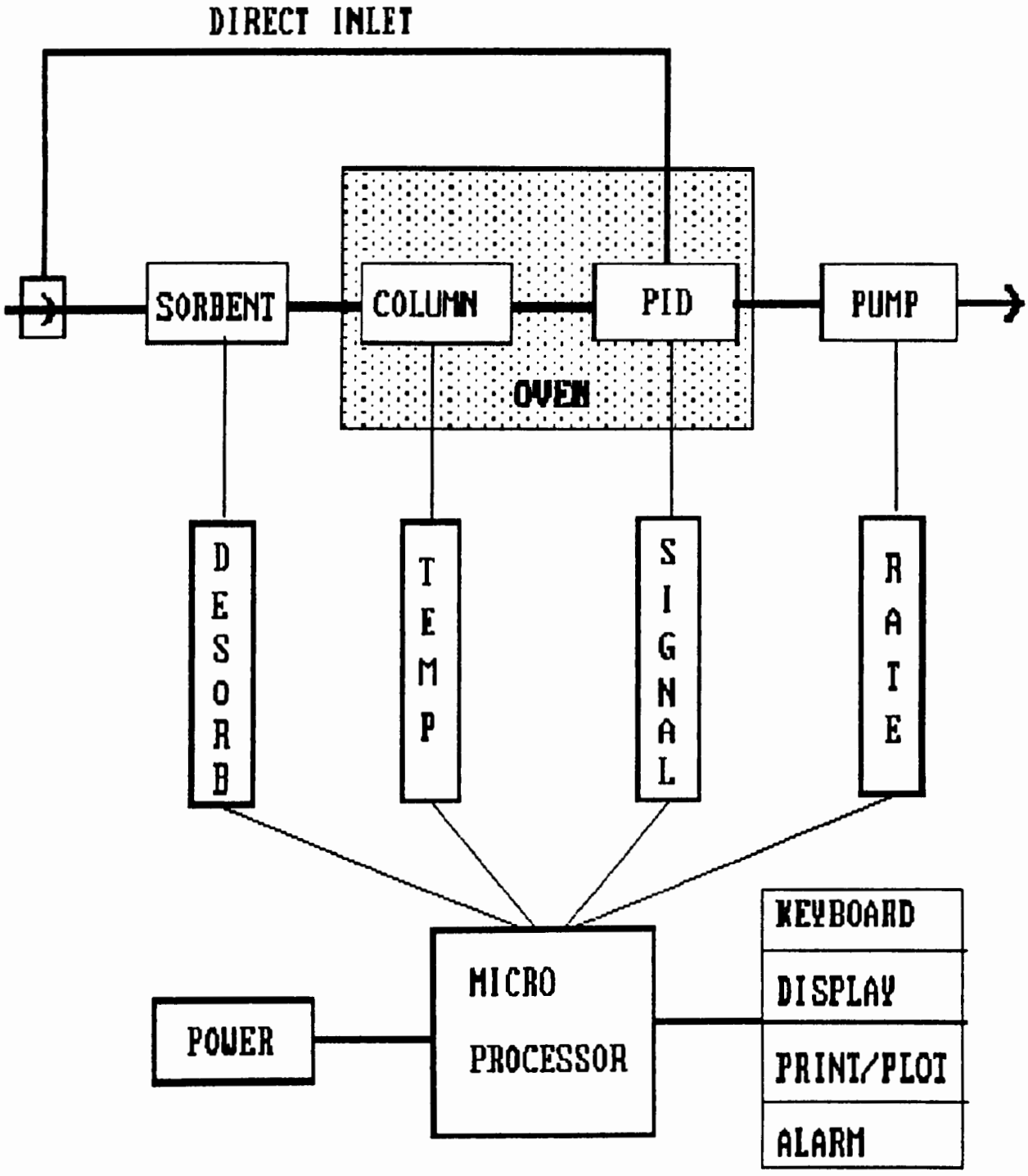

Figure 6
PID BASED GAS CHROMATOGRAPH

GMD "AUTOGRAPH"

PID GC Improvements (continued)

Operating parameters such as column temperature, length of sampling period, etc., can be programmed by the operator either via an integral keypad or via a serial data link from an external laptop or other personal computer, which also serves to download and analyze data which is stored in the instrument's memory during field use.

Typical analysis cycle times are around 4 minutes, and it will be appreciated that a new sample is being collected during this cycle, since the sorbent continues to act as a filter to the incoming air. However, longer sampling periods can be used, giving increased sensitivity of detection, since the mass of sample on the sorbent is increased. Sensitivities down to 0.01 ppb have been achieved in this way.

The versatility of the technique is enhanced by providing a sample bypass valve which diverts the incoming air directly to the PID. This permits rapid qualitative screening of the test atmosphere with the concentration displayed in analog bar-graph format on the graphic display. If organics are detected, the instrument can then be put into "GC" mode for identification if required.

The complete instrument is compact in size (approximately 4-1/2" high x 10" wide x 12.0" deep) and weighs approximately 10 pounds. It is battery operated and runs for up to 8 hours on a single charge.

The Autograph demonstrates the degree to which it is possible to simplify and miniaturize these techniques and shows the potential for carrying out many analytical functions with a field-portable instrument.

Conclusions

It has been shown that there are around 1,250 organic compounds in general use requiring organic vapor monitoring. Approximately 96% should be considered as listed or potentially toxic and, therefore, there may be a need for toxic level monitoring. This group of compounds represents by far the most numerous family of substances for which specific monitoring is required.

The range of toxic concentrations is mainly from 0.1 --> 1000 ppm with only very small numbers outside this range. Specific detectors are often available for particular organics at ppb levels, but the remainder require a good general purpose monitoring technique.

Conclusions (continued)

Improvement in PID-based instruments have made them more available and easy to use in recent years. High sensitivity and broad-ranging response are the advantages, while cost of the detector and non-uniformity of relative responses are the main disadvantages.

PID-based portable GC systems are now widely available. This combination of sensitivity, selectivity and portability is unique. However, not all instruments take full advantage of the technique as regards true portability, elimination of carrier gases, etc. The development of the GMD "Autograph" has been described as an example of good exploitation of this potential.

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DISCUSSION

JUDD POSNER: My question relates to using air as a carrier gas. My recollection way back when I was using PID was that there was a negative beat for oxygen and that might be a problem with using air as a carrier gas. Does it not, in fact, lower your sensitivity somewhat?

The second thing is, having spent so much time arguing with people that tubes are not really a very good design for passive monitoring, I'm appalled that you should come up here and tell me that you can use that little external tube as a passive monitor.

GERALD MOORE: You got me with a tube, I have to admit. It's kind of a neat feature of particular techniques, so why not use it. If I could have made it look like a passive monitor, I really would have done it out of principle.

As to the more serious point about the oxygen, we haven't actually seen any interfering peaks that interfere with the identification. I think the more serious problem that's been raised by several people we've talked to is possible oxidation of the thermally unstable compounds with an air carrier either in the system, on the column, or wherever. Not having the advantage of a nitrogen carrier, I think that is going to be a problem for some compounds. We don't have enough experience to know how many. We hope that the advantages of the technique considering the wide field we're dealing with here will be greater than the disadvantages.

RAPID ASSESSMENT OF SUPERFUND SITES FOR HAZARDOUS MATERIALS WITH X-RAY FLUORESCENCE SPECTROMETRY

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Abstract

Field-portable X-ray fluorescence (FPXRF) is nationally recognized as an excellent screening tool for inorganic contaminants on hazardous waste sites. However, FPXRF is more than a screening tool when used correctly. Properly calibrated and monitored, FPXRF produces quantitative data of known quality. Albeit, the data are often of lower quality than intensive laboratory analytical methods, but one must consider the end-use of the data. In many situations, definition of the spatial distribution of the contaminants can be accomplished most cost effectively by taking numerous FPXRF measurements rather than a limited number of laboratory analyses of higher precision and accuracy.

INTRODUCTION

Sampling procedures traditionally employed for site characterization revolve around the analytical laboratory. Physical samples are collected onsite, packaged, decontaminated if necessary, and shipped to a laboratory for analysis under chain-of-custody restrictions (see Figure 1). Laboratory residence time is typically 20 to 40 days, with analytical costs of $150 or more per sample using contract laboratory program (CLP) procedures. Analytical results are compiled into data packs and shipped to site personnel for review. Clearly, this approach is costly, time consuming, and affords many opportunities for the incurrence of errors and data loss. It discourages multistage sampling and, in some cases, has led to development of inadequate sampling plans in order to avoid the inherent expense.

The disadvantages of the foregoing approach have prompted new emphasis on the development of rapid, inexpensive field analytical methods. In the case of inorganic contaminants, X-ray fluorescence (XRF) is particularly applicable, especially for heavier elements such as the transition metals. XRF spectrometers capable of being transported to field sites and operated thereon are commercially available. Some require operation in a field laboratory, whereas others can be transported manually and operated directly on the site surface. Availability of the latter has led to development of a field portable X-ray fluorescence (FPXRF) approach by Lockheed Engineering & Sciences Co. (LESC) as part of the U.S. Environmental Protection Agency (EPA) effort to evaluate and develop field screening and analytical methods.

The FPXRF approach consists of performing in situ analyses with a field portable instrument (see Figure 2). Maximum flexibility and minimum data turnaround can be achieved when the portable instrument is supported with a field laboratory containing equipment for sample preparation, data analysis and display, and a laboratory grade XRF instrument for analyzing calibration standards and confirmatory sample. If desired, data and a report can be delivered to site personnel prior to demobilization.

X-MET 880 FIELD SPECTROMETER

Field implementation employed in LESC studies to date is limited to the X-Met 880. This instrument is a field-portable, energy-dispersive spectrometer commercially distributed through Outokumpu Electronics, Inc., Langhorne, PA. It is self-contained, battery powered, and weighs 8.5 kg. These characteristics, and the fact that it is hermetically sealed and can therefore be decontaminated, allow operation directly onsite. X-ray fluorescence is induced by a low intensity ^{244}Cm or ^{241}Am gamma-ray source housed, along with a gas proportional detector, in the sampling probe. Operational safety is maintained by a shutter approved by the Nuclear Regulatory Commission.

Analysis with the X-Met 880 consists simply of placing the probe in direct contact with the sampling medium and opening the shutter with a trigger. Fluorescent x-ray photons are counted over a user-specified period of time by a counting circuit and classified into discrete energy levels by a multichannel analyzer to produce a spectrum characteristic of the elements in the sampling medium. Net intensities for each target element are calculated by software deconvolution of the characteristic spectrum and converted to concentration values by means of a calibration model. This model is derived empirically by measuring the net intensities of the target elements in a set of calibration standards, and fitting a linear function that relates net intensity to concentration by a multiple regression procedure.

As is the case with all XRF systems, the relationship between net intensity and concentration varies with the characteristics of the sample matrix. In the case of solid, inhomogeneous particulate media such as soils or sludges, the concentration-intensity relationship is particularly influenced by variability in the grain size distribution, bulk density, and the geometric relationships between discrete grains containing the target element(s) and the detector. The geometry problem is exacerbated by the very small volume (roughly 0.04 cubic inch) measured by the probe. Net intensities can be artificially enhanced or absorbed by certain non-target elements that may be present. Moisture has also been reported to affect intensities(1). Data quality can be significantly influenced by any or all of these matrix effects which must therefore be taken into account in the calibration procedure, a subject that is discussed in greater detail in the next section.

ROUTINE FIELD PROCEDURES

Calibration

The X-Met 880 has no fundamental parameter capabilities which would allow for standardless calibration. It uses calibration curves based on matrices similar to those of the routine samples. The instrument has 32 calibration models, each of which can contain up to 6 calibration curves. Therefore, each calibration model can simultaneously quantify up to six analytes. The number of calibration standards required for each calibration model depends on the number of analytes of interest; generally eight to ten standards per analyte.

Site Typical

A site typical calibration curve is based on samples similar in composition, but not necessarily matrix matched. Extreme caution should be exercised when using a site-typical calibration curve. The authors have encountered the situation where increased iron levels in mine tailings relative to the calibration standards resulted in anomalously high chromium results (in excess of several wt% Cr!). Corroboratory analyses found chromium in the zero to 40 mg/kg range.

Site Specific

To minimize enhancement/absorption and spectral interference errors, calibration standards should be collected from the specific site in question. These Site Specific Calibration (SSC) standards must closely emulate the physical and chemical matrix of the routine samples. The SSC standards are prepared as loose soils (screened through 2 mm but unpulverized) so that the particle size bias of the routine samples is included in the instrument calibration.

Characterization of the SSC standards must be done using a total digestion procedure rather than a partial extraction (i.e., CLP "Total Metals"(2)), because XRF is a total analyte method regardless of phase or speciation.

Co-calibration

If more than one X-Met is used on a site, the two instruments should be co-calibrated with the same SSC standards. Even with co-calibrated instruments, there can be inter-instrument bias. This should be tracked and quantified by using splits of the same check samples (discussed below) to monitor the instruments.

The authors were involved in a site screening which was restrained to using 2 X-Mets that were not co-calibrated. The instruments produced two very different populations of data for chromium, an order of magnitude apart. The higher concentration set exceed the state regulatory levels. Despite the low chromium values in the laboratory corroboratory samples, the high FPXRF values are still an issue with the state health agency involved (approximately 1.5 years later).

Sampling

In situ analysis does not require that a physical sample be removed from the ground. The FPXRF probe is placed on the ground and the analysis mode is activated by pulling the trigger. Acquisition time can be preset at any desired length; 30 to 120 seconds is the most common range. FPXRF in situ analyses are very beneficial during remediation. FPXRF can be employed in iterative passes following contaminated soil removal efforts and quickly produce the results of each remediation attempt.

In situ analyses are the quickest way to obtain soil chemistry data but these data also contain the highest degree of variability (error). A large source of error is the extreme heterogeneity of most soils. The radioactive source in the probe is exciting a very small cross section of the soil (20 mm diameter by 2 mm depth). When the probe is moved laterally 5 cm, the detector is 'seeing' a very different sample. Another source of error is the extremely wide range of particle sizes in the sample. This produces a known negative bias[3] that can be somewhat compensated for by using loose, unpulverized SSC standards. A third source of error is surface microvariability which is caused by such physical factors as wind or running water, vehicles or footsteps, and by chemical alteration of the surface. An excellent example of a rapid chemical change in surface phenomena was encountered by the authors at a mine tailings site in New Mexico. A white precipitate of $ZnSO_4$ (?) formed surface crusts in the late morning as the tailings piles dried out. Every afternoon, thunder storms washed the precipitate back into the soil. No precipitate was apparent the next morning until the sun began to dry the soil. Different daily spatial patterns could radically alter concentration maps.

Surface microvariability can be mitigated by in situ homogenization or by collecting intrusive samples, i.e. samples that are physically removed from the sampling media[4].

DATA QUALITY

The procedures in this section address only in situ analyses. Intrusive samples have several sources of variability that do not occur with in situ sampling such as collection, handling, and preparation errors.

Quality Control Procedures

Replicate Analyses

All FPXRF routine samples are analyzed in triplicate and the means are the reported values. The three in situ measurements are made in a 6 by 6 by 6 inch triangular pattern around the sample location marker. After the third measurement of every fifth sample location, the probe is left in place and analysis is repeated two more times (stationary probe triplicate).

Before the first in situ sample location and after every tenth sample location low- and mid-calibration range quality control (QC) check samples are analyzed in triplicate. QC check samples are loose soils in a 31 mm diameter by 2.5 cm cup, approximately one half full. Each QC check sample is analyzed in triplicate, by removing the cup from the detector between each analysis, shaking the soil in the cup, then lightly tapping the cup on a smooth surface before replacing it on the detector. Analyzing these samples periodically will warn the technician of gain change or other instrument problems. The authors have found this particularly helpful in detecting a low battery before the X-Met software gives the "low battery" warning.

Confirmatory Samples

The number of samples for laboratory confirmation of the FPXRF instrument results are based on the overall number of FPXRF samples points and the budget of the onsite coordinator. One confirmatory in 40 routine samples is adequate on a site with approximately 300 sample locations. Confirmatory sample frequency can decrease with increased sample locations.

Quality Assurance Parameters

Precision

Different levels of precision can be determined. Minimum instrument variability in the field is measured from the stationary probe triplicate. A more comprehensive assessment of precision is measured from the performance of the QC check samples. Physical agitation of the sample between measurements yields some component of the soil microvariability. The QC samples are analyzed over the entire time span of analyses and, consequently, yield an overall FPXRF system precision.

Accuracy

Accuracy is also determined from the low- and mid-calibration range QC check samples. QC values are plotted in control charts (one for the low range sample and one for the high range samples) with concentration on the ordinate and successive measurements on the abscissa. Accuracy and the instrument bias from the "true" values can be quickly determined from the control charts. Table 1 compares FPXRF accuracy and precision performance to that of the CLP Data Quality Objectives (DQOs)[2].

Detection Limits

Detection limits are defined as three times the standard deviation (SD) of the low-calibration range QC check sample. CLP contract required detection limits[2] are compared to FPXRF detection limits in Table 2.

Data Quality Objectives

Tables 1 and 2 give some indication of levels for precision and accuracy that can be achieved under conditions deemed to be typical for the types of waste sites investigated. These values should be viewed with some caution, however, recalling that the matrix-specific nature of the intensity-concentration relationship dictates that achievable QA levels are also site-specific. Precision, accuracy, and detection limits may vary significantly from matrix to matrix, in contrast with "wet chemical" procedures in which physical matrix effects are eliminated by taking samples into solution prior to analysis. QA levels displayed in Tables 1 and 2 probably represent neither the best or worst cases. Evaluating the applicability of FPXRF to meet DQOs for a given site therefore requires careful evaluation of matrix character and variability when using empirically calibrated instruments such as the X-Met 880.

In the authors' experience, there seems to be some reluctance to consider FPXRF as anything more than a screening tool. Part of this problem stems from the failure of site personnel to consider the end-use of the data when defining DQOs and evaluating potential analytical methods. Examples come from site managers who have asked if specific detection limits can be achieved for certain target elements when those limits are one or more orders of magnitude lower than potential action levels. Perhaps an even more widespread problem concerns spatial applications. When determination of the spatial distribution of target elements constitutes the data end-use, DQO definition almost invariably focusses on errors relating to sampling and analysis and not on errors relating to spatial interpolation. This problem is so significant in terms of the application of FPXRF that it warrants some detailed consideration.

The inferential link between samples and the spatially distributed population they are intended to represent is established through the process of spatial interpolation. This process consists of estimating concentration values at unsampled points, usually located at the nodes of a regular grid, by applying an appropriate algorithm to sample values. It results in a spatial model of target element concentration, and serves as the basis of such graphical decision-making tools as isometric diagrams and contour plots. The reliability of decisions based upon a spatial model ultimately depend on estimation errors incurred at the grid nodes.

Geostatistical theory shows that spatial estimation errors consist of several components related to sample collection, preparation, and analysis, and of a component related to spatial extension of the sample value to an unsampled location[5]. Extension error is a function of the spatial variability of concentration and of the distances between samples and grid nodes, and is usually much larger than sample-related errors[6]. Thus, the largest source of error can be reduced most effectively by increasing sampling density rather than by improving the precision and accuracy of the analytical method. It follows that DQO definition for spatial applications should focus on spatial estimation errors rather than on analytical errors. It is possible to meet or exceed high DQOs with an inexpensive method such as FPXRF, even though its precision and accuracy may be less than those of CLP wet-chemical methods. This is achieved by employing higher sampling densities, at less cost, thereby reducing the largest source of error in the spatial model that represents the instrument of decision. The proviso, of course, is that the concentrations of interest exceed the detection limit of the FPXRF for the target element under the prevailing matrix conditions.

To demonstrate the foregoing points, Figure 3 shows a variogram model describing the spatial variability of lead concentrations obtained with the FPXRF method in contaminated soil at a Superfund site. Intersection of the model at a high value along the GAMMA axis indicates high analytical error. A second variogram in Figure 3 represents a model with no analytical error, clearly an ideal but unachievable situation. Using these models, the spatial errors incurred in estimating the average lead concentration of a 50' x 50' x 1' remediation block were calculated for different densities of samples taken on a square grid pattern within the block (see Table 3). Direct analytical cost of $150 per sample was assumed for the ideal analytical case, and $13 per sample location was assumed for the FPXRF case. The latter value is based on CLP laboratory analysis of 25 calibration samples at $150 per sample, and a sampling campaign totaling 300 hundred sample locations. Applying these values to the number of samples for each sampling density results in the total costs shown in Table 3. Spatial estimation error, expressed as relative standard deviation, are plotted against sampling costs for each case in Figure 4. These plots show that FPXRF can achieve levels of spatial estimation error similar to those of the best laboratory methods, and that a given level of error can be achieved by FPXRF at significantly less cost than laboratory methods. This means that FPXRF should not be restricted to screening, but can also be employed for site characterization and remedial evaluation sampling in many situations. As before, these conclusions are based on the assumption that concentrations of interest are above the FPXRF detection limits for the given situation.

CONCLUSIONS

Based on results achieved thus far, FPXRF has demonstrated the capability of providing data necessary for screening and characterizing many inorganic contaminants, both rapidly and inexpensively. The authors believe that it will play an important and perhaps central role in site remediation in times to come. Like any other analytical method, FPXRF has limitations as well as strengths. Many of these will be improved by recent and future improvements in technology. Sensitivity and detection limits, for instance, can now be materially improved with high resolution detector systems designed for field portable instruments. Calibration constraints can be relaxed with incorporation of fundamental parameter techniques and better software systems. However, several points need to be emphasized for attainment of optimal results when field sampling with the X-Met 880 and similar instruments:

- Site specific calibration standards are absolutely necessary to obtain defensible quantitative data.
- Proper sampling protocols must be designed to allow quality assessment of the data.
- DQOs must be correctly defined.
- Geostatistical procedures are essential for proper definition of DQOs and for QA evaluation of spatially distributed FPXRF data.

If these points are followed, the authors believe that FPXRF can meet or exceed

traditional CLP procedures more cost-effectively in many situations.

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Table 1. Comparison of CLP DQOs to FPXRF Performance for soil samples.

Analytical Method	Accuracy	Precision
CLP Spectroscopic (AA/ICP)	+/- 25 %	+/- 35 %
FPXRF	+/- 50 %	+/- 35 %

Table 2. Comparison of Detection Limits for CLP and FPXRF. (all values in mg/kg)

Analytes	CLP*	FPXRF
Cu	5	410 - 470
Zn	4	105 - 200
As	2	100 - 250
Pb	0.6	120 - 513

* Assumed soil weight of 1 g and end volume of 200 mL.

DISCUSSION

JIM PASMORE: I have a question on the data you showed for precision. What was your measurement time on that, or the precision measurements, table 2.

BILL COLE: Thirty seconds.

STEPHEN KNOLLMEYER: I was just wondering why you didn't have any detection limits for the cadmium? Didn't you take it?

BOB ENWALL: That was just a slight mistake on our part. We haven't really had any experience with cadmium that would give us a number.

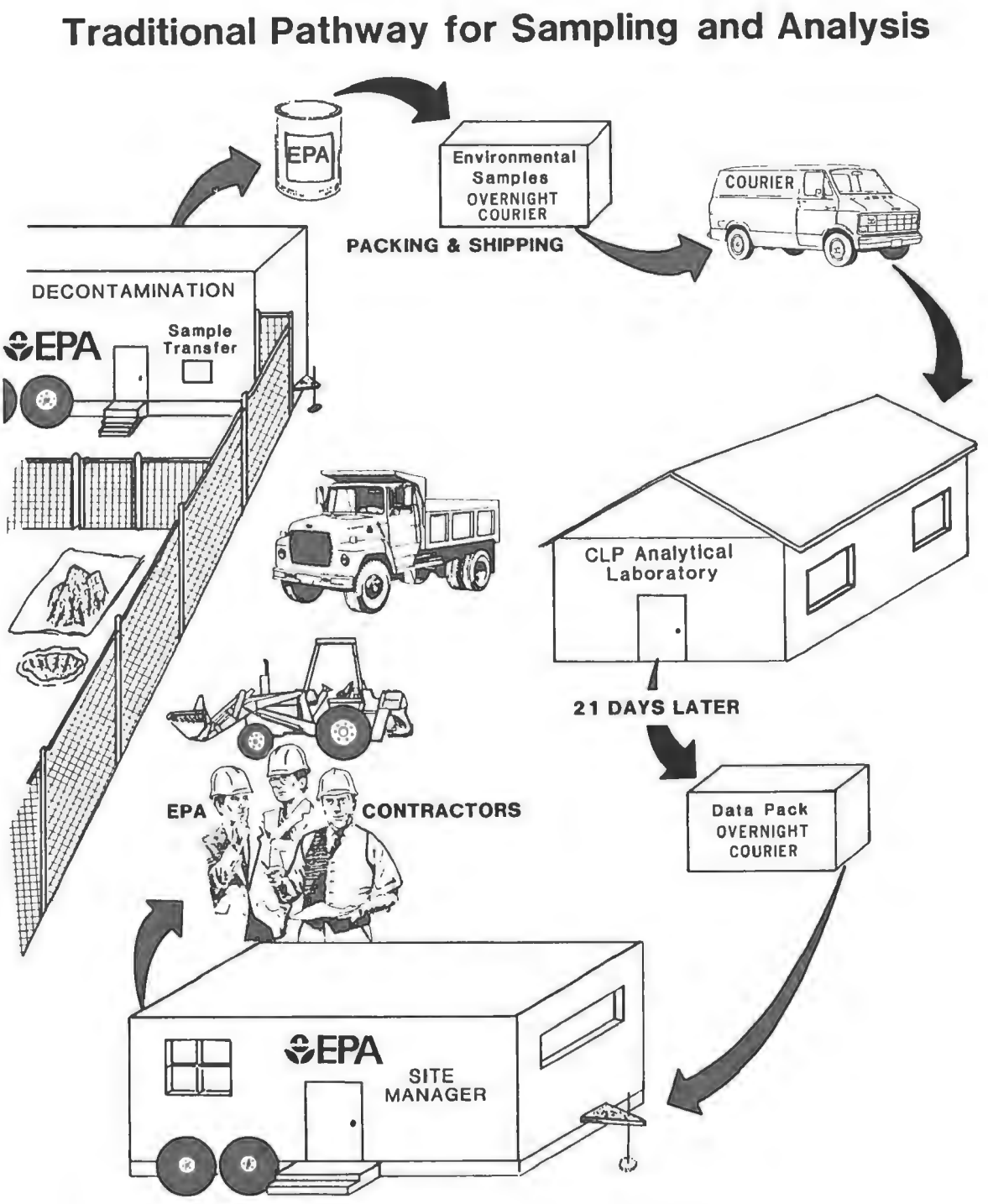

FIGURE 1. Traditional Approach to Site Characterization.

Table 3. Comparison of Costs for Estimating the Average Concentration of a 50' x 50' x 1' Remediation Block Using Different Sampling Densities.				
SAMPLE DENSITY (# SAMPLES)	ESTIMATION ERROR FPXRF	ESTIMATION ERROR IDEAL ANAL.	COST $ FPXRF	COST $ IDEAL ANAL.
1	1.8298	0.9211	13	150
4	0.8447	0.2977	52	600
9	0.5510	0.1604	117	1350
16	0.4094	0.1067	208	2400
25	0.3268	0.0825	325	3750
36	0.2709	0.0629	468	5400
49	0.2318	0.0522	637	7350

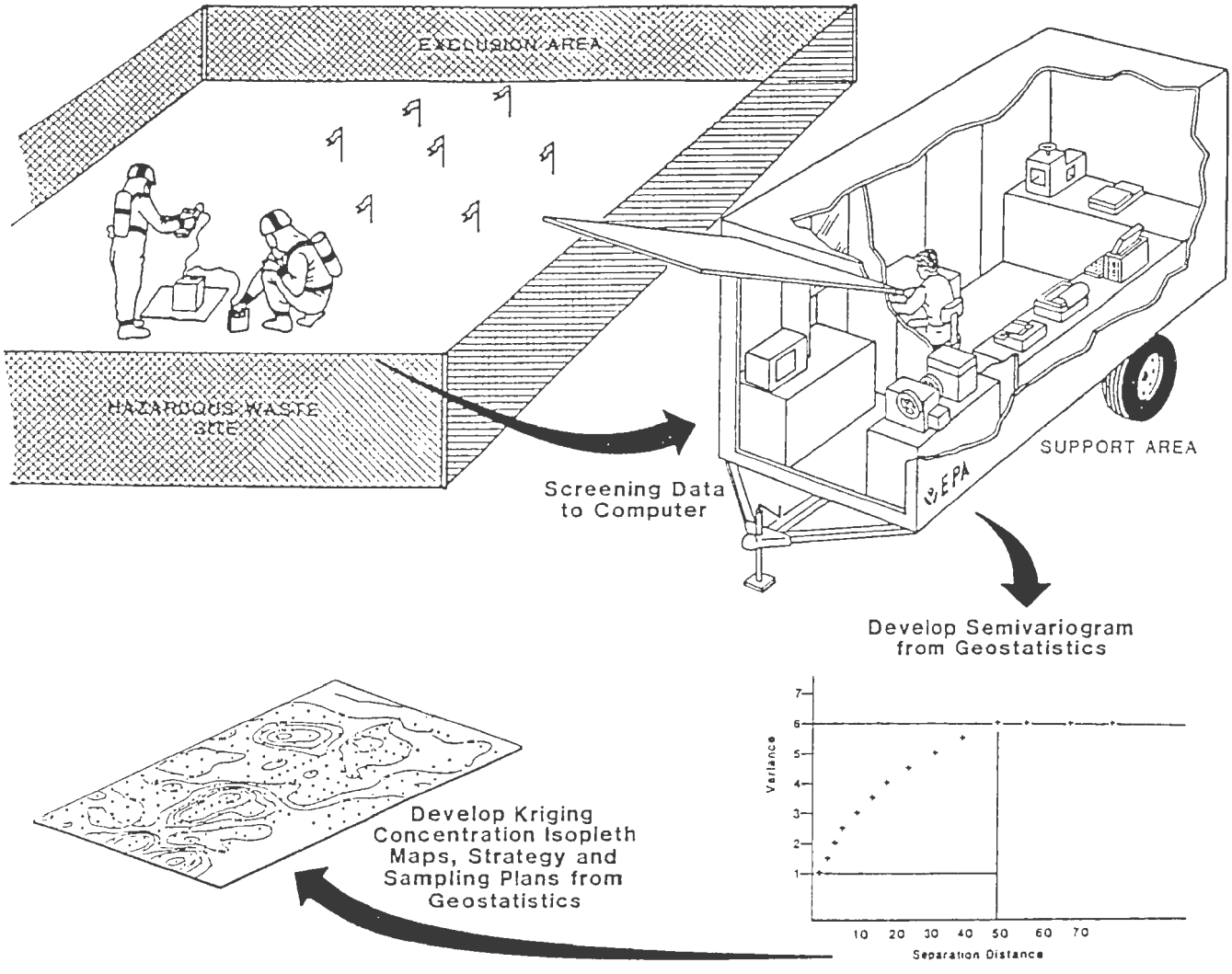

FIGURE 2. FPXRF Approach Employing In Situ Measurements.

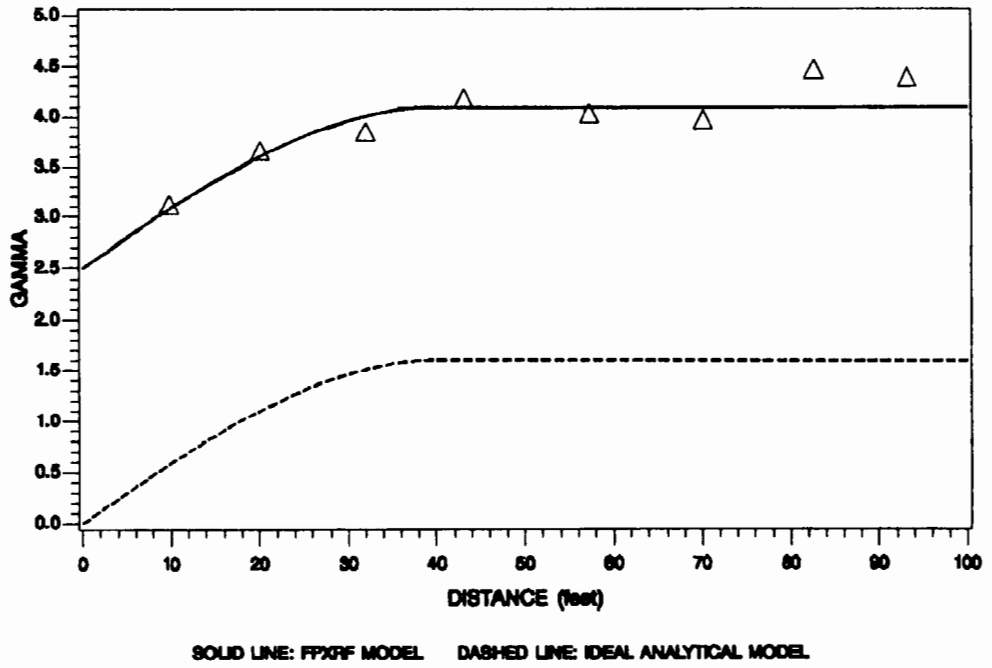

FIGURE 3. RELATIVE VARIOGRAMS FOR FPXRF AND IDEAL ANALYTICAL CASES.

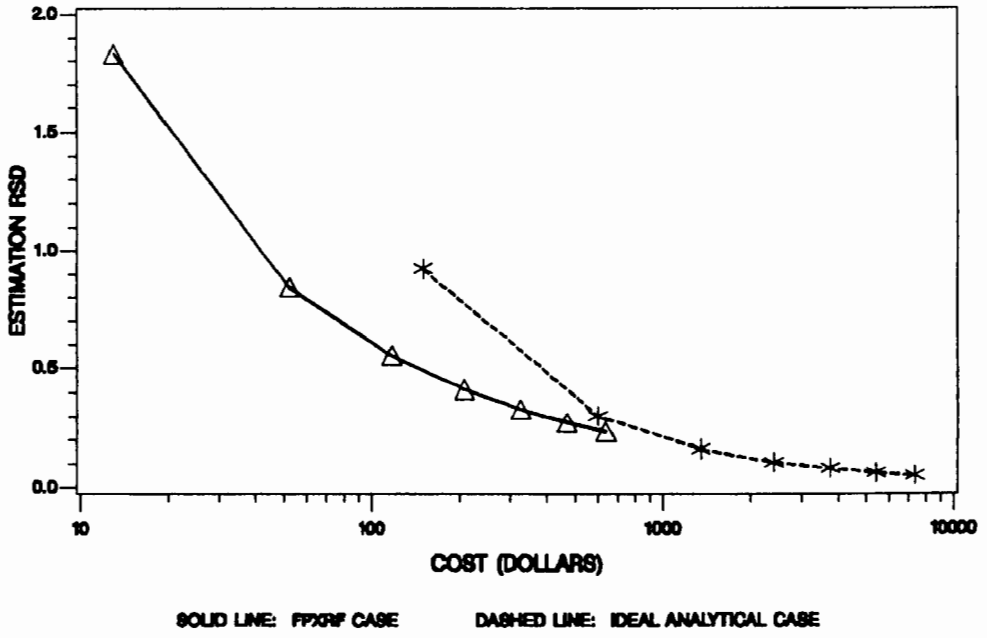

FIGURE 4. ESTIMATION OF A 50' X 50' X 1' REMEDIATION BLOCK. ESTIMATION ERROR VS. COST FOR FPXRF AND IDEAL ANALYTICAL CASES.

A HIGH RESOLUTION PORTABLE XRF HgI_2 SPECTROMETER FOR FIELD SCREENING OF HAZARDOUS WASTES.

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ABSTRACT

A field portable XRF spectrometer based on a mercuric iodide (HgI_2) semiconductor x-ray detector is described. Its multi-element capabilities will be illustrated with measurements on chemically-analyzed samples representing materials collected from several hazardous waste sites containing different metallic pollutants in a variety of soil matrices.

The range of the analyzer extends from Ca to U, and a typical configuration provides for about 20 elements which are simultaneously reported together with the analytical precision. Minimum detection limits for most elements are in the range of 50 -200 mg/kg with a 200 second analysis time.

The solid state detector is operated near ambient temperature and affords an energy resolution of better than 300 eV for the Mn K x-rays. Intrinsic detector efficiency exceeds 60% for energies up to 100 keV. Dual radioisotopic source excitation is provided from the list: Fe-55, Cd-109, Cm-244, Am-241. A 6.5 kg battery-powered Data Processing Unit features menu-driven operation and on-board dual 2000 channel MCA spectrum display capability. Internal storage provides for the retention of 30 spectra and 100 multi-element analytical reports.

A "fundamental parameters" based analysis algorithm is used to compute elemental concentrations. This computational approach, together with the comprehensive element coverage, permits "standardless" measurements over a wide range of material compositions.

INTRODUCTION

Soil contamination by hazardous metallic waste is present at the level of concern on more than 50% of the sites on the National Priorities List. Complete evaluation of the degree of hazard and measurement of the spatial extent of those hazards involves the analysis of literally millions of samples. Although procedures have been approved by the Environmental Protection Agency for use under the Contract Laboratory Program for performing enforcement quality analyses on environmental samples, a need still exists for rapid, reliable, and cost-effective assays to expedite the characterization and remediation of sites. Ideally such assays could be accomplished by direct measurement in the field.

Several investigators (1-15) have reported on the application of energy dispersive x-ray fluorescence (XRF) to the assay of metal-contaminated soil. Savings in time and analysis cost over the standard EPA-approved chemical methods are significant (1,5,11). Essentially a nondestructive technique suited to the measurement of almost any kind of material in powder, liquid or solid form, XRF is further distinquished by its ability to analyze for many elements, including the unexpected, in a truly simultaneous fashion. Thus it offers low cost and rapid turnaround time per analysis.

By means of XRF, two environmental application methodologies - in situ assay with field portable instruments and intrusive sample analysis with laboratory grade equipment - are currently being pursued and are reported to yield good definition of the magnitude and extent of contamination -

particularly when coupled with geostatistical sampling methods and data analysis (12,14). Laboratory-grade instruments generally offer better precision, higher accuracy and greater sensitivity than portable equipment since, with no weight and power restrictions, x-ray tube excitation (as opposed to radioisotopes) and high resolution spectrometers of the cryogenically-cooled semiconductor Si(Li) detector type can be used. Portable instrument designs have so far employed gas proportional detectors and their capability for multielement application has been somewhat impaired by the limited energy resolution of that type of detector. The in-situ measurement capability of a portable instrument, albeit at some trade-off in analytical performance, is of advantage in reducing the time delays and data-integrity risks associated with sample handling procedures. Other benefits are its low cost per analysis, its utility in delineating hot spots as an aid in the collection of samples for enforcement quality assay or to guide the work of site remediation.

Quantitative XRF application always requires an appropriate calibration, usually by measurement on a representative suite of chemically known standards. Alternatively, as is now the option on most laboratory-grade instruments using Fundamental Parameter (FP) methods of analysis, only pure elements or a few standards (which need not be of site-specific composition) are required. Currently available portable instruments with their lower x-ray resolving power are more restricted to the use of an empirically structured analysis algorithm of limited element coverage. They, therefore, require a multi-sample calibration on site-specific material (11). This is a major drawback to their general use, and the quality of the resultant analyses is operator sensitive and highly dependent on the validity of the calibration samples.

The development of a high-resolution non-cryogenic semiconductor x-ray detector has made possible a new field-portable instrument design which can provide for the application of FP analysis of soils using a site-independent calibration based on pure elements standards. Our paper will present some of the results obtained with this instrument.

INSTRUMENTATION

The instrument used to evaluate the application of an FP-based XRF method for field analysis of metal-contaminated soil is shown in Figure 1. Similar instruments are now used industry-wide for on-site verification of alloy materials (16). The system operates

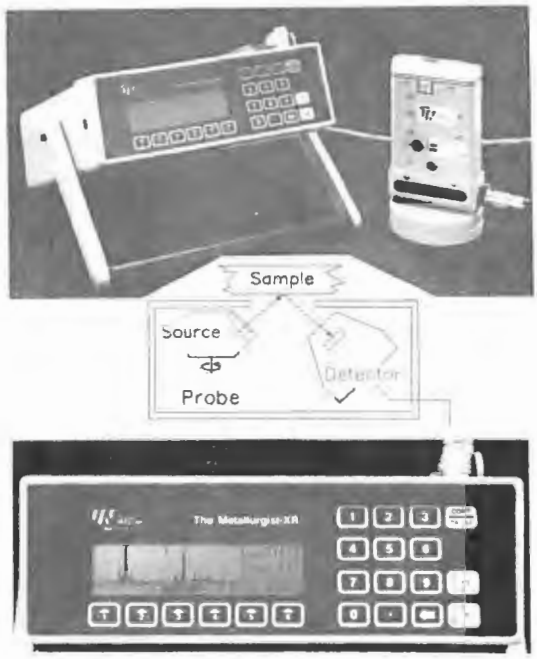

Figure 1
Field-Portable XRF Spectrometer

off either AC-power or rechargeable NiCd batteries and weighs approx. 17 lb (8kg). Compared to the alloy-analysis design, the soil application unit was modified only in regard to the type of isotopic excitation sources contained in the hand-held probe, and minor revisions to the PROM-based operating software in the data processor module. The sample measurements we report were performed with an isotope combination of Cd-109 and Am-241; each of an effective 3mCi source activity. The sources are separately shielded in a motorized turret and are positioned for measurement under program control. An on-screen set-up menu allows the individual source exposure time to be selected from 1 to 999 secs. All reported measurements used a 200 sec. selection.

Probe accessories such as a detachable base, shown in the figure, and clip-on front-end attachments, facilitate the measurement of contained samples, but the main utility of the probe is afforded by its compact, hand-size, design for direct application to in-situ material. Measurement is initiated by momentary push-button action, either at the probe or on the instrument panel, so free-standing long period assay and, as required, operation within an environmentally sealed plastic enclosure are quite practical. A tough replaceable x-ray entrance window also seals the probe face over a measurement aperture of 0.5 x 0.75 inch (1.25 x 2.0 cm).

Spectrometer-Analysis Operations

The x-ray analytical capability of the instrument is established mainly by its use of a new-technology, high resolution energy dispersive x-ray detection device based on semiconductor HgI_2. This detector is contained in a capsule within the probe and operates at a controlled, less-than-ambient temperature by low-power thermo-electric cooling. The energy resolution, expressed as FWHM, is of the order of 300 eV for the Mn K x-ray line.

The data processor performs all of the necessary analog/digital electronic functions to translate the detected x-ray information into quantitative analytical results. Pulse-amplitude records, for instance, representing the sample x-ray fluorescence spectra are generated and stored for each excitation source in a 2x2000-channel memory. These spectra, if desired, can be presented on the instrument's LCD panel accompanied with the usual control features of a multichannel analyzer. Peak identifiers, regions of interest, and element-line markers, for example, are operative in that mode and are displayed in calibrated x-ray energy units. Non-volatile RAM storage allows up to 30 spectra to be retained together with the analytical results for more than 100 field measurements. An RS-232 serial port is provided for printer and computer communication.

All operations are prompted by on-screen menus which indicate the available options and how to proceed. An example of the "turn-on" menu is as follows:

```
MAIN MENU
Enter Choice of Operation
1 SOILS ANALYSIS
2 RECALL STORED RESULTS
3 REVIEW/CHANGE SET-UP
4 STORE/RECALL SPECTRUM
5 OTHER FUNCTIONS
```

Routine operation proceeds by option #1, which leads to a set up of the data acquisition times per source and initialization of the probe controls for measurement. Measurement concludes with an audible signal followed by an on-screen report of the analyzed elements. Results are labelled by element symbol and, as later described, include both element concentrations and an indication of the computed standard deviations. Options, such as the storage and printout of results, follow the on-screen report if pre-selected from the Main Menu. Spectrum operations, available as shown, are normally by-passed in the routine measurement sequence which returns directly to a "ready" status after the analysis report.

Element concentrations are computed using Fundamental Parameter derived coefficients in an algorithm of the form:

$$CONC = R \times S \times (1 + SUM\{a_n x C_n\})$$

Where, "R" is the measured analyte x-ray intensity relative to the pure element: "S" is a calculated sensitivity coefficient: and the quantity SUM{} is a summation of "n"-element absorption-enhancement terms containing calculated alpha-coefficients (17) and iteratively computed element concentrations. Preparation of the instrument for the measurements reported in the next sections entailed only a normalization to the pure element response. No other calibration was performed. X-ray intensities are processed for more than 20 elements but only those determined to be in excess of three-times the standard deviation are presented in the analysis report. All element x-ray intensities, however, can be viewed on the screen.

SAMPLE MEASUREMENTS

Although the instrument is capable of performing in-situ measurements, the effectiveness of an FP-analytical approach was evaluated by analyzing intrusive samples so that comparative analyses could be obtained. A total of 55 samples were measured representing material from four NPL sites characterized by complex metallic contaminations. The samples were air dried, disagglomerated but not ground, and passed through a 20 mesh screen (.84 mm hole). The oversize was discarded. The undersize was split so that replicate samples were available for the chemical and x-ray assays. The powdered samples, ranging in mass from 2 to 8 gms, were placed in 30mm sample cups and covered with a 0.005 mm polypropylene x-ray window for measurement in the upright probe geometry. Sample thicknesses ranged from 8.5 to 16 mm and bulk densities of the loose powders ranged from 0.26 to 1.2 gm/cc. The chemical assays of the sample splits were performed by a commercial laboratory (18) using flame Atomic Absorption (AA) analysis for the elements of interest.

Two of the sampled sites (noted as Sites 1 and 3 in the results) are inactive metal plating locations. The samples were collected from settling lagoons and consisted of plating sludges mixed with the local soils. Site 2 had been the location of a smelter; a metal working facility; and, in recent time, a Ni-Cd battery manufacturing operation. It is an estuary location, submerged except during low tide, and the soil would

be best described as contaminated bay sediment. Site 4 was a scrap metal storage-segregation facility, involving a wide variety of metals and metallic compounds in open areas throughout the site.

An example of the instrument-generated pulse height spectrum (excited by Cm-244) for one of the soil samples from a plating lagoon is shown in Figure 2, overlaid with a spectrum for the same sample obtained on a gas-filled proportional-detector instrument. The superior x-ray resolving power of the HgI_2 detector is obvious and is seen to provide well for quantitative analysis of minor elements in the presence of adjacent atomic-number elements at high concentration.

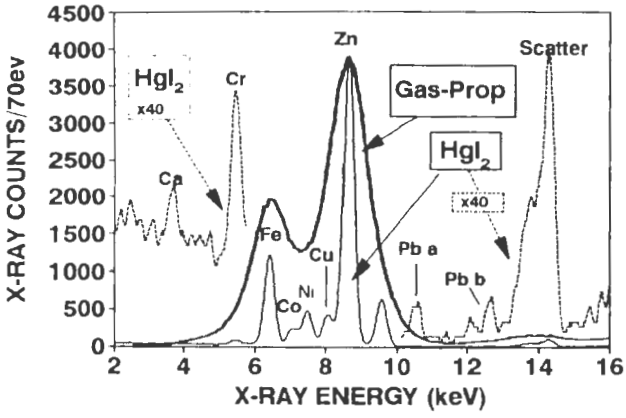

Figure 2. Example XRF Spectra for a HgI_2 and a Gas Proportional Detector on the Same Soil Sample (Cm-244 Excitation).

The instrument-reported XRF assay results of a Cd-109/Am-241 excitation measurement on the soil sample are given in Figure 3. Where available, the results of prior analysis by Atomic Absorption are tabulated.

DATE: 07/10/90
TIME: 10:15:55
MODE: STANDARD

COMPOSITION:

	CONC. (PCNT)	ST. DEV. (PCNT)	X-RAY (mg/kg)	ATOMIC ABSORP. (mg/kg)
Ca	5.035	0.705	50,035	*
Cr	0.513	.055	5,130	6,600
Fe	8.453	.064	84,453	*
Co	.118	.024	1,180	*
Ni	1.570	.020	15,700	16,000
Cu	1.661	.015	16,610	*
Zn	11.865	.053	118,865	110,000
Cd	.683	.005	6,830	7,900
Sn	.453	.005	4,530	*
Pb	.047	.002	470	430

* = Not Analyzed

Figure 3. X-Ray Analysis Report and AA Assay Data for the Soil Sample of Figure 2.

The format of the XRF results shown in the left-hand columns of Figure 3 is that of the resident operating software which reports both the element concentrations and the computed statistical uncertainties in units of weight-per-cent-element. For comparison with the AA mg/kg assays in the figure, and for the results discussed in the next section, a factor of 10^4 has been applied to the x-ray data. In this single-sample comparison, the XRF and AA results are seen to be in good agreement for the elements measured by both techniques. However, a number of contaminants not known to be at the site were detected at a statistically significant level by XRF.

COMPARATIVE RESULTS

Graphical comparisons of the XRF results with AA analyses for the 55 split samples from the four sites are presented in Figures 4-9. Because of suspected intra-sample heterogeneity, a statistical comparison of the results of the two measurements on a simple point-by-point basis was not considered appropriate. Under such circumstances, global data comparisons are more valid. Two global methods were used: The XRF results were regressed against the AA results to reveal any relative biases in the data sets; and the relative percent difference (RPD) between the two determinations were calculated to indicate the average disparity between the analyses. Any disparity would reflect the imprecision of each determination and real chemical differences in the sample splits. Where the measurements span a range of values well above the detection threshold, the average RPD should be a good indicator of the intra-sample heterogeneity uninfluenced by the analytical precision of either technique. The average RPD's from samples with contamination levels greater than 10 times the standard deviation were computed for each analyte and are shown in Table 1 along with the main results of the regression analysis:

Table 1 Some XRF vs. AA Correlation Data

ANALYTE	RANGE (mg/kg)	REGRESSION DATA SLOPE	σ slp.	R^2	RELATIVE % DIFF (RPD)
Cr	0 - 28,000	1.02	.09	0.84	38
Fe	0 - 350,000	1.36	.05	0.98	23
Ni	0 - 20,000	1.11	.05	0.96	30
Zn	0 - 150,000	0.99	.02	0.98	28
Cd*	0 - 10,000	0.84	.07	0.90	33
Cd**		1.10	.06	0.95	17
Pb	0 - 580,000	1.06	.09	0.85	30

* Cd uncorrected for bulk density
** Cd corrected for bulk density (see text)

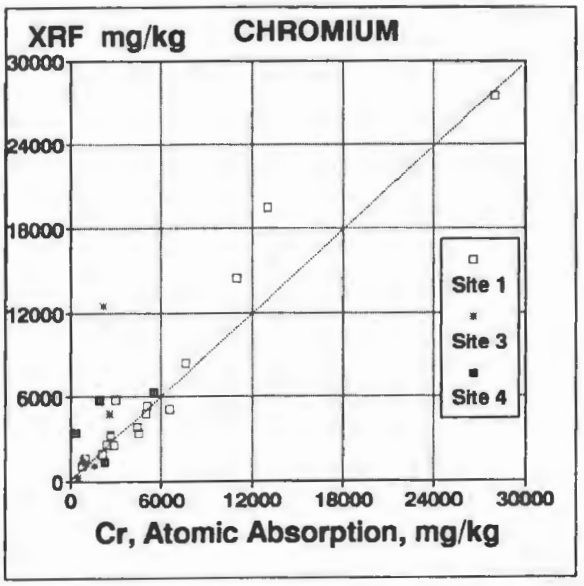

Figure 4
Comparative Assay Results for Chromium

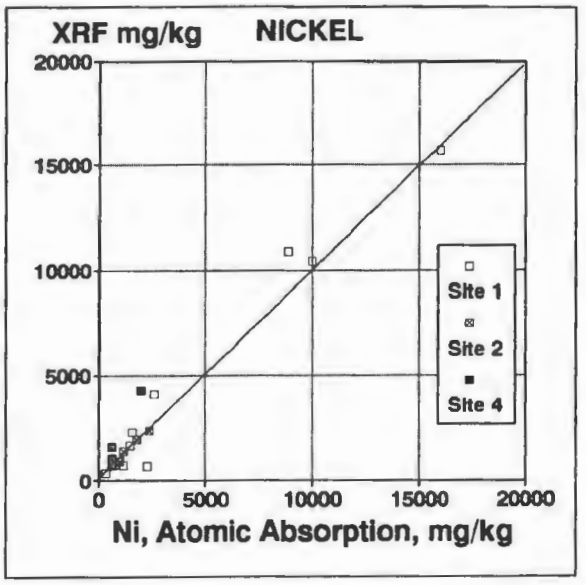

Figure 6
Comparative Assay Results for Nickel

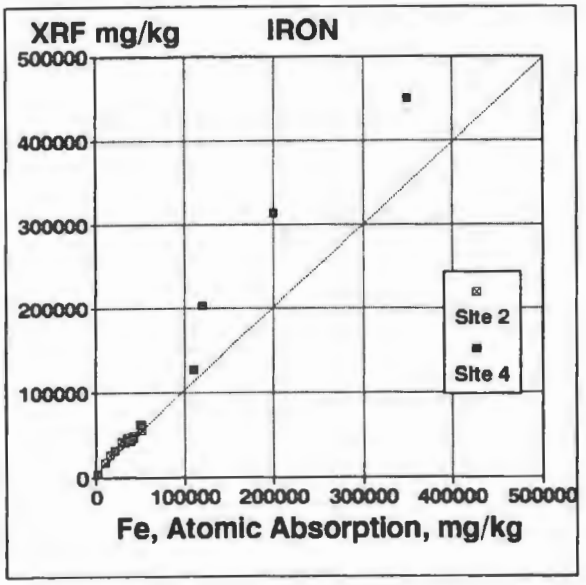

Figure 5
Comparative Assay Results for Iron

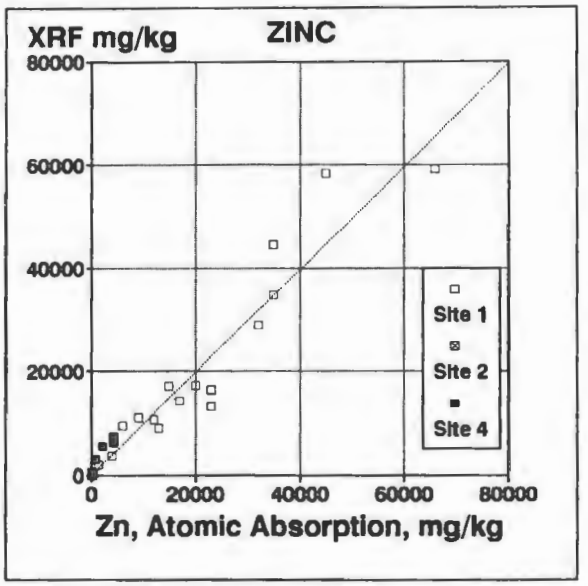

Figure 7
Comparative Assay Results for Zinc

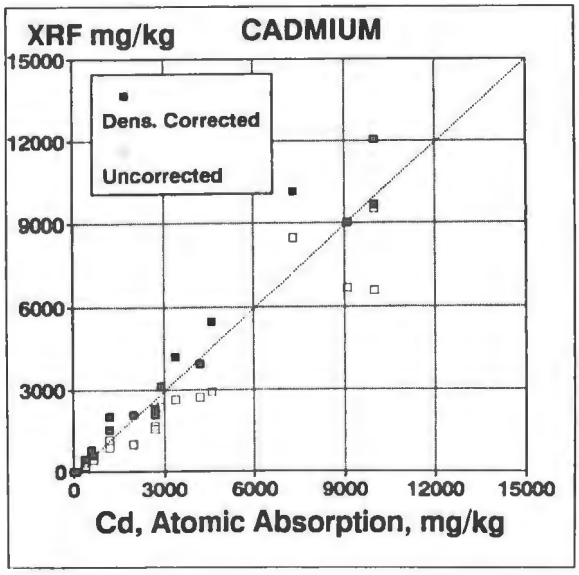

Figure 8
Comparative Assay Results for Cadmium
(Illustrating Bulk Density Corrections)

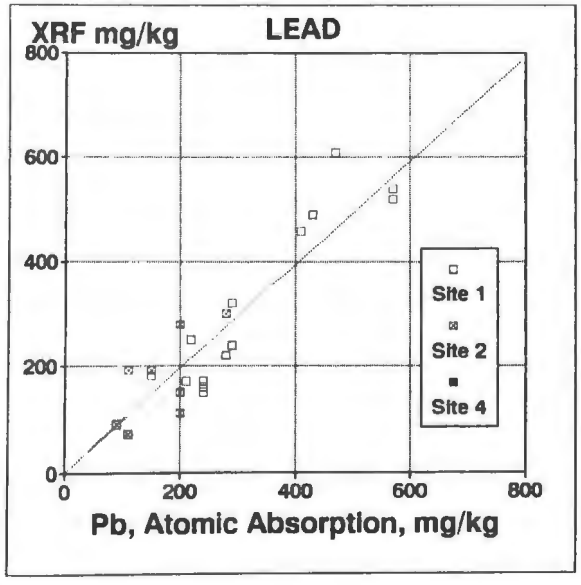

Figure 9a
Comparative Assay Results for Lead
(Low Range)

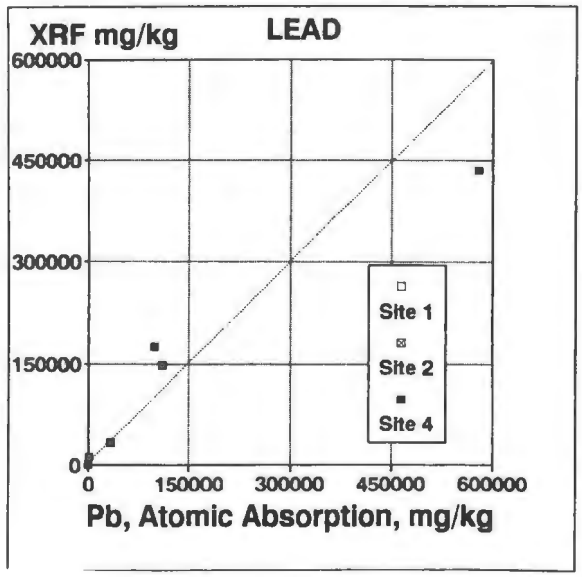

Figure 9b
Comparative Assay Results for Lead
(High Range)

Concerning the density correction on the Cd assays (noted in Table 1), it is generally recognized that for XRF analysis of loosely packed powder material there is always some influence of bulk density on the measured x-ray intensity. The magnitude of the effect depends on the excitation and fluorescent x-ray energies and was investigated by measurement on a specially prepared suite of "doped" samples covering a density range of 0.2 to 2.0 gm/cc. A functional dependence of the x-ray intensity, relative to a "high density" sample, was derived to be of the form;

$$(mu*rho)/(mu*rho+1)$$

where "rho" is the bulk density and "mu" is a calculated absorption coefficient for the analyte x-rays. The value of "mu" decreases with increasing x-ray energy and, in low bulk density material, becomes a factor in the XRF analysis of elements such as Cd, Sn, Sb, etc., excited by the relatively high energy emission of Am-241. Over the density range of the measured samples (0.26 to 1.2 gm/cc) the values of the calculated x-ray intensity correction were in the range of 1.2 to 1.9. The results are illustrated in the data of Figure 8.

The XRF precision data reported alongside the assay values (as previously noted in Table 1) are based on the calculated statistical errors associated with each analyte x-

ray intensity and include the compounding effect of the iterative solution of the multielement analysis algorithm. The data, therefore, can convey a realistic indication of analytical detection limit, consistent with all of the conditions of measurement. An evaluation of the precision was conducted by repeated independent analysis on the same undisturbed sample over a three-day period and the results are shown in Table 2.

Table 2 Precision Evaluation Data

ANALYTE	ANALYTE CONCENTRATION (mg/kg)	COUNTING STATISTICS (mg/kg)	REPEATED MEASUREMENTS (mg/kg)
Fe	2204	190	147
Ni	247	60	63
Cu	937	70	101
Zn	396	40	44
Cd	5487	80	97
Sn	663	30	31
Pb	494	30	28
Bi	377	20	15

It is seen that the "repeated-measurement" results are in excellent agreement with the instrument-calculated values, thus verifying the method of calculation and the absence of any significant instrument drift.

The Minimum Detection Limit (MDL) for an analyte is a measure of the analytical sensitivity of the technique. It is conventional (19) to define the MDL as three times the standard deviation of analysis for a blank or low analyte concentration sample. Table 3 lists the standard deviation and MDL for several analytes. The standard deviation as presented is a composite of measured and calculated values and represents an estimate of performance under the experimental conditions with these soil matrices.

Table 3 Minimum Detection Limits for Selected Analytes

ANALYTE	STANDARD DEVIATION (mg/kg)	MINIMUM DETECTION LIMIT (mg/kg)
Cr	330	1000
Fe	200	600
Ni	80	240
Cu	70	200
Zn	50	150
As	17	50
Cd	50	150
Sn	33	100
Hg	17	50
Pb	17	50

COMMENTS ON RESULTS

Accuracy and precision are two indicators of analytical data quality that are most informative of the technique. It is generally recognized that the AA method has good accuracy over the ranges of contamination presented by these samples, so global measures of the correlation with results of AA analysis - derived from linear regression and the "relative-percent-differences" - should provide good indications of accuracy for XRF; and, in particular, of this method of implementation using Fundamental Parameters. It is, however, important to also recognize the possibility of real disparities in chemical composition between the samples presented for comparative analysis due to highly heterogeneous nature of soil. There are several cases, for example, shown in the graphs, of significant differences in assay. All of the graphed data, however, were included to obtain the correlation indices of Table 1.

The regression coefficients obtained show generally good agreement between the two techniques. Most element slopes are equal to 1.0 (with a high degree of correlation) which lends support to the Fundamental Parameter analysis calibration. There is some departure from unit slope in the case of Fe mainly over the range represented by some samples of unusually high Pb content (up to 58%). We suspect this to be due to an overcorrection for the influence of Pb on the Fe fluorescent x-ray emissions; as calculated from the Fundamental Parameters. The application of the density correction on the Cd data is seen to improve both the FP-calculated slope correlation and the value of the regression coefficient.

The average RPD value of approximately 20% suggests that significant intra-sample heterogeneity remains after crushing to -20 mesh and "homogenizing". It is the more significant with the lighter elements, but evident with all analytes. This further demonstrates the difficulty in assessing the performance of a technique using normal soil samples. Generally recognized high quality standard reference soil materials with high ppm to percent level contaminants do not exist, but are needed.

The precision indicator of data quality - as was measured directly and as reported by the instrument - is well illustrated by the results in Table 2. There is seen to be excellent agreement between the calculated and measured values. The uncertainty in the measured standard deviations for the conditions of the test was about 20%. It is to be

expected that similar accuracy and precision values would be achieved for other analytes in the same part of the periodic table as those reported here.

The MDL's reported in Table 3 were determined under the available but less-than-optimum instrumental parameters. Count rates with the sources employed were substantially lower than the practical limit of the system. The detector head, shown in Figure 1, is designed for optimum presentation of small metallic samples commonly encountered in alloy-sorting applications. A sample presentation geometry of more appropriate design for soil assay should yield a significant improvement in the measurement efficiency. Most data were acquired with the source pair of Cd-109 and Am-241. Chromium, and perhaps other analytes, could be more sensitively assayed with other isotopic sources. Improvements in these areas of the instrument design are expected to lower the MDL of all analytes by at least a factor of two, and should lower the MDL of Cr into the 150 - 200 mg/kg range.

CONCLUSIONS

The results obtained from this study clearly show the potential of a Fundamental Parameter approach to the analysis of soil contamination with a high-resolution energy-dispersive XRF analyzer of field portable design. The operational convenience of a calibration based only on measurement of pure element standards is well demonstrated. Considering the diversity of soil types tested and their wide variation in the level of contamination, the overall accuracy is good and certainly adequate for screening tests where operational requirements are generally set at +/- 50% accuracy and +/- 10% precision (20). The results reported here easily satisfy those requirements.

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DISCUSSION

JOHN MORRIS: The fundamental parameters technique assumes that it's dealing with all the components of the system. This question is twofold. Do you routinely switch over radionuclide sources to span spectrum for all samples to do this? And do you make assumptions about the light component, or do you calculate that with the Raley-Compton ratio?

PETER BERRY: The value of the fundamental parameters is only really achieved if you measure all of the elements. And so naturally we do expose all of the sources to obtain the data to apply that model. The light elements are not practically measured in the field, so everything is expressed relative to a lighter element like silica. Elements like calcium can be determined and the coefficients derived, but we cannot measure silica and quantify that. So that one is assumed to be the balance of the material.

LOW CONCENTRATION SOIL CONTAMINANT

CHARACTERIZATION USING EDXRF ANALYSIS

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INTRODUCTION

Effective assessment and remediation of hazardous waste sites dictates that analytical methodologies be developed which assist in the evaluation of site contamination and simultaneously make efficient use of sampling time and resources (1). Optimally, a technique would provide on-site personnel with immediate and accurate information concerning the identity and concentration of inorganic soil contaminants (2).

Inorganic pollutants can be readily determined in contaminated soils with energy dispersive X-ray fluorescence spectrometry (EDXRF) using a thermoelectrically cooled Si(Li) detector (3). A field mobile laboratory van or trailer can accommodate the EDXRF system because the electrically cooled detector, which provides high resolution EDXRF spectra, does not require cryogenic cooling. Soil sample preparation for EDXRF analysis is minimal, therefore, short turnaround times are realized between sampling and reporting results.

This report will describe an EDXRF method developed to determine four inorganic soil contaminants: lead, arsenic, zinc, and cadmium at four sampling depths. The EDXRF results for approximately one hundred eighty soil samples will be compared to results obtained for sample splits submitted for analysis at an independent laboratory. Evaluation of low concentration arsenic detectability with elevated lead concentrations in these samples will be discussed. Accuracy and precision of the EDXRF method will also be compared to the independent methods using a standard reference material and soil samples submitted in triplicate to both laboratories.

EXPERIMENTAL

The field mobile EDXRF spectrometer used in this work was a Spectrace 6000 (Spectrace Instruments, Inc., Mountain View, CA). The EDXRF system consists of three modules: the spectrometer, the control/pulse processing electronics, and the data analysis computer. The compact size and weight (90 lbs.) of the modules permits installation of the system in a laboratory trailer or van.

The bench top spectrometer module, which can accommodate a single soil sample, is powered by 110 V line or generator feed. The excitation source used is a low powered Rh anode X-ray tube (50 kV, 0.35 mA (17 W) maximum output) positioned at a 45° incident angle to the sample. Three primary radiation filters permit optimum spectral acquisition conditions to be computer selected.

The thermoelectrically cooled Si(Li) X-ray detector is mounted at a 45° take-off angle in an inverted geometry with respect to the sample. The 20 mm2 Si(Li) crystal, which is protected by a 0.5 mil Be window, is cooled to -90°C for operation using a multi-stage thermoelectric (Peltier effect) cooler. The 300 watts produced at the detector heat sink are dissipated by forced ambient air. Thermoelectrically cooled detectors provide typical resolutions of 185 eV (Mn Kα).

A card cage module is interfaced between the spectrometer and an IBM PS/2 or PC/AT series computer. The card cage components include the detector high voltage supply, the pulse processing electronics, and the control circuit board for the EDXRF spectrometer. The data analysis software executed on the PC is capable of either a fundamental parameters or empirical data treatment scheme using a combination of standard reference materials and/or site specific standards.

Sampling of the suspected waste site was performed using EPA approved protocols in a 9500'x 3500' rectangular area. Forty three (43) cores were collected and partitioned into four depth levels: surface to 2"; 2" to 6"; 6" to 12"; and 12" to 18", and designated levels 1 through 4, respectively. At the site, samples were first homogenized and then split into two fractions. One was submitted for EDXRF analysis and the other sent to an independent lab for analysis.

The independent laboratory used EPA SW 846 (methods 3050 and 6010) methodology to determine Cd, Pb, and Zn concentrations in the soil sample splits. Arsenic was determined in those splits using SW 846 method 3050 and EPA method 206.4 (spectrophotometric).

Sample preparation for EDXRF analysis consisted of drying the sample for 4 minutes in a microwave oven followed by sieving the dried sample. Material passing through the 2 mm sieve was collected as sample and was free of large foreign objects such as pebbles and sticks. Drying the sample was required due to the variable moisture content in the submitted soils; some surface samples had the consistency of mud. The sieved soil was then ground in a Spex shatterbox grinder (Spex Ind., Edison, NJ) using tungsten carbide cups for 2 minutes. Grinding cups were subsequently cleaned using soap and tap water. The cleaned cups were rinsed with distilled/deionized water followed by isopropanol. Approximately 5 grams of prepared sample were poured into a disposable 32 mm X-ray sample cup and covered with a 6.3 μm polypropylene film. Five grams of dried sample gave the equivalent of a 15 mm sample depth in the cup. Approximately twenty five samples were prepared and analyzed per day.

STANDARDIZATION METHOD

Two sets of excitation conditions were employed to determine seven elements in the soil samples, four of which are of specific environmental concern: Zn, As, Pb, and Cd. Table 1 lists the two sets of spectral acquisition conditions and which conditions were used to determine each analyte. Figure 1 is a mid Z spectrum of a soil sample that was found to contain 125 ppm As, 1100 ppm Pb, and 729 ppm Zn. A multiple linear least squares peak fitting routine was used for deconvolution of overlapped peaks.

The soil characterization method was standardized using four standard reference materials (SRM): NBS 1648 (urban particulate); NBS 2704 (river sediment); SO-1 and SO-3, two soil standards available from the Canada Centre for Mineral and Energy Technology. Standards labeled NBS are available from the National Institute for Standards and Technology (NIST). These SRMs have certified concentrations of Fe, Mn, Cu, Zn, Pb, and Cd.

A fundamental parameters (FP) method (5) was employed as the data treatment scheme and used certified concentrations of Fe, Mn, Cu, Zn, Pb, and Cd in the four standard materials. To compute instrumental sensitivity (emission peak counts per second per ppm), the balance of the standard was assumed to be comprised of SiO5 to account for the contribution of the matrix on the measured analyte X-ray intensity. The balance component SiO5 was selected to mimic the concentration of Si and O in typical soils, approximately 24% Si and 45% O. Since none of the selected SRM's contain arsenic, As sensitivity (cps/ppm) was determined using a fundamental parameters theoretical calculation based on the computed Zn sensitivity. Table 2 lists the analyte sensitivities computed by the FP method.

There are some advantages to using an FP method for standardization compared to site specific soil standards. The FP method can use readily available, well characterized SRMs to measure analyte sensitivities. Site specific soil standards, by contrast, are usually collected with a separate sampling mobilization. The FP method standardized with SRM's can provide accurate analyte

concentrations to be determined in samples with fairly wide matrix variations without restandardization, unlike methods incorporating site specific standards.

RESULTS

Table 2 lists the lower limits of detection determined using the two sets of spectral acquisition conditions (Table 1). The pertinent equation is: LLD (ppm)= $3\sqrt{Ib}/m(\sqrt{T})$, where Ib is the background intensity (cps), m is the analyte sensitivity (cps/ppm), and T is the acquisition livetime in seconds (6). Calculated LLD values are dependent upon spectrum acquisition times, sample matrix, and excitation conditions. The conditions in Table 1 were selected to optimize the Pb and Cd spectral regions. Improved LLD's are possible with EDXRF using longer spectrum acquisition livetimes and optimized excitation conditions for selected spectral regions.

Results for the determination of four analytes by EDXRF in 180 samples (43 cores at 4 levels, two SRM's, three samples in triplicate) were compared to independent analysis results in order to evaluate the level of agreement between the two methods. Table 3 lists the correlation plot data for the analytes in terms of actual slope, intercept, errors, and the correlation coefficient of the fit. Each analyte correlation plot included approximately 150 data points.

As shown in Table 3, slopes of the plots for Pb, Cd, Zn, and As are within 8% of 1.00 and all correlation coefficients are greater than 0.92. The calculated slope near 1.00 and correlation coefficients greater than 0.90 indicates agreement between the two analytical techniques. Figure 2 is a plot of 94 data points in the range of 0 to 300 ppm Pb. Figure 3 is a plot of 110 EDXRF and ICP analyzed samples in the range of 0 to 100 ppm Cd and also indicates agreement between the results of the two methods.

EFFECT OF LEAD ON EDXRF ARSENIC DETECTABILITY

Figure 1 illustrates the spectral interference between the emission lines of lead and arsenic in the EDXRF measurement. The As Kα (10.53 keV) and the Pb Lα (10.55 keV) peaks are directly superimposed. Peak deconvolution software must, therefore, rely on the relatively low intensity As Kß (11.73 keV) peak for unobstructed arsenic peak shape data. However, to the low energy side of the As Kß is the Pb Ln (11.35 keV) and to the high energy side of the As Kß are the Pb Lß6 (12.14 keV), the Pb Lß4 (12.31 keV), and the Pb Lß1 (12.61 keV) peaks which appear as a single peak shape in the spectrum. As the Pb emission lines increase in intensity with increasing lead concentration the arsenic Kß peak becomes indistinguishable.

The nature of the arsenic/lead interference in the EDXRF spectrum has a detrimental effect on the arsenic lower detection limit (LLD) in soils containing high Pb concentrations. The magnitude of the interference effect is directly related to the resolution provided by the EDXRF spectrometer. EDXRF spectrometers with improved resolutions would exhibit reduced As/Pb spectral interference. Reduced spectral interference thereby reduces the detrimental effect of elevated Pb concentrations on the As LLD.

To quantify the effect of As/Pb spectral interference on the EDXRF arsenic LLD, 148 samples in this study were evaluated. Of the 148 samples, 43 samples were reported as not detected for arsenic by EDXRF. Of those 43 samples, 31 were reported by the independent lab as containing 12 ppm As or higher. Arsenic non-detects, reported by EDXRF, were evaluated with respect to the As and Pb concentrations reported by the independent lab for the same sample.

The overall findings of the 148 samples can be illustrated using analysis results of four samples (Table 4) as examples. Two of the samples have non-detected As reported by EDXRF and two had detected EDXRF arsenic concentrations. In sample A, the independent lab reported an As concentration of 12 ppm while EDXRF reported a non-detected (ND) arsenic concentration. Note that 12 ppm is the EDXRF arsenic detection limit. Calculating the ratio of As to Pb concentrations, as determined by the independent lab, a value of 0.083 was obtained. Nearly the same ratio was found for sample B, again where EDXRF reported a ND while the independent lab determined 17 ppm As.

The largest absolute As concentration found by the independent lab that was reported as ND by EDXRF was 67 ppm As. That sample contains 1310 ppm Pb (1217 ppm Pb determined by EDXRF) which is an As/Pb ratio of 0.051. EDXRF reported a non-detected As result for all samples containing an As/Pb concentration ratio below 0.046.

Table 4 also lists two examples of EDXRF successfully analyzing low concentrations of arsenic in the presence of lead. The As/Pb concentration ratios for samples C and D were 0.046 and 0.053, respectively.

From the data in Table 4 and the correlation data shown in Table 3, three findings emerge. First, the EDXRF spectrometer used here is unable to determine arsenic in samples containing an As/Pb concentration ratio of less than 0.046. Secondly, arsenic determination by EDXRF is unreliable for samples containing As/Pb concentration ratios in the range of 0.046 and 0.083. This is due, in large part, to the errors in counting statistics for EDXRF measurements near the arsenic LLD. Lastly, EDXRF results show excellent correlation with the independent lab results for samples containing As/Pb concentration ratios above 0.083.

ACCURACY AND PRECISION

To evaluate the accuracy provided by the EDXRF method two SRMs were submitted as unknowns for EDXRF analysis as well as being submitted to the independent lab for analysis. Table 5 lists the results for SRM SO-2. EDXRF analysis of SO-2 provides results that are in good agreement with certified values. The independant ICP analysis of zinc in SO-2, however, is biased low by a factor of one-half.

Precision was evaluated by submitting three samples a total of three times for independent and EDXRF analysis. Table 6 shows the results for the two methods along with the calculated standard deviation (in ppm) of the three replicate analyses. Note that Cd in sample C was only reported by EDXRF to the nearest 1 ppm and three values of 9 ppm Cd were determined, hence the zero standard deviation for the three replicates. EDXRF precision is better than 10% relative standard deviation in all but one case (As in sample C) and compares well with that provided by the independent lab.

CONCLUSION

Field mobile EDXRF analysis of soils suspected of being contaminated provides information concerning the nature, extent, and magnitude of the contamination. Due to the minimal sample preparation necessary for EDXRF analysis, sampling to result turnaround time is relatively short so the most effective use of sampling resources is realized. EDXRF detection limits below 20 ppm were obtained for the elements of environmental concern. The effect of increasing lead concentration on arsenic detectability was quantified. Using the EDXRF method described here, reliable As results were found for those samples containing As/Pb concentration ratios above 0.083. Accuracy and precision for the analytes of interest using the EDXRF method was shown to be comparable to results obtained by independent analysis. Comparable results for Cd, As, Pb, and Zn between independent and EDXRF methods validates the use of EDXRF analysis for hazardous waste site investigation and remediation.

ACKNOWLEDGMENT

The author would like to acknowledge James P. Walsh and Associates for site sampling and providing the independent analysis data.

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Table 1. Spectral acquisition conditions for the EDXRF analysis of soils.

SPECTRAL REGION	CONDITIONS	ANALYTES
MID Z	35 kV, 0.35 mA, 0.13mm Rh filter, 200 s livetime	Mn, Fe, Cu Zn, Pb, As
HIGH Z	50 kV, 0.35 mA, 0.63mm Cu filter, 200 s livetime	Cd

Table 2. Sensitivity and lower limits of detection for the analytes of interest.

ANALYTE	SENSITIVITY (cps/ppm)	LLD (ppm)
Mn	0.010	21
Fe	0.015	19
Cu	0.046	26
Zn	0.067	19
Pb	0.084	7
As	0.132	12
Cd	0.107	4

Table 3. Correlation plot data for the four analytes of environmental interest.

ANALYTE	SLOPE	INTERCEPT	CORRELATION COEFFICIENT
Pb	1.01±0.03	10.0±13.8	0.96
As	1.08±0.05	0.98±3.54	0.92
Cd	1.02±0.03	3.09±2.19	0.94
Zn	1.02±0.02	63.0±13.6	0.98

Table 4. Examples of four samples illustrating the effect of lead concentration on the arsenic lower limit of detection. All concentration values are in ppm.

SAMPLE	As XRF	Pb XRF	As AA	Pb AA	As/Pb
A	ND	153	12	144	0.083
B	ND	200	17	209	0.081
C	28	381	16	349	0.046
D	16	217	11	209	0.053

Table 5. Results of the analysis of SRM SO-2 by ICP and EDXRF methods. All values in ppm.

SAMPLE	ANALYTE	ICP	EDXRF	CERTIFIED
SO-2	Pb	19	17	21
	Zn	55	123	124

Table 6. EDXRF and independent lab results for three soil samples each analyzed in triplicate. All values in ppm.

SAMPLE	ELEMENT	IND. LAB	EDXRF
A	As	45 ± 4	41 ± 3
	Cd	20 ± 2	31 ± 3
	Pb	286 ± 28	312 ± 12
	Zn	185 ± 15	134 ± 10
B	As	17 ± 3	14 ± 1
	Cd	80 ± 6	58 ± 4
	Pb	141 ± 15	158 ± 3
	Zn	556 ± 39	529 ± 46
C	As	17 ± 1	19 ± 4
	Cd	10.0 ± 0.9	9 ± 0
	Pb	117 ± 8	142 ± 14
	Zn	173 ± 26	128 ± 3

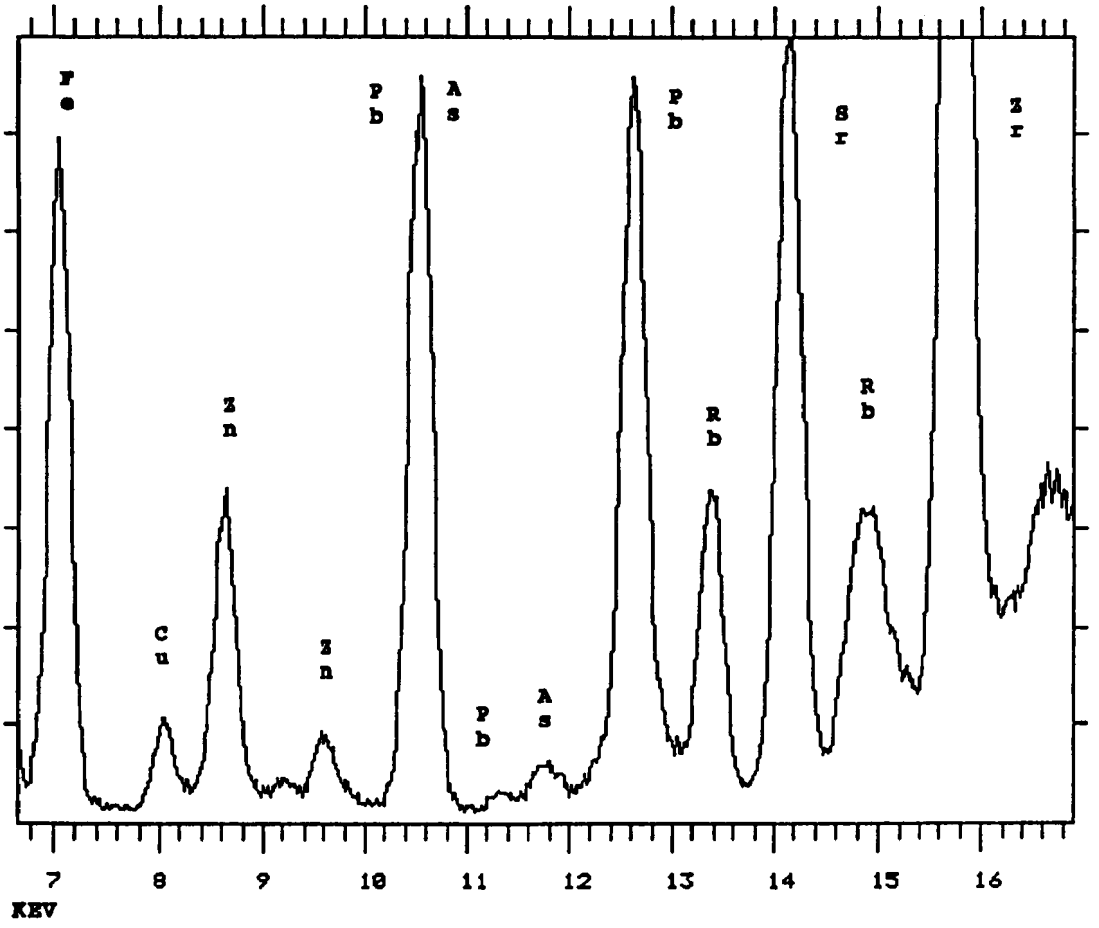

Figure 1. Mid Z spectrum of a soil sample containing 1100 ppm Pb, 729 ppm Zn, and 125 ppm As. Full scale on the y-axis is 2,000 counts.

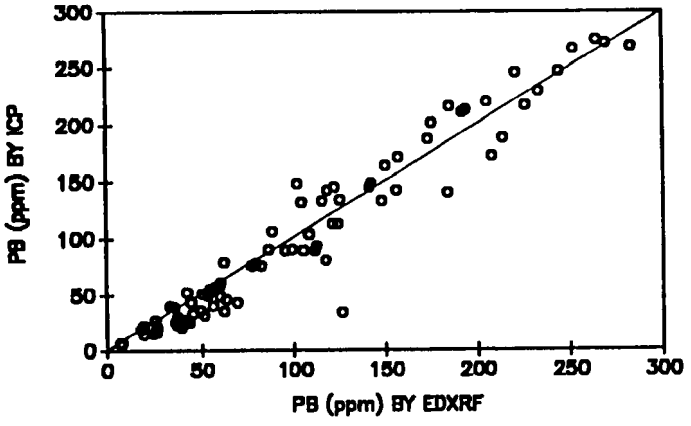

Figure 2. Pb correlation plot for 94 samples.

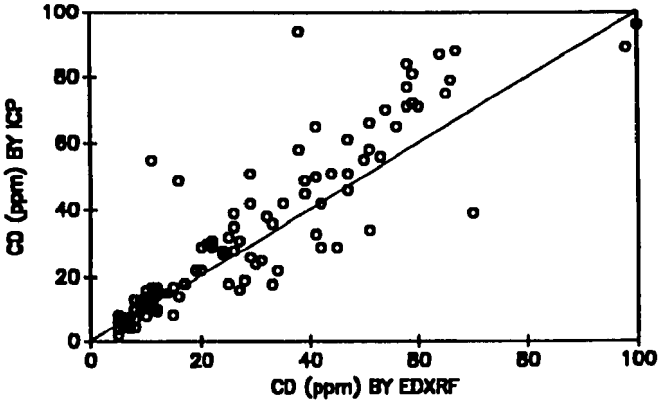

Figure 3. Cd correlation plot for 110 samples.

DISCUSSION

ROGER JENKINS: Would you care to speculate on the effect of the microwave heating on any mercury that might be in the sample. Do you think that would drive it off or not?

ANTHONY HARDING: I don't have any experience with mercury in soils and heating. I'm sorry.

ROGER JENKINS: Secondly, the drawings, sieving and grinding adds a considerable amount of time to the total sample analysis time. How much do you think that buys you in terms of increased precision or accuracy? In other words, if we eliminated that, and just sort of mainly chopped up the sample and stuck it in the x-ray system, what could we get?

ANTHONY HARDING: In terms of precision degradation, it would probably be a factor of two or three. In other words, your coarsely graded sample would be about a factor of three more or imprecise relative to the method that we took here. And of course, if your precision has degraded, your accuracy is likely to have degraded as well.

MARTY HARSHBARGER-KELLY: I'm familiar with medical x-ray generating devices, and they typically use a tungsten or molybdenum target for the mammographic units. What is the target material in your x-ray source?

ANTHONY HARDING: Rhodium.

MARTY HARSHBARGER-KELLY: And you use a rhodium filter to attenuate the beam too, for the mid-range Z?

ANTHONY HARDING: Yes, we modify the spectral distribution from the x-ray tube to minimize the background and produce improved excitation efficiency for a spectral region.

MARTY HARSHBARGER-KELLY: And the rhodium is used for both the mid-range and the high Z metals?

ANTHONY HARDING: Rhodium is selected because it's a very good general purpose anode material. Typically unless there is a specific excitation advantage to going to a tungsten anode, molybdenum anode, silver anode, most applications are done quite adequately with the general rhodium anode tube.

RUDOLF GREULICH: I'd like to ask you to comment on the background labels you might expect in your samples. You are talking about low soil concentrations. Those you have been showing are rather high and rather low. Some of them might be influenced by the background. Do you know anything about that?

ANTHONY HARDING: The detection limits were determined as interference free detection limits in the soil matrix.

RUDOLF GREULICH: You don't know what the background levels might be?

ANTHONY HARDING: The background levels are going to be varying site to site, in different regions.

MARK BERNICK: I'd like to comment on the, what appeared to be, 50% recoveries of the AA lab and the zinc. And what that means in terms of the actual accuracy of the digestive and analytical method.

ANTHONY HARDING: I wish I could comment on that particular effect. Because it does have some ramifications in terms of our correlation data counted later, or earlier, whatever. I really don't have a particular reason. All I know is we submitted that sample to two different laboratories. They were both using ICP for that particular soil, and they both got 55 ppm. So, unfortunately, I can't explain it.

JOHN MORRIS: On your arsenic lead peak stripping, most of your arsenic data were fairly low. I was wondering if you had tried MBS SRM 1645. It's the older river sediment. It's no longer commercially available, but you ought to be able to find some somewhere in some labs. Arsenic was 66. And the lead was 715, I believe.

ANTHONY HARDING: That's about 10%.

JOHN MORRIS: Yes. I was just wondering whether you could do it with the higher levels.

ANTHONY HARDING: We were able to do it from up to 125 ppm arsenic. But that correlation plot data was up to 125.

JOHN MORRIS: Your actual points that you showed were lower.

ANTHONY HARDING: Well, yes. I didn't show the arsenic correlation.

JACK HERNDON: I was wondering how long it takes for the detector to stabilize after, say, a period of 24 hours or longer if the unit is turned off for that period. How long does it take to stabilize before you can start taking readings?

ANTHONY HARDING: From room temperature the detector takes about 45 minutes to an hour to cool down to operational temperature. I'd give it another 30 minutes for temperature stabilization an the pulse processing electronics. We're pretty insensitive to temperature variations that are normally obtained in a laboratory van or trailer.

JACK HERNDON: What is the range of metals that your unit can detect? How light?

ANTHONY HARDING: We can detect sodium through uranium, atomic numbers 11 through 92.

JACK HERNDON: Do you have a vacuum system for lower ranges?

ANTHONY HARDING: Yes. That particular chamber that I showed is evacuable.

DATA QUALITY ASSURANCE/QUALITY CONTROL FOR FIELD X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Because of the nature of field screening with portable x-ray fluorescence (XRF) spectrometry, the majority of quality assurance/quality control is performed prior to and following the field activity. Prior to any field screening activity, the calibration of the instrument is the most vital area for QA/QC in the analysis. It is recommended that a suite of site specific calibration samples be prepared with soil which is representative of the site to be investigated. This soil should be collected at the site to be investigated and should include a set of both clean samples and contaminated samples, if possible. The concentrations of these samples should be verified by laboratory techniques. These samples are then mixed and spiked with the appropriate analytes to give the suite of calibration samples. From this suite of calibration samples is selected one or more samples to be used for initial and continuing calibration verification (ICV and CCV). During a sampling activity, the QA/QC measures are the assurance of representativeness of the sample, particle size , the CCV and duplicate analysis. Samples must also be collected periodically, approximately 10% of samples analyzed, for laboratory verification of the result. The results of two field screening activities are presented with the protocols for quality assurance of the data.

INTRODUCTION

The use of x-ray fluorescence(XRF) spectrometry as a method of screening hazardous waste sites for inorganic contaminants has become a viable option due to the commercial availability of field portable instrumentation (1). The usefulness of a method as a screening tool depends on portability of the instrument, the speed of the analysis, and the precision and accuracy of the data. The size of the instruments makes them highly portable and the results from the analyses can be presented immediately for interpretation. The question of precision and accuracy of that data is then of the highest priority. In studies at mines and hazardous waste sites, the usefulness of data obtained from field portable XRF units has been reported (2).

As with any analytical method, the quality of the data must be maintained to protect the ultimate usefulness of any data obtained. The USEPA defines the parameters of data quality as the precision, accuracy, representativeness, completeness, and comparability (3). The methods for meeting the requirements of data quality are, for the most part, universal for all types of chemical analysis and field screening techniques, however, there are some special situations in XRF spectrometry that require unique forms of quality control. These special situations include particle size affects(4), and preparation of calibration samples(5). The other, standard, QA methods are calibration of the instrumentation(linear correlation of the calibration), calibration verifications, duplicate analyses, laboratory verification, and sample representativeness. This paper will describe the quality control protocols used in field screening of various hazardous waste sites.

PROCEDURE

The field portable XRF unit used in acquiring all data was an X-MET 880 manufactured by Outokumpu Electronics. The X-MET 880 is an

energy dispersive x-ray fluorescence unit with two radioactive sources (^{244}Cm and ^{241}Am). For the examples which are presented in this paper, only the low energy source (^{244}Cm) is used. The calibration curves are calculated with the instruments linear regression software utilizing all of the calibration sample.

Prior to explaining the quality assurance/quality control associated with the field use of the instrument, a rudimentary knowledge of the procedures used will assist in the evaluation of the QA/QC protocols. Below is the general outline used when sampling with the X-MET 880 X-ray fluorescence spectrometer.

1. Calibration of the instrument.

    a. only necessary if elements not previously calibrated for are required, or if a close match between the matrices of the calibration standard and the samples is desired.

    b. calibration can be performed with spiked samples or previously analyzed samples. A minimum of four samples per element (up to 20 samples) should be used for the calibration.

2. Check the calibration of each model to be used (A model is a calibration including up to six elements). This is to be done by measuring a check sample (a control standard). If the values of the elements in the sample are outside of one sigma (1 σ), the STA command on the X-MET 880 can be used to reslope the calibration curve.

3. Prepare the instrument for field use. Check the charge on the batteries (each battery is good for 8 hours of use), inspect the instrument to see that all cords are in place and in good condition , and cover the probe window with the polypropylene film to keep it clean during use. Bring extra polypropylene film for replacement if necessary.

4. Upon arrival at the site, the instrument is to be turned on and allowed to equilibrate for at least 30 minutes. The instrument also needs to be allowed to gain control for 5 minutes after each 20-25 minutes of use. If the surrounding temperature is changing rapidly, the gain control should be performed at shorter time intervals.

5. Prepare the site for sampling

    a. determine the frequency of sampling

    b. make a map of where sampling is to occur (these two steps may be performed prior to arrival)

    c. determine the number of measurements per point on the map which will give a representative value for the points. This number will be between four and seven (seven giving a confidence interval of >90%)

6. Preparation of each point for measurement

    Immediately prior to taking the measurements at a point on the map, a representative sample to be measured must be exposed.

    a. for surface studies, organic matter (stick, grass, bugs, etc.) and any large unrepresentative objects should be removed. The surface may be scraped with a rake or a shovel.

    b. for subsurface studies, the proper amount of surface material must be removed. This can be done using a shovel or other digging apparatus and getting to the level of interest, or

by obtaining a core sample (with a coring tool) and measuring at the proper depth.

c. the samples (four to seven) are homogenized by the quartering technique and sieved to 9mm.

7. After preparing each point, the measurements can be obtained. One measurement is required for each model used the analysis. A counting time of 50 seconds should be used for each measurement. This value can be adjusted by the operator if the matrix characteristics are such that longer or shorter counting times are indicated. Factors influencing this decision include particle size, moisture content and homogeneity of the matrix.

   The data to be recorded for each measurement are:

   a. Concentration response for each element
   b. counting statistic for each element (gives the standard deviation due to the measuring time used)
   c. intensity data for each element

8. For quality assurance, the control sample should be measured before the measurements begin, after each 10 measurements, and after the final measurement. As indicated earlier, the control sample should fall within ten percent (10 %) of the actual value or the model should be restandardized using the standardization function on the instrument. A duplicate analysis should also be performed for precision analysis.

9. Repack the instrument for travel back to the lab, inspecting for any problems.

It should be noted that the quality control referred to in section 8 is that associated with only the field analysis and not the pre-screening QC.

The QA/QC involved in the process of field screening for metals with a field portable XRF unit can be divided into two main categories, the pre-screening QA/QC followed by the field (screening) and laboratory (post-screening) QA/QC. These two main categories can then be further separated into the individual elements that make up the protocols involved in the assurance of the quality of the data.

PRE-SCREENING QA/QC

Prior to any field screening activity, a number of procedures can be followed to assist in the quality control of the final product. The first of these is in the calibration of the instrumentation. There are two primary methods for obtaining a calibration curve for a field screening application which will produce data of acceptable quality ; a site specific calibration and a generic calibration. For the site specific calibration, a number of samples with varying concentrations of interest must be obtained for each site which will be screened. For a generic calibration, a suite of samples prepared by the spiking of a generic, or common, soil with various levels of the analytes of concern. The former of these methods will be more time consuming and therefore have a greater cost associated with the analysis, while the latter may not take into consideration matrix affects from the soil on the site. Of the two methods the one that appears to give the best results is the site specific calibration.

The best way of preparing site specific calibration samples is to have a series of analyzed samples obtained from the site of interest which contain the proper ranges of analytes of interest. This method would give a reliable calibration but would defeat the purpose of having an instrument to screen a site for possible contamination since the site would already be well characterized. An alternative involves the spiking of samples obtained at the site to be screened. In some cases it is not possible to obtain samples prior to a screening activity and in these cases a generic calibration will be the only option.

When a request for screening at a site is made, a minimum of two samples from the site are required to be used in creating the calibration samples. One of the samples must be from a part of the site which is considered to be uncontaminated, or "clean", while the subsequent samples should be obtained from what is expected to be highly contaminated areas of the site. These samples are dried, sieved through a 9mm pore size sieve, homogenized and analyzed in the laboratory. The method for analyzing the samples to be used in the calibration will depend on the type of results are desired. The XRF can emulate whatever method is called for in the project plan. If the analysis is to emulate a total contaminant digestion, then the calibration samples should be analyzed using SW846 Method 3051 (6) followed by ICP-AES. The data can also emulate a TCLP type digestion or a total digestion (i.e. hydrogen fluoride). In addition to using this data in preparing the calibration samples, the analysis may also give some idea as to what unexpected contaminants may be present at the site. The clean soil is used as the blank, the soil to be spiked, and the diluent for the contaminated soil. The contaminated soil is used as the limit for the calibration curve, unless a greater range of concentrations than this will account for is requested. In this case, the clean soil can be spiked at higher levels or spikes can be added to the contaminated soils.

From the samples obtained at the site, five calibration samples are prepared. These five consist of the clean soil, the contaminated soil, a 25/75 mixture of the two samples, a 50/50 mixture of the two samples, and 75/25 mixture of the two samples. The next 15 to 25 samples are prepared by spiking these five mixtures with the analytes of interest, giving 20 to 30 calibration samples to create the calibration curve. The spiking of the samples is preformed with the oxides and nitrates of the analytes of interest in varying ratios as is seen in the table below:

Table 1 Site 1 Calibration Samples

#	As	Cr	Pb	Zn	Fe
1	<3.0	12	201	200	12200
2	<3.0	136	2590	6870	47800
3	<3.0	110	2110	5540	40680
4	<3.0	90	1630	4200	33560
5	10000	6012	4590	7870	12200
6	6000	4012	12590	9070	12200
7	5100	1112	8590	16870	12200
8	2000	10012	3590	10870	12200
9	1000	2012	6590	12870	12200
10	5000	5012	7590	11870	12200

all concentrations in mg/Kg

The use of the oxides and nitrates is due mainly to their availability and ease of handling. The above table is a partial list of the values used in the calibration for the screening of a superfund site in region 10 (see results section). The preparation of the calibration samples normally requires three to four labor hours. Twenty gram samples of the dried and sieved clean soil are measured out, one for each element to be analyzed. To these samples is added a nitrate or an oxide of the analyte of concern in a proportion to give a sample concentration of ten weight percent. These samples are then homogenized and used in the proper ratios with the clean soil to give the calibration samples. Three of these samples are analyzed using Total digestion and ICP-AES to verify the concentrations. One of the three samples is chosen as the control sample for the ICV and CCVs. For this site the sample chosen as the control sample was # 10. Normally one of the samples which has not been spiked is used as the control sample but since there was little or no arsenic or chromium in the sample, it was decided to use a sample which contained all of the analytes of interest.

When preparing the calibration curves, the correlation coefficient shows the linearity of the calibra-

tion. Since there is a direct correlation between intensity and concentration in XRF spectrometry, the quality of the data will be dependant on the linear correlation. The acceptance limit for the linear correlation used in this study was 0.990. If the correlation falls below the limit, the intensities for the calibration samples are recollected and if the correlation is still low, the samples with low values (far off the calibration line) are re-prepared and reanalyzed.

FIELD AND LABORATORY QA/QC

In the field portion of the analysis, there are a number of areas where the quality of the data must be documented. As with any instrumental technique, there are QC requirements in XRF spectrometry including the initial and continuing calibration verification and duplicate analysis. An aspect of XRF spectrometry which can cause unique problems is that particle size can affect the results and so must be controlled. Finally, the field analysis itself gives rise to possible sources of error, such as how representative the sample collected is and laboratory verification of the results. All of these factors must have associated QC/QA to document the quality of the results.

The normal QC which is followed with any instrumental technique include the initial and continuing calibration verification (ICV and CCV respectively). The ICV is performed prior to any sampling and the CCVs are performed after every ten sampling sites. If any of the verifications are out of the control limits, the control limits being $\pm$ 20%, then the calibration needs to be restandardized. The X-MET 880 software has a restandardization function built in so that all that is required is a remeasurement of a standard sample. Since there are no moving parts within the instrument, there is rarely a need for a restandardization during a field screening activity. A duplicate analysis is run to give an idea as to the precision of the analysis. A sample is chosen at random for the duplicate analysis.

Particle size affects can cause discrepancies in XRF data and so it is necessary to minimize these affects. One way of proceeding to this end is to match the field sample particles size to that used in the calibration samples as closely as possible. By avoiding a difference in particle size, the affect of particle size should be a minimum. To accomplish this, all samples are sieved with a standard sieve to less than 9mm. This size of sieve was used so that all particles that can be considered soil are included in the analysis. To get an even closer match in particle size would require some sort of particle size reduction which would greatly increase the time required for the field screening procedure.

The problem of obtaining representative samples will be of concern when the site is large and the sampling areas are spaced some distance apart. There is a need to make sure that the readings obtained are a reasonable reflection of the contamination at the sampling site. To obtain a statistically representative sample, seven unique portions are obtained from the site and then homogenized using the quartering technique. The homogenized sample is then sieved (see above) and analyzed with the XRF spectrometer.

The final QC requirement for the field analysis is the collection of samples to be used for laboratory verification. The samples are to be collected from the sieved material at a frequency of approximately 10% of the total samples. This gives a range of sample concentrations to help in the interpretation of the field data. These samples will then be analyzed by the USEPA approved method at a laboratory to determine the accepted concentrations of contaminants at the site.

RESULTS

This section will give the result obtained at two hazardous waste sites using the X-MET 880 to analyze for a variety of elements. Both of the sites were analyzed using a site specific calibration. In both cases, the calibration samples were prepared using two samples from the site, one contaminated and the other uncontaminated, with spiking of the soils.

Site 1 is a junkyard which at one time contained transformers and lead-acid batteries in addition to other types of scrap metal. This is an eleven acre site with many type of soil including fill brought in from other places. The element of most concern at this site was lead. The three figures below (Figures 1, 2, and 3) show the correlation between the laboratory results and the field XRF spectroscopy results. In the preparation of the calibration curve, the analysis on the preliminary samples was performed using SW846 method 3051 (6) for the digestion and ICP-AES for the analysis (see Table 1). The laboratory analyses on the verification samples used the same procedures.

Figure 1 Site 1 correlation for lead results

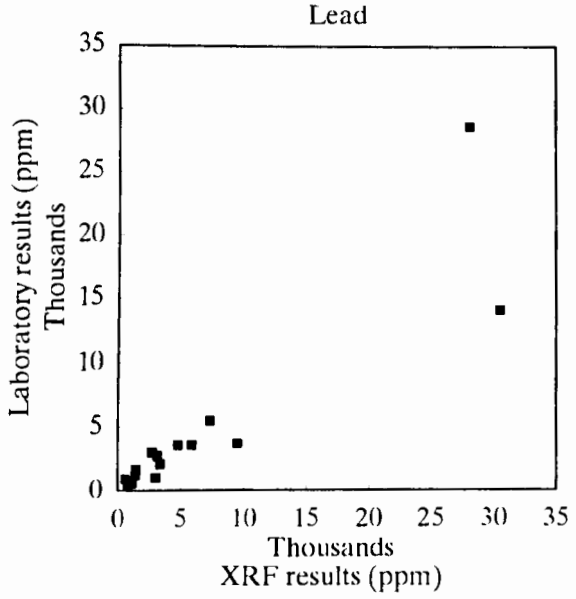

Figure 2 Site 1 correlation for zinc results.

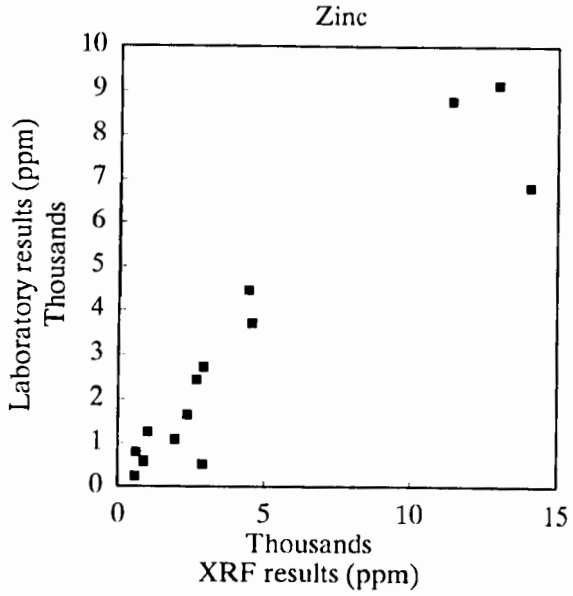

Figure 3 Site 1 correlation for iron results.

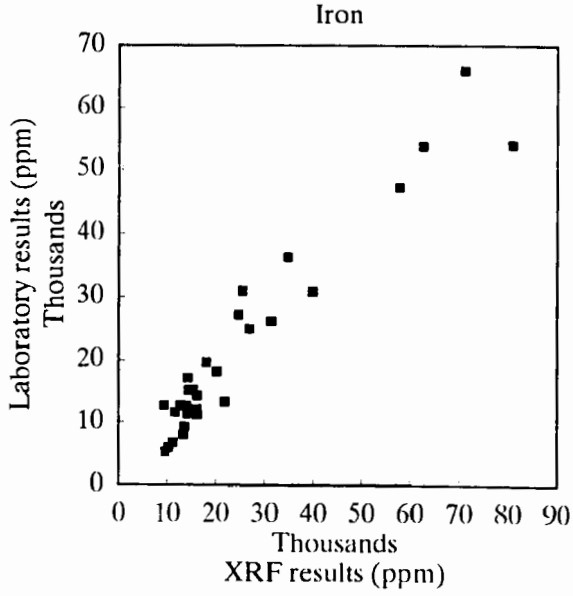

Table 2 Duplicate XRF Analysis for Lead at Site 1

Sample #	Analysis #1	Analysis #2
1	8600	7270
2	28630	9370
3	12600	6970
4	12580	15200
5	16480	9500
6	5430	5870
7	14110	14370
8	8540	7250
9	7910	7290
10	10270	13100

From the Figures and Tables above, it is apparent that the analysis simulated the laboratory data fairly well. Other elements were analyzed for (As, Cr, and Cu) but they were all present below the detection limit of the calibration. The discrepancies in the duplicate analysis can be explained as a problem in the variability of the contamination at the points and the difficulty in obtaining a large amount during the duplicate analysis. The large variability may be due to one small nugget in the first sample which contained a large amount of lead.

There were no problems encountered in the continuing calibration verification. All of the values for the control sample were within 10% of that found in the laboratory analysis so restandardiation was not required during the analysis.

Site 2 is a former Oil filtering operation for the reclamation of used oil. The filtercake material was buried and the covered over with gravel to make a parking lot. The samples were obtained using a drilling rig. This was a very small site with the sampling occurring at 12 boring holes. The main element of concern was lead. Table 2 shows the comparison of the field readings and the laboratory values for the two samples used in the verification. The ultimate purpose of the XRF screening was to determine, on the site, the hot spot for lead contamination. In the preparation of the calibration curve, the analysis on the preliminary samples was performed using SW846 method 3051 for the digestion and ICP-AES for the analysis. The laboratory analyses on the verification samples used the same procedure.

Table 3 Results from Site 2

	Hot Spot		Representative	
	Lab (ppm)	XRF (ppm)	Lab (ppm)	XRF (ppm)
Pb	15384	15500	4608	5050
As	18.11	<180	24.99	<180
Cr	41.57	<100	90.39	110

The results show that the X-MET 880 XRF spectrometer gave results that were close to that found during the laboratory verification.

No problems encountered in the continuing calibration verification. All of the values for the control sample were within 10% of that found in the laboratory analysis so restandardiation was not required during the analysis.

SUMMARY

This study has shown the quality objectives for utilizing XRF as a screening tool for metals at hazardous waste sites. The results from the field screening appear to emulate the data obtained from the laboratory verification. A major factor in the quality of the results would appear to be the site specific calibration. The use of the site specific calibration appears to give good quality data without adding a great amount of time to the pre-screening process. The data presented is the product of two sites which had very different soil types which could create difficulties when using a

generic calibration.

The other methods of quality control are also responsible for the quality of the data received from the screening process. These methods include the calibration verification, duplicate analysis, assurance of the representativeness of the sample, particle size, and laboratory verification. These steps are already accepted methods in the collection and analysis of any environmental samples.

When the protocols listed above are followed, the data obtained from the screening of hazardous waste sites for inorganic contaminants by x-ray fluorescence spectroscopy correlates well with confirmatory results and require minimal reanalysis in the field. The use of XRF spectroscopy as a screening tool will meet the criteria establish for these tools, those being speed of analysis, accuracy of the method, cost effectiveness and quality of the data.

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ACKNOWLEDGEMENTS

The authors would like to thank the U.S. Environmental Protection Agency for funding this work. We would also like to express our thanks to Mr. Roy R. Jones for his many useful discussions and assistance throughout this project.

DISCUSSION

RUSS SLOBODA: My question involves the site specific calibration. Most soil studies usually involve a variety of matrices at a specific site and it would seem to be rather naive to say that one calibration is specific to the whole site. What type of protocol do you have to help you decide? Is it a geologist helping you to decide if these are different mineral matrices? Or do you test in your base lab every single thing that might be a different matrix before you decide on how may site-specific calibrations are necessary for the types of matrices you're encountering.

CLARK CARLSON: What we like to do, of course, is to have enough samples from the site. We require at least two. But depending on the size of the sites (because most of the sites that I've done haven't been that large), the assumption that just a few samples will get us a fairly good correlation as to the matrix over the whole site, I feel, is a good one. But when you're talking about very large sites, you may run into some problems with the matrix, and you may have to do more than one site-specific calibration.

JOHN BARICH: When specifying a job, what is your rule of thumb as to what percentage of your budgeted dollars and what percentage of your performance period should be devoted to the QA program?

CLARK CARLSON: As far as the time allotted, it usually takes on the average, about four or five hours to make our calibration samples. And depending on the size of the site, of course, that's going to affect the percentage of time that you're going to use for that particular portion of the QA/QC. But other than that, since we're doing the duplicate samples and the sample verification, the rule of thumb that I've been using is roughly between 20% and 25% of the time.

A Study of the Calibration of a Portable Energy Dispersive X-ray Fluorescence Spectrometer

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ABSTRACT

Generation of reliable concentration information from portable energy dispersive X-ray fluorescence necessitates the development and use of appropriate calibration methods. The present study considers some of the difficulties encountered with the use of empirical calibration, which is obtained from the measurement of standards with a similar matrix to that of the samples being investigated. The effectiveness of two sets of empirical calibration standards have been investigated, namely a set of site specific samples analyzed using a referee method, and a set of artificially prepared calibration samples produced by spiking an uncontaminated soil matrix. It was found that sample matrix variation unaccounted for in the calibration leads to uncontrolled bias in the analytical results.

INTRODUCTION

Of major concern in the characterization of many hazardous waste sites is the rapid and accurate determination of metal concentrations in solid and liquid samples. Generally, these determinations are carried out in an off-site laboratory using techniques such as atomic absorption (AA) spectrophotometry or inductively coupled plasma (ICP) atomic emission spectrometry. These methods, while relatively accurate, are time consuming and expensive; they also cannot practically provide on-site, real-time results. Thus, there is a need for a supplementary technique that can provide adequate information about a site in a timely and less expensive manner. Portable energy dispersive X-ray fluorescence (FPXRF) spectrometry is a promising method to meet this need. Instrumentation is commercially available which utilizes radioisotope sources and gas-filled proportional counters.

Problems exist, however, which are inherent to X-ray fluorescence (XRF) methods that must be addressed to provide useful concentration data for unknown samples. Some of these problems, such as particle size and mineralogical effects, are common to all types of XRF and can be minimized by preparation of all samples and standards to a uniform state. Other well-known problems consist of interelement effects, which include spectral overlap, primary and secondary absorption, and enhancement. Absorption and enhancement effects are commonly addressed in laboratory XRF using computational procedures such as the "Fundamental Parameters" approach (Jenkins, 1974). With contemporary laboratory wavelength- and energy-dispersive instrumentation, spectral interferences present little difficulty in all but a few cases. Thus, in laboratory implementations of XRF, results comparable to AA and ICP are routinely achievable.
To date, the aforementioned problems have not been adequately addressed in applications of FPXRF to environmental monitoring; of major concern is the relatively poor spectral resolution of the proportional counter detectors, which require larger overlap correction factors for adjacent elements than solid

state dectectors. In addition, approaches such as "Fundamental Parameters" are not practical to implement in FPXRF because of the presence of many unresolved spectral interferences, computation requirements, and the inability to measure all components in the sample. Thus, empirical calibration approaches have been used in FPXRF; these relate the measured spectra of a "training set" (calibration set) to the concentrations of elements present in the training set samples, typically using an approach such as multiple linear regression (MLR). Two types of training sets are common, namely real samples analyzed by referee methods (site-specific models), and synthetically prepared standards (generic models). For both types of training sets, the analyst attempts to match the matrix of the training set to the anticipated unknown samples. Obviously, selection of a proper training set matrix and the determination of its applicability to unknown samples are critical problems.

This study involved the application of empirical calibration-based FPXRF to an environmental monitoring situation, namely, the determination of the elements chromium, zinc, and lead in a soil-like waste material. Samples from a site contaminated with heavy metals were collected and analyzed by ICP. These samples were used to evaluate the performance of site-specific and generic training sets.

XRF THEORY

The first step of any X-ray analysis is the removal of inner shell electrons from the atom. A vacancy is then created which is immediately filled by an electron from a higher energy shell. The resulting free energy is emitted as radiation that is characteristic of the excited element. The second stage is the selection of an emission line from the element of interest by means of a wavelength or energy dispersive spectrometer. Next is the detection and integration of the characteristic emission line of interest, and finally, the conversion of intensity to concentration by the use of some calibration procedure.

Until the late 1960s nearly all X-ray spectrometers were the wavelength dispersive type in which wavelengths are separated by Bragg diffraction from a single crystal. Although wavelength dispersive X-ray fluorescence (WDXRF) spectrometers have high spectral resolution, they are bulky, expensive, and require a high power x-ray tube as an excitation source.

More suited for field work are energy dispersive X-ray fluorescence (EDXRF) spectrometers. EDXRF spectrometers, being more efficient than wavelength dispersive spectrometers, can utilize small radioactive sources for excitation instead of large X-ray tubes. In addition, the separation of emission lines does not require the use of a large crystal chamber and goniometer as does a WDXRF spectrometer. There are several types of detectors that are employed in FPXRF spectrometers: scintillation counters, solid state detectors, and gas-filled proportional counters. The scintillation counter has very poor resolution and requires the use of balanced filters to discriminate between lines. The need for filters increases the mechanical complexity and limits the flexibility of an instrument. Solid state detectors use a crystal of lithium drifted silicon. Silicon detectors have very good resolution (~0.16 KeV full width at half maximum for the 5.89 KeV Mn-K_a) but require the use of liquid nitrogen or thermoelectric cooling to minimize electronic noise. Gas filled proportional counters have an intermediate resolution (~0.77 KeV for Mn-K_a) between the scintillation counter and the solid state detector but do not require cooling. Thus, the combination of radioisotopic source for excitation and gas-filled proportional counters for detection are more suited for field portable instruments.

EXPERIMENT

Samples and Standards. Contaminated soil samples were collected from a site bearing potentially hazardous waste material. Initially, 25 samples were taken from soil that was contaminated with heavy metals from a metal recycling plant. Fifteen of these 25 samples were used as a site-specific training (calibration) set, referred to hereafter as TRAIN1. The TRAIN1 samples were selected to provide the maximum range of concentrations for both the analytes and major elements. The remaining 10

samples were used as an "unknown" testset; these are referred to as TEST1. An additional testset (TEST2) of eleven samples, taken from a different area on the same site, consisted of material from the same process produced at an earlier time. ICP analysis showed that the levels of iron, calcium, and silicon were higher in the TEST2 samples than in the soil from the TRAIN1 group (refer to Table 1).

The generic training set (TRAIN2) consisted of synthetically prepared standards obtained commercially. These standards had been produced by spiking an uncontaminated sandy soil matrix with chromium, copper, zinc, arsenic, cadmium, and lead.

Sample Preparation. Approximately one kilogram of each soil sample was air-dried to constant weight and sieved through a two millimeter nylon sieve. A 50 gram subsample was selected by randomly taking approximately 50 one gram aliquots from the primary sample. This subsample was then ground in a tungsten carbide rotary ring mill to minus 200 mesh particle size. From the ground subsample, an analytical sample was selected for FPXRF analysis, which consisted of approximately 30-40 increments of about 0.25 grams each, which were then placed in a polypropylene cup for the analysis. Analysis of replicates by ICP verified the homogeneity of the ground samples (less than five percent relative standard deviation between 0.25 gram aliquots). These measures minimized subsampling and particle size effects.

Samples were prepared for ICP by fusing 0.25 grams of ground material with 2.0 grams potassium hydroxide (KOH), followed by dissolution of the melt in hydrochloric and nitric acid ($HCl-HNO_3$). Fusion was selected over commonly used acid digestions such as EPA Method 3050 because of greater accuracy for critical elements such as chromium and iron; procedures such as Method 3050 tend to yield low results for many elements because of poor attack of silica-based minerals. This fusion procedure produced reliable analytical results for thirty elements of interest, as evidenced by acceptable results for spiked samples, replicate samples, and reference materials. Accuracy of these results was further verified by determination of the analytes using a laboratory-based EDXRF.

FPXRF Measurements. An Outokumpu X-MET 880 FPXRF, containing a 30 mCi ^{244}Cm excitation source and an argon proportional counter, was used in these studies. Data was acquired using a 200 second measurement time, and a consistent sample presentation geometry. Chromium, zinc, lead, and backscatter (BS), as well as several potential interfering elements were measured in the training set. The K_a emission lines for chromium and zinc were selected and the L_a line for lead was used in Train1 because no arsenic was present in the samples. The L_b line for lead was used in Train2 due to the presence of arsenic in the standards. Spectral interferences were treated using a Gaussian elimination algorithm (subtracting the portion of signal due to the interferant after measuring interferant intensity and using a pre-established correction coefficient) provided for in the X-MET software (Outokumpu Oy). Stepwise multiple linear regression was used to develop models accounting for absorption and enhancement effects; interference-corrected spectral intensities were used as dependent variables; concentrations of the elements were used as independent variables. The significances of independent variable effects were determined using t-tests. Some standards were omitted from the model if significant improvement in r^2 was achieved by doing so. A summary of the models generated is presented in Table 2.

RESULTS AND DISCUSSION

Examination of Table 3 reveals that bias for all elements generally increases in the order (TRAIN1 ; TEST1) < (TRAIN1 ; TEST2) << (TRAIN2 ; TEST1 or TEST2). Chromium could not be effectively quantitated in any samples by the TRAIN2 (generic) model. Indeed, chromium was not detected for most samples even though 400-600 mg/kg Cr was actually present. The bias problem was not due to lack of measurement precision (see Table 4). A possible explanation is as follows: The Cr-K_a, being of low energy, is particularly susceptible to sample matrix effects, such as the presence of iron at varying levels. The analogous effect is not as pronounced

for the higher energy Zn-K_a and Pb-L_a. Additionally, the Cr-K_a line is subject to spectral interference from the Fe-K_a line, which is problematic when the concentration of the interferant (Fe) is high compared to the analyte (Cr).
A difficulty with the TRAIN2 (generic) calibration model is the lack of definition of the sample matrix effect (differing absorption/enhancement correction coefficients). Elemental analysis of the TRAIN2 standards by lab-based EDXRF revealed very little range in the concentrations of major elements such as iron, silicon, and calcium. Empirical training models containing no variance in influential parameters (e.g. matrix, concentration of interferants) cannot be expected to produce models which are robust with respect to these variations. For TRAIN2, t-values for iron and backscatter were statistically insignificant in this set of standards, indicating that no variances exist for major elements in the TRAIN2 materials.

Differences in matrices are thus a main pitfall in FPXRF. It is unrealistic to believe that, for field applications, the matrix will be identical for all samples encountered. It is also difficult to determine, in real time, the applicability of a specific training set to a particular sample. A specific training set may be inadequate due to the presence of unanticipated spectral interferants, or large matrix differences, or both problems. In this study, changes of less than a factor of two in the concentrations of iron, calcium, and silicon between TEST1 and TEST2 strongly influence the biases of the resulting data.

FPXRF calibration models are frequently evaluated based upon the value of the regression coefficient, r^2. It is essential to note that good correlation alone does not ensure accurate results. The regression coefficients for all analytes using TRAIN1 and TRAIN2 were close to unity, yet many predictions were highly biased. While a model with a low r^2 value lacks any predictive capability, a high r^2 alone does not guarantee its predictive capability for a specific test sample.

CONCLUSIONS

FPXRF is an analytical technique which is not highly robust with respect to spectral interferences and sample matrix effects. Even with site specific empirical calibration, the applicability of a particular model to a specific sample cannot be ensured. In some cases several models might have to be employed to cover the entire range of analytes, inteferents, and matrices. Quantitative analyses of varying, unknown hazardous waste streams present a challenge of the highest order to FPXRF application; substantial possibility exists for false positive and false negative readings, as well as highly biased quantitation. Low atomic number elements and lower concentrations appear to be more susceptible to quantitation problems. However, FPXRF is presently very useful as a field analytical device for problems such as contamination delimination and segregation of waste streams. Qualitative, semi-quantitative, and quantitative analytical results are all potentially achievable on a case-by-case basis. Assuming present instrumental hardware, additional research in FPXRF should be directed towards development of more robust calibration methods, for example chemometric calibration.

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Table 1

Matrix and Analyte Concentration Ranges (mg/Kg)

Element	TRAIN1	TEST2
Fe	83900-127000	87500-196000
Ca	17900-30700	27600-49100
Si	64400-146000	121000-220000
Cr	497-766	307-567
Pb	4740-8230	3210-8560
Zn	9280-20100	5840-26800

Table 2

Summary of Calibration Data

TRAIN1 (Site-Specific) Calibration Model

Analytes	Interfering Elements	Points Omitted	Regression Coefficient
Cr	Cr, Ti, Fe, BS	2	.990
Pb	Pb, Fe, BS	3	.990
Zn	Zn, Fe, BS	1	.991

TRAIN2 (Generic) Calibration Model

Analytes	Interfering Elements	Points Omitted	Correlation Coefficient
Cr	Cr, Mn, Fe, BS	0	.998
Pb	Pb, BS	0	.996
Zn	Zn, BS, Pb	0	.998

Table 3

Bias Data for Samples
Absolute Percent Relative Error

TRAIN1 (Site-Specific) Calibration Model

	Chromium	Lead	Zinc
TRAIN1	7.0	9.3	5.6
TEST1	8.9	5.3	3.5
TEST2	100.0	23.3	13.1

TRAIN2 (Generic) Calibration Model

	Chromium	Lead	Zinc
TRAIN2	12.0	15.1	8.9
TEST1	97.9	33.8	39.8
TEST2	86.0	38.4	49.6

NOTES: The training set rows refer to the mean magnitude of the relative errors produced by re-measurement of the training set using the developed model. The testset rows refer to the mean magnitude of the relative errors produced by measurement of the samples using the developed model.

Table 4

Measurement Precision
Percent Relative Standard Deviation

TRAIN1 (Site-specific) Calibration Model

Samples	Chromium	Lead	Zinc
TRAIN1	4.2	2.1	1.3
TEST1	8.4	1.7	0.7
TEST2	ND	1.9	1.9

TRAIN2 (Generic) Calibration Model

Samples	Chromium	Lead	Zinc
TRAIN2	1.3	4.7	0.5
TEST1	ND	2.7	1.8
TEST2	ND	2.9	0.8

NOTE: "ND" means only values of zero were measured; precision was therefore not determined.

DISCUSSION

STEVE KNOLLMEYER: I have two questions. One, does the X-MET 880 have an internal measurement capability? That is, needing no external calibration. And two, if so, do you compare errors using that internal calibration method versus your matrix specific calibration standards?

DONALD SMITH: As far as I know there's no internal calibration available with that. So, no we didn't.

Use of Long-path FTIR Spectrometry in Conjunction with Scintillometry to Measure Gas Fluxes.

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ABSTRACT

Fourier Transform Infrared (FTIR) spectrometry is rapidly becoming a technique of choice for analyzing volatile hazardous waste emissions (1). We have developed a field portable system that is capable of measuring gas concentrations at up to a 1 Km pathlength. The advantage of such a system is that it can analyze samples virtually in real time for myriad compounds simultaneously without introduction of any artifacts from sample collection. Because detection sensitivity increases with path length, analysis of compounds can often be made down to ppb levels. While we have concentrated on measuring gas emissions from biologic sources, we are also capable of monitoring hazardous gas emissions that have characteristic infrared absorbance peaks in regions of the IR spectrum that are not dominated by water or CO_2. Numerous volatile organic compounds such as chlorinated hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, ethers and aldehydes fall into this category.

While gas concentrations are of interest, emission rates are needed to accurately evaluate waste sites. Obtaining such flux rates has become the focal point of our research. Recently, the Wave Propagation Lab (WPL) at NOAA (Boulder CO) has demonstrated that an optical-scintillation instrument can measure path-averaged momentum and heat fluxes. Development of scintillometers by WPL, which is currently in progress, will allow long-path measurement of water flux as well. Combining these long-path flux measurements with measurements of gradients of gas concentrations using the FTIR has the potential to provide an estimate of flux rates for numerous gases simultaneously. This technique will then have application in natural, agricultural and human impacted areas such as landfills and hazardous waste sites.

INTRODUCTION

Fourier Transform Infrared (FTIR) spectrometry is rapidly becoming a technique of choice for analyzing volatile hazardous waste emissions. A particular advantage of FTIR spectrometry is that it can be configured for long-path analysis. Large areas from which potential emissions are occurring can be analyzed at one time. We have developed a field portable system that is capable of measuring a number of infrared absorbing trace gases over long paths of up to a kilometer (Fig. 1). Many of these gases have either natural and/or anthropogenic sources and/or sinks. Increased path-length provides several advantages such as increased detection level (ppb levels) and long-path averaging of the high variability in gas emissions that may often be the case on a smaller scale (2).

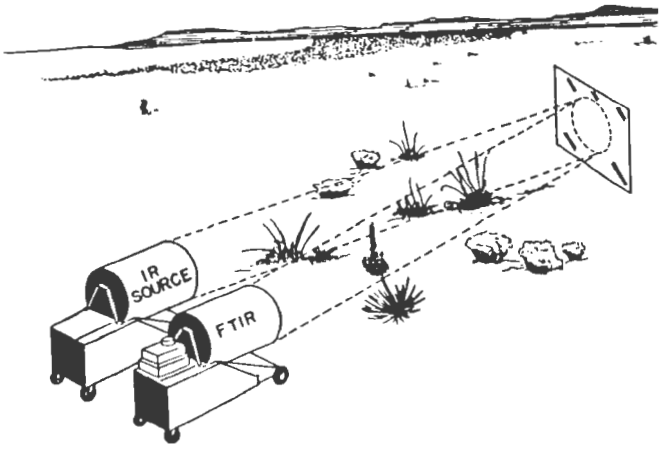


Figure 1. Schematic of an infrared radiation source and Fourier transform infrared (FTIR) spectrometer equipped with telescopes to allow long-path analyses. The flat mirror allows rapid manipulation of optical pathlength and analyses over undisturbed terrain.

The detection of the presence or absence of a particular IR absorbing contaminant is diagnostic of what volatile constituents are being released from a site. An even more valuable piece of information would be an estimate of the total flux of that contaminant through the site into the atmosphere over time. Such an estimate requires knowledge of the micrometeorological conditions of the site during the period when long-path FTIR spectrometry measurements are being made. Ideally, the micrometeorological measurements would also be path-averaged over a comparable path being sampled by the FTIR spectrometer. Scintillometry techniques, presently under development by atmospheric scientists at the NOAA wave propagation laboratory in Boulder, Colorado, provide a potential method to link path averaged FTIR spectroscopic profiling and micrometeorological characterization of the near surface atmosphere. Such a combined data base may make estimates of large scale contaminant fluxes possible.

The purpose of this article is to describe our long-path FTIR spectrometer instrument, to present some analyses of various IR absorbing trace gases measured using a long-path configuration, and to discuss means of combining micrometeorological data with long-path trace gas concentrations to obtain estimates of fluxes. In particular, combining of long-path scintillometry with long-path FTIR gas concentration data shows the promise of providing a better tool for quantifying gas fluxes from both natural and polluted sources.

MATERIALS AND METHODS

FTIR Spectrometer

Our FTIR instrument is a Nicolet 740 optical bench interfaced with a Nicolet 660 work station having a storage module capable of storing 344 Mbytes of data. The 740 unit is capable of 0.3 cm-1 wavenumber resolution (3,4). The optical bench is mounted on a wheeled cart in conjunction with a 60 cm diameter Cassegrain telescope. The infrared source (1000-W halogen quartz lamp or globar) is mounted at the focal point of a second 60 cm diameter Cassegrain telescope. The infrared beam is transmitted to a 60 cm square flat mirror and returned to the receiving telescope which focuses it on an adjustable aperture (Fig. 1). The beam is then recollimated and transmitted into the optical bench and subsequently through the interferometer to the detector. The 740 bench is equipped with an Hg-Cd-Te (MCT-A) detector. All sample collection and processing is handled using Nicolet software. Each collected sample can be either a single scan or a composite of a series of scans. Sampling rates are a function of scans per sample and the pathlength of the moveable mirror. Most samples discussed in this paper were collected at 0.5 cm-1 wavenumber resolution. Each scan takes about a second at this resolution. Generally 16 scans per sample were collected although in some cases a 1-minute sampling rate was desired which resulted in 60 scans per sample. Each sample yields an interferogram (Fig. 2) which must then be processed to give an absorbance spectrum (Fig. 3) from which gas concentrations can be calculated. This quantification is performed using a multivariate least squares fit (LSF) program developed by Haaland and Easterling (5). This technique allows quantifying of multiple components whose lines overlap in a given spectral region with better precision and accuracy than can be obtained from a single peak analysis.

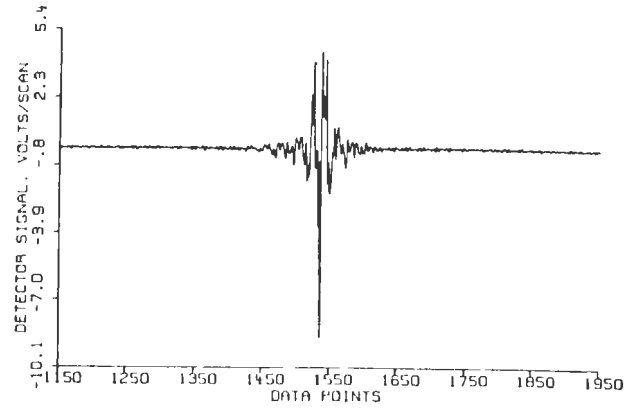


Figure 2. Example interferogram from the FTIR. The energy source was a quartz-halogen lamp, pathlength 407 m, atmospheric pressure 724 torr and instrument resolution 0.3 cm^{-1}.

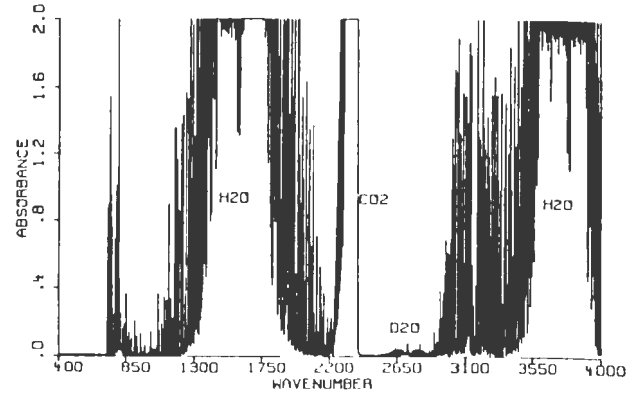


Figure 3. The raw data of the interferogram is processed to give an absorbance spectrum that allows calculation of gas concentrations. This interferogram was collected at Maricopa, Arizona over a cotton field, 10:26 hrs, 12 June 1988, pathlength 407 m.

Optical Scintillometer

Scintillometers are devices that sense the scintillation (intensity variations) in propagating electromagnetic (EM) waves. The refractive index structure parameter C_n^2 characterizes the magnitude of this scintillation. EM scintillation results from turbulent fluctuations in the atmospheric refractive index which in turn result from fluctuations in atmospheric temperature and humidity fields. The scintillometer currently being used is an optical scintillation inner-scale meter. In the experiment reported here, it is deployed on a horizontal path of 150 m at a height of 4 m. This instrument measures the variance of the log intensity of diverging Laser light detected through a 1mm-diameter hole as well as the variance of the logarithm of aperture-averaged intensity from a 4.4-cm diameter, phase incoherent uniformly-illuminated source. The ratio of these variances gives the inner scale of turbulence l_o. The refractive index structure parameter C_n^2 is also determined from this instrument's data. An approximate correction for saturation of scintillation of the Laser variances is computed to extend the range of validity of the instrument. The heat and momentum fluxes are deduced from C_n^2 and l_o using Monin-Obukhov similarity relationships. This is the "inertial dissipation" method of determining these fluxes. In this configuration the instrument can be considered a fluxes scintillometer.

For comparison purposes, a three-axis sonic anemometer having platinum resistance-wire thermometer near its center is also deployed at a height of 4 m on a tower near the optical scintillation instrument. The sonic anemometer measures all three fluctuating components of velocity at a 25 Hz data rate. The correlation of the vertical component of velocity with the streamwise horizontal component gives the momentum flux (divided by air density). The friction velocity U_* is the square root of the negative coefficient of this correlation. The correlation of the vertical component of velocity with the temperature from the resistance-wire thermometer gives the temperature flux (heat flux is temperature flux multiplied by the air's heat capacity.)

RESULTS AND DISCUSSION

FTIR

Much of our initial work has involved testing the utility of the long-path FTIR for monitoring gases from natural as well as anthropogenic origins. Gases that we most routinely analyze include H_2O, CO_2, CH_4, N_2O, and CO but many other gases can also be quantified simultaneously or at some later time. This points up one of the primary advantages of FTIR. Spectra collected can be reprocessed at a future time to look for gases that may not have been of primary interest at the time that the original analysis was carried out. Below are examples of some uses of our long-path FTIR.

Gas Emissions

The FTIR was set up to measure a 100 m path over a small shallow lake on the Isleta Indian Reservation near Albuquerque, N.M on June 26, 1989. A series of samples was taken to establish ambient gas concentrations. The bottom sediments were then disturbed by a person walking around to force degassing of the sediments. A second series of samples was collected during this period (Fig. 4). Emission of CH_4 is readily apparent. These emissions were in fact point source emissions and the measured concentrations denote a mean concentration for the entire 100 m path, most of which was not undergoing degassing. This artificially induced gas emission points up the ability of the FTIR to quantify such emissions but the experiment was designed to test our ability to measure changes in path-averaged atmospheric concentrations and was not meant to estimate gas fluxes.

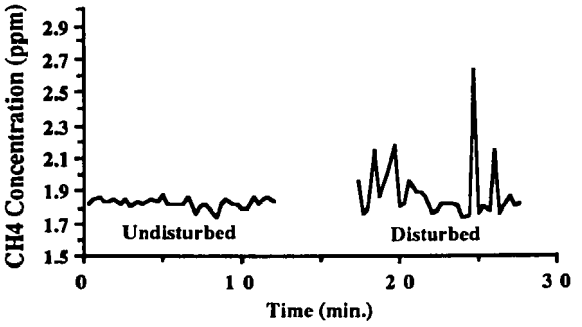


Figure 4. Field demonstration of the ability of long-path FTIR to detect CH_4 emissions from a shallow lake in New Mexico. Measurements were made over the lake on June 26, 1989 before and after bottom sediments were disturbed along a portion of the pathlength.

Gradient Profiling

A primary focus of our study is to develop the capability to measure gas fluxes over a long path which should average out the large spatial variability encountered using small scale techniques such as chambers. Micrometeorological techniques such as Eddy correlation and Bowen Ratio techniques have been shown to be capable of measuring heat and water fluxes under certain ideal conditions. We have explored the possibility of using the diffusivity constants obtained from Bowen stations and eddy correlation stations to plug into a flux gradient equation:

$$F = k \cdot dc/dz \qquad (1)$$

where F is the mixing ratio flux, dc is the difference in a gas concentration (in ppm) measured at two heights and dz is the difference in those two heights. We experimented with this technique over a tall grass prairie site near the Konza Prairie Long Term Ecological Research (LTER) site near Manhattan, KA in July of 1989. The FTIR source and spectrometer were mounted on the lift gate of a truck so that the instrument could be raised from near-ground level at 1 m to a 2 m level. Samples were collected at one height for 10 minutes then moved to the other height for a 10 minute collection period. This procedure was repeated over a 3 day period (July 25, 26, 27, 1989 - Julian days 206, 207, 208).

Our initial results were encouraging as a significant gradient could be detected for most gases. In some cases, such as for water vapor, this gradient agreed reasonably well with that measured by a Bowen Ratio station in the same vicinity (Fig. 5). During some of our measurements the gradient was opposite to that expected. Presumably, this was the result of the rapid changes in surface layer conditions that were missed due to the time required to move the instrument from one height to another and realign it.

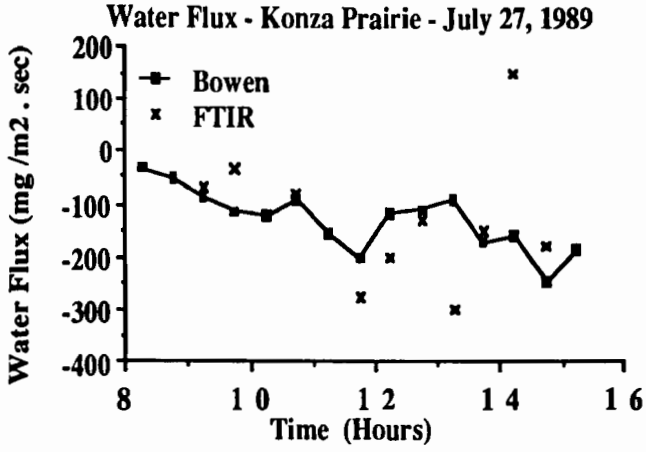
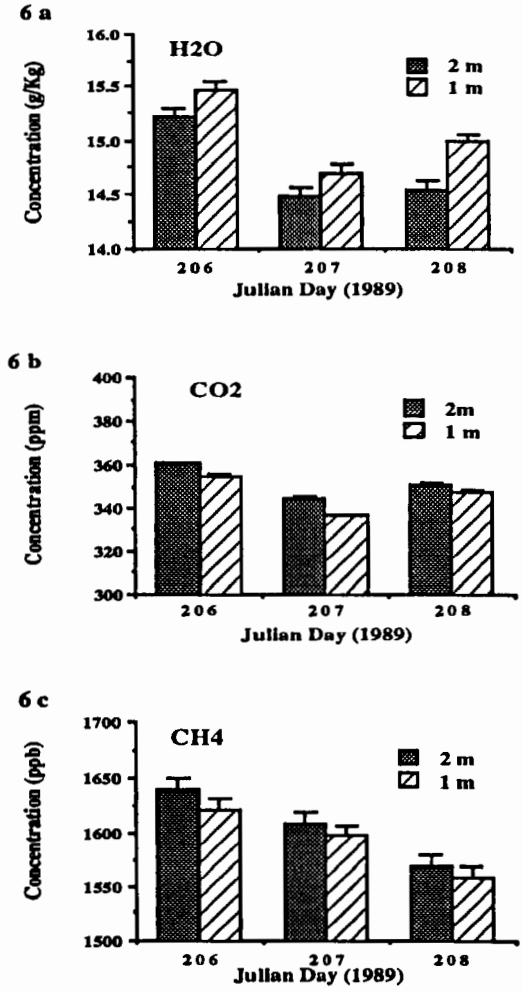


Figure 5. Water fluxes as quantified by long-path FTIR and a Bowen Ratio station at the Konza prairie research area on July 27, 1989. The values are based on the concentration gradient at 2 m and 1 m heights above the ground. Negative values indicate that the direction of the flux is away from the soil and vegetation.

Figure 6 shows the concentration gradients that were monitored for the 3 days of sampling. There are several noteworthy items: 1. Water gradients were always negative as should be the case under stable surface layer conditions (concentration at 2 m < concentration at 1 m). 2. Daytime CO_2 gradients always showed a positive gradient presumably reflecting the active CO_2 absorption by plants. 3. Of even greater significance was the positive gradient for CH_4 coupled with the significant daily decreases in CH_4 concentrations. A rain event on July 23 (Julian day 204) was followed by a drying period for the remainder of the sampling days. The sequence is likely due to a high rate of oxidation of CH_4 by methane oxidizers in the local soils coupled with a decrease in atmospheric concentrations as the general area dried. The regional source of the CH4 is not known. 4. CO concentrations also demonstrated a constant drop through the sampling period. A shift in the wind away from the direction of an interstate that ran just north of the site to a more southeasterly direction is a likely explanation for this change as anthropogenic sources far exceed biological sources.



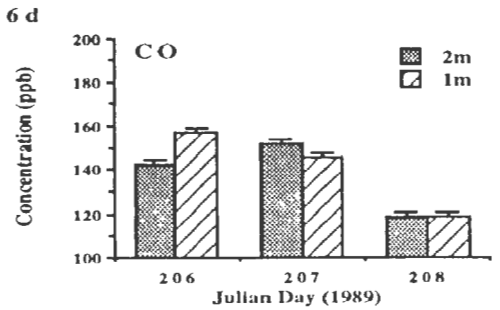


Figure 6. Concentration gradients for H_2O (6a), and trace gases - CO_2 (6b), CH_4 (6c) and CO (6d) measured by long-path FTIR on the Konza Prairie research area during the period July 25-27,1989.

Air Quality Monitoring

In an effort to explore the possibility of using the FTIR to monitor air quality in the metropolitan area of Albuquerque, N.M., we set up the instrument to analyze over a path of about 500 m. A portion of this path was just over the level of automobile traffic on one of the main traffic arteries in Albuquerque. The sampling period extended from rush hour through the period of peak fireplace smoke emission. A primary purpose of the experiment was to determine if methyl chloride (an indicator of wood smoke source) could be detected. Concentrations of this gas were found to be too low to be detectable even at the 500 m pathlength due to both low concentrations and relatively poor absorption by this molecule. However, examination of the spectra showed that a number of gases which are not normally detectable under clean air conditions were present in elevated levels. Ethylene and methanol were easily detected while ammonia and formaldehyde were also above detectable concentrations.

These tests were carried out on two nights during the winter of 1989-90. The first was on Dec. 8, 1989. This had been declared a no-burn night by the City's Environmental Health Department meaning that no wood burning in fireplaces or stoves was permitted. Gas sampling began at about 5:40 PM and continued until 11:00 PM. Figure 7 shows the level of gas concentrations for N_2O, CO, CO_2, CH_4, H_2O and C_2H_4. Values are means of 10 - one minute samples. All of the gases, with the exception of N_2O, increased until about 7:30 PM at which time they began a steady decline. The second sampling date was Jan. 12, 1990. This night was not declared a no-burn night by the city although it was expected to be marginal with respect to weather conditions which could assist with the dispersal of gases emitted by wood burning or automobiles. Indeed, surface wind conditions for both nights were quite similar. On Jan. 12, most of the data for the period 7:40 to 9:15 were lost due to problems with the FTIR instrument (Fig. 8). As with the Dec. 8 date, all gases tracked each other with the exception of N_2O which showed an inverse pattern. However, unlike the December collection, the gases showed a steady increase from 5:00 PM until about 10:00 PM when they began to decline. While the time of peak levels was different, concentration of peak levels for all gases were generally comparable. Table 1 gives the maximum, minimum, and mean concentrations for all of the gases measured for the two sampling dates. The sampling intervals for the two dates were not the same although total sample numbers were similar.

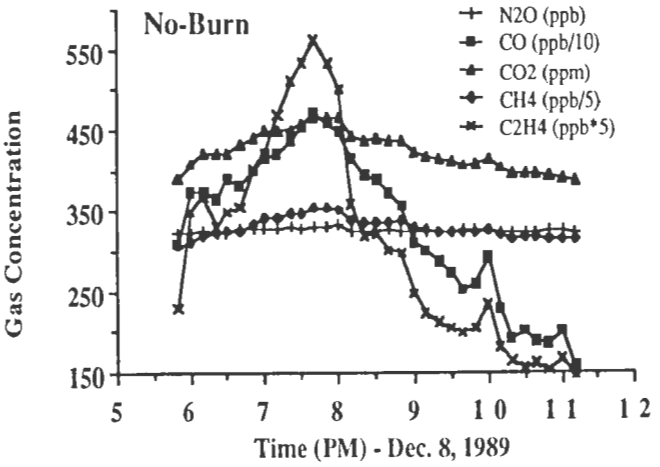


Figure 7. Trace gas concentrations measured by long-path FTIR during a no-burn (no wood burning allowed) night in Albuquerque, New Mexico. Values are concentrations from the means of 10 - 1 minute. samples on the night of December 8 1989. Pathlength was 500 m.

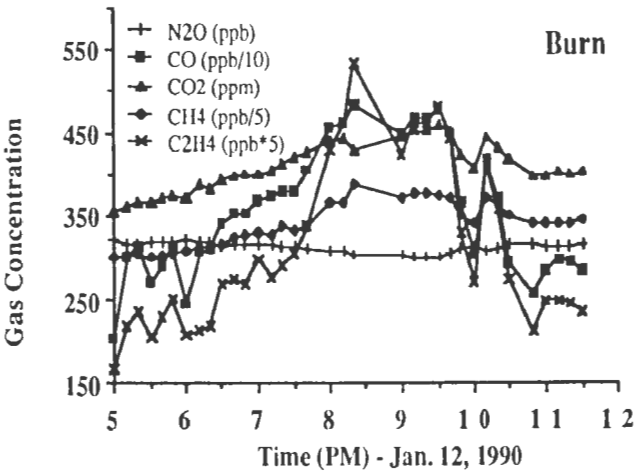


Figure 8. Trace gas concentrations measured by long-path FTIR during a night when wood burning was allowed (Jan. 12, 1990). Pathlength was 500 m.

Table 1. Mean, maximum and minimum concentrations of trace gases measued with long-path FTIR on Dec. 8, 1989 (No-Burn) and Jan. 12, 1990 (Burn) in Albuquerque, NM.

		Mean		Maximum		Minimum	
Gas	Units	No-Burn	Burn	No-Burn	Burn	No-Burn	Burn
N_2O	ppb	328	314	337	324	317	297
CO	ppb	3316	3438	4980	5274	1518	1763
CO_2	ppm	426	405	472	463	386	353
CH_4	ppb	1659	1678	1790	1946	1522	1494
H_2O	ppm	2037	2204	2181	2300	1926	2127
CH_3OH	ppb	7.7	15.2	31	30	0	3
C_2H_4	ppb	61.6	59.2	120	110	23	30
NH_3	ppb	16.7	19.7	36	26	9	14

While the small sample size precludes any definitive conclusions as to the relative contribution of wood-burning and automobiles to the elevated levels of the sampled gases, some things are suggested by the data.

1. The timing of the peak CO level on the burn night suggests that wood-burning contributes a considerable quantity of CO to the city air when permitted.

2. Based on mean and maximum CO levels for the two nights, firewood burning contributes proportionately more CH_4, CH_3OH and NH_3 than vehicle emissions while automobile exhaust shows a greater contribution of CO_2, N_2O and C_2H_4.

3. On the burn night, the CO concentrations were extremely erratic during the time of maximum traffic. This indicates a nearby source due to heavy vehicle traffic. Later in the evening, the concentrations were less erratic suggesting a less proximate source which would likely be the case for wood smoke.

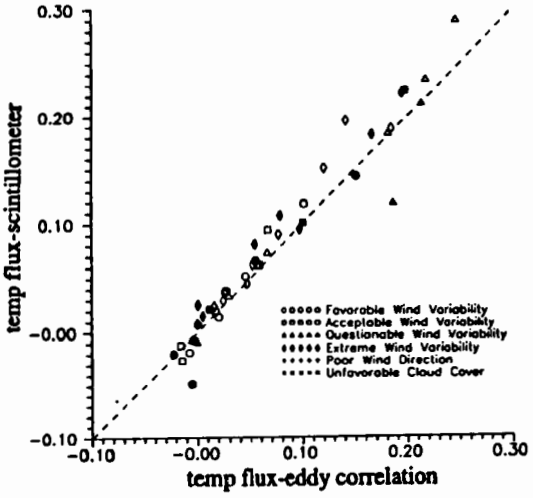


Figure 9. Temperature flux measured by the flux scintillometer compared with temperature flux from eddy correlation. Units are ^oC m s^{-1}.

Scintillometry

Comparison of the temperature flux and friction velocity determined from the fluxes scintillometer with that obtained from the point sensors are shown in figures 9 and 10. These data show that the fluxes scintillometer gives good values even in nonideal atmospheric conditions. Even during periods of intermittent cloud cover and unfavorable wind conditions, when the validity of the Monin-Obukhov similarity is limited or unknown, measurements obtained from the fluxes scintillometer compared well with the point sensor measurements.

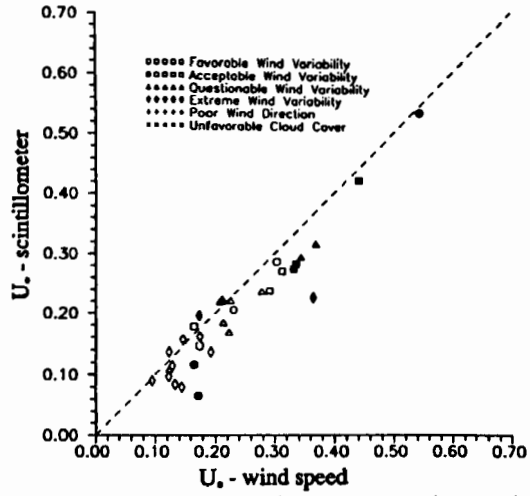


Figure 10. Friction velocity measured by the flux scintillometer compared with friction velocity deduced from wind speed, surface roughness, and eddy-correlation temperature flux. Units are m s^{-1}

Integration of FTIR and Scintillometry

Our next step in the integration of the FTIR system with the long-path measurement of water and heat fluxes involves two steps. The first is the development of 2 scintillometers by the WPL. One uses a 10.6 μm wavelength Laser source; the other uses a 3 mm wavelength Gunn diode source. The combination of thes two scintillometers with the fluxes scintillometer allows long-path measurement of the fluxes of latent heat sensible heat and momentum. Modification of the FTI system to allow it to measure gas concentrations at tw heights almost simultaneously is the second proposed modification. This will be accomplished through the use of a periscope system that will eliminate the lengthy delays in realignment that are necessary when the entire instrument must be moved vertically as was the case in th Konza Prairie experiment.

Two related methods will be used to derive gas fluxes from FTIR and scintillometry measurements. These are outlined

by Andreas (6). The first uses the Obukhov length L from measurement of vertical momentum, u_* and the temperature and water vapor fluxes. These, combined with the gas concentrations, G_1 and G_2 measured at the two heights z_1 and z_2 by the FTIR, will give an estimate of the corresponding flux scale g_* from the relation

$$\Delta G = G_2 - G_1 = (g_*/K)[\ln (z_2/z_1) - u_g(z_2/L) - u_g(z_1/L)] \quad (2)$$

as suggested by Hicks and Liss (7). The gas flux is then given by $F_g = -u_* g_*$. The second method will use a modified Bowen ratio method which is based on the belief that u_g should be the same for all conservative scalars. In particular, the difference in water-vapor mixing ratio, ΔQ, also satisfies equation 2

$$\Delta Q = Q_1 - Q_2 = (q_*/K)\ [\ln (z_2/z_1) - u_q(z_2/L) - u_q(z_1/L)] \quad (3)$$

where q_* is the water vapor flux scale. Since $-u_* g_* = F_g$ is the gas flux we are seeking and $-u_* q_* = F_q$ is the water flux, and since we assume ug=uq, Equations 2 and 3 yield:

$$F_g = F_q\ (\Delta G/\Delta Q) \quad (4)$$

To use equation 4, we obtain ΔG and ΔQ from the FTIR and F_q from the scintillometers.An important assumption of the application of gradient profiling is that the various gases for which fluxes are being derived behave similarly to heat and water vapor in the atmosphere. The scintillometry system measures path averaged fluxes of heat, momentum and humidity with scintillometers measuring at 1 mm, 10μm, and 1μm. Gaseous flux estimates are then based on these measurements of atmospheric conditions. All gases might not have identical flux profile relationships that lead to equation 2; that is it may be that $u_g \neq u_q$ (8). It will be critical in future work to determine the flux-profile relationships for trace gases.

CONCLUSIONS

Our research to date with long-path FTIR spectroscopy and path-averaged scintillometry has resulted in the following conclusions.

1) Long-path FTIR has the analytical sensitivity to measure numerous atmospheric trace gases both anthropogenically and naturally derived at ambient concentrations.

2) Increased pathlength commonly adds to the sensitivity with which we can measure atmospheric trace gases.

3) Optical scintillometry is a potential tool for measuring path-averaged fluxes of heat, momentum and humidity in the atmosphere over the same path in which gas concentrations are being determined by long-path FTIR.

4) Gradient profiling using long-path, path-averaged FTIR spectroscopy has been used to show distinct vertical structure of H_2O, CO_2 and CH_4 in the atmosphere over a prairie.

5) Coupling gradient profiling of atmospheric trace gases with the long-path FTIR and path averaged scintillometry is a promising means to begin to estimate gas fluxes at larger spatial scales from various landscapes. Applications are seen for both field screening of hazardous waste and toxic chemical emissions to the atmosphere and for many global greenhouse gases.

ACKNOWLEDGEMENTS

This work was supported by a grant from the National Science Foundation (BSR 8618487). We also wish to acknowledge Bill Herget of Nicolet Instruments for his technical assistance in getting the FTIR instrument set up and operational, Tom Garrison and Greg Shore for help with collection and processing of FTIR data and Yorgos Marinakis for help in collecting and interpreting micrometeorological data. We would also thank Shashi Verma for sharing his micrometeorological data from the 1989 FIFE experiment at Konza Prairie.

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DISCUSSION

JOHN EVANS: I was just curious how you calibrate the instrument and secondarily, what sort of precision and accuracy of the path length average concentration you get for something, like methane, for example.

DOUG MOORE: We calibrated FTIR using white cell, .25 meter white cell in the laboratory. And for things like methane we get detection limits of about 30 ppb, plus or minus.

JOHN EVANS: What sort of precision and accuracy can you get on normal measurements say, in the atmosphere?

DOUG MOORE: Well, yes, that's going to be path dependent. I'm not sure I understand. What numbers do you want it in?

JOHN EVANS: Well, we see a graph up there with some numbers up and down. Are they 1%, 10%, 50% accuracy precision?

DOUG MOORE: We're better than 5% accuracy. Probably better than that on the long path.

TOM PRITCHETT: When you were actually measuring this flux, do you have to shine the beam directly over the source, or do you shine the beam downwind of the source in looking at any downwind transport?

CLIFF DAHM: Our applications are quite a bit different than many other people who are looking at point source. We're not looking at point source emission. We're looking at something that's broadly distributed across the environment. So, what we're looking at is something where we really need to know something about fetch length from which the sources are generated. But we're not looking at a point source. If we are looking at a point source, we would go into point source analysis, we would have to be downwind and perpendicular to that point source, or over that area of point source. What we're looking at, though, is landscape emissions of things that tend to be distributed rather, at least reasonably, uniformly over the environment.

TOM PRITCHETT: So, basically you're looking at the flux as coming directly underneath your beam, essentially?

CLIFF DAHM: That's a very difficult question as to exactly where those gases are coming. They're coming from downwind. It's very dependent, of course, on wind field conditions at the time you're making the measurements. But you can be generating input terms to your vertical structure of the atmosphere that can be anywhere up to 100 times the height you are above the ground, 100 times upwind of that direction. Again, it depends very much on meteorological conditions at the time of the emission.

PATTERN RECOGNITION METHODS FOR FTIR REMOTE SENSING

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ABSTRACT

Digital filtering and pattern recognition methods are described that implement an automated detection algorithm for passive Fourier transform infrared (FTIR) remote sensing data. The detection is performed with only a 76-point segment of the FTIR interferogram, thereby enabling a "short-scan" interferometer to be used. Two novel pattern recognition methods are introduced that provide for the intelligent selection of training set patterns and for the calculation of collectively optimized piecewise linear discriminants. This methodology is evaluated with a large quantity of passive FTIR remote sensing data and is shown to perform in a highly effective manner.

INTRODUCTION

Fourier transform infrared (FTIR) remote sensors are environmental monitoring devices that employ an interferometer-based optical system to collect infrared spectral data in the outdoor environment. The resulting data can be analyzed for the presence of characteristic spectral bands corresponding to target analytes.

Infrared remote sensors can be operated in two ways. The spectrometer can be used with an external blackbody infrared source, or the sensor can be employed in a passive mode simply to collect whatever ambient infrared background radiation is present in the field of view. The passive technique is the more flexible of the two implementations, as the sensor consists of a single unit.

Specific application environments for passive FTIR sensors include monitoring at hazardous waste sites, leak detection at chemical plants, and regulatory monitoring of smokestack emissions. In these applications, the spectrometer can be positioned in a stationary configuration or mounted in a ground or airborne vehicle.

Two fundamental problems limit the applicability of passive FTIR sensors in demanding monitoring applications. First, the sensor must be rugged enough to operate under the conditions required for the application. For example, in an airborne implementation, the spectrometer must be stable enough to allow data collection under conditions of moderate vibrations or varying G-forces. Second, in the passive FTIR experiment, no stable infrared spectral background exists for use in processing the collected data. Standard laboratory spectral processing techniques that employ a background or reference spectrum cannot be used.

The most fragile component of a typical FTIR remote sensor is the interferometer drive mechanism, which must allow the collection of a stable interferogram of 1024 or 2048 points. The required interferogram length is dictated by the spectral resolution required to detect the target analyte(s) of interest. This relationship between interferogram length and spectral resolution derives from an inherent characteristic of the Fast Fourier Transform (FFT), the data processing tool used to extract infrared spectra from the collected interferograms. The FFT assumes that the interferogram is an infinitely long waveform that contains zeros for all points not explicitly collected. This has the effect of adding $\sin(x)/x$ components to the computed spectrum, resulting in spectral broadening. As the number of collected interferogram points is increased, the $\sin(x)/x$ contribution

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is decreased. Correspondingly, spectra computed from very short interferograms are severely distorted due to these effects.

One approach to increasing the potential ruggedness of an FTIR remote sensor is to adopt a simplified "short-scan" interferometer design. The drive mechanism for such a system would allow only the collection of a 100-200 point interferogram segment. Conceptually, this system would be much more rugged than a conventional design, as the moving mirror of the interferometer would need to maintain optical alignment for only a very short distance. The drawback to such a system is that a conventional spectral-based analysis cannot be performed, due to the characteristics of the FFT noted above.

Recently, we have introduced an alternative FTIR data processing strategy that is compatible with short interferograms (1). The approach used is based on the application of bandpass digital filters directly to short interferogram segments. If the filter bandpass is chosen to coincide with the frequencies of the spectral band(s) of a target analyte, the application of the filter has the effect of extracting specific spectral information directly from the interferogram segment. This approach overcomes the limitations of the FFT, but still allows the data analysis to be based on selected infrared frequencies. Additionally, judicious choice of the interferogram segment allows the analysis to be performed without the use of data describing the infrared background.

The principal drawback to this scheme is the difficulty in interpreting the filtered interferogram data. Virtually every application of FTIR remote sensing requires that the collected data be interpreted automatically and a decision made as to the presence or absence of the target analyte(s). In application scenarios such as leak detection, a positive decision regarding the presence of the analyte is used to trigger an alarm. Clearly, in such cases, the decision-making aspect of the analysis is critical.

In the work presented here, pattern recognition techniques are described that allow the implementation of an effective decision-making algorithm for use in analyzing filtered interferogram segments. The utility of this methodology is demonstrated through the use of a large quantity of passive FTIR remote sensing data.

EXPERIMENTAL

The FTIR remote sensing data used for this research were collected with a passive FTIR sensor built by Midac Corp. (Costa Mesa, CA) to the specifications of the U.S. Army Chemical Research, Development, and Engineering Center, Edgewood, MD. The spectrometer design is based on a linear-drive Michelson interferometer coupled with a liquid-nitrogen-cooled Hg:Cd:Te detector that responds in the range of 8-12 um. The collected data consisted of 1024-point interferograms, with a corresponding spectral resolution of approximately 4 cm^{-1}. The data collection was performed with the instrument placed on a tripod. Under a variety of infrared background conditions, a test analyte, SF_6 (Matheson Gas Products, Secaucus, NJ), was released in the field of view of the spectrometer. SF_6 was selected as a target because of its use as a standard test compound in pollution monitoring. It has a single strong absorption at 940 cm^{-1}. Due to the great variety of infrared backgrounds observed, the collected data contained both SF_6 absorption and emission bands.

The data analysis described here was performed by use of software written in FORTRAN-77 and assembly language. The design of digital filters and the selection of the pattern recognition training set were performed on a Prime 9955 computer system operating in the Gerard P. Weeg Computing Center at the University of Iowa. The pattern recognition analysis was performed on a Hewlett-Packard Vectra RS/20c, a 20-MHz 80386 IBM PC-compatible microcomputer with 4 Mb RAM (Hewlett Packard, Inc., Sunnyvale, CA). The MS-DOS 3.3 operating system was used. The compilers, assembler, and operating system used with the Hewlett-Packard system were manufactured by Microsoft, Inc. (Redmond, WA). This software was executed under the Desqview-386 multi-tasking environment (Quarterdeck Office Systems, Santa Monica, CA).

OVERVIEW OF INTERFEROGRAM-BASED ANALYSIS

Figure 1 displays the action of a bandpass digital filter in the spectral domain. A single-beam spectrum is displayed with an absorption band at 940 cm^{-1} from the analyte, SF_6. The interferogram producing this spectrum was collected with the remote sensor positioned on top of a building looking down at a ground source of SF_6, approximately 180 feet away. Superimposed on the spectrum is a Gaussian-shaped frequency response function of a digital filter. The frequency response has a width at half maximum of 33.0 cm^{-1}, and is centered on the SF_6 absorption band. This filter can be applied in the spectral domain by multiplying the frequency response function by the single-beam spectrum. The resulting filtered spectrum is zeroed outside of the filter bandpass, and the SF_6 absorption is superimposed on the filter bandpass function.

The same filtering procedure can be performed in the interferogram domain. Here, the correspond-

ing operation is the convolution of the interferogram and the time-domain representation of the frequency response function.

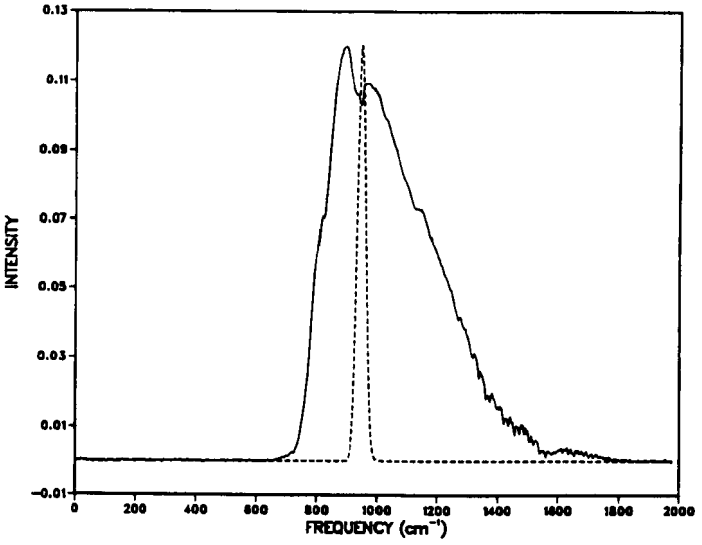

Figure 1. Single-beam spectrum (solid line) with filter frequency response (dashed line) superimposed.

In mathematical terms,

$$H(f)X(f) \longleftrightarrow \int_{-\infty}^{\infty} h(k)x(t-k)\,dk \qquad (1)$$

where H(f)X(f) is the product of the frequency response function, H, and the single beam spectrum, X. The Fourier transform pair of H(f)X(f) is the convolution of the raw interferogram, x, and the interferogram-domain representation of the filter bandpass, h (termed the impulse response of the filter). H and X are functions of frequency, f, while h and x are functions of the time variables, t and k.

In the interferogram, the filtering operation suppresses those sinusoidal signals whose frequencies lie outside of the filter bandpass. The filtered interferogram is thereby reduced to two features: (1) the interferogram representation of the Gaussian frequency response function and (2) the corresponding representation of the analyte band. As the Gaussian feature is wider than the absorption band, its interferogram representation damps at a faster rate. Thus, beyond the point in the filtered interferogram where the representation of the Gaussian feature has damped to zero, the dominant information is a sinusoidal signal whose amplitude is related to the height of the analyte absorption band.

Figures 2 and 3 illustrate these concepts. Figure 2 depicts points 160-235 (relative to the centerburst) in two unfiltered interferograms. The lower interferogram corresponds to the single-beam spectrum in Figure 1. The upper interferogram was collected during the same experiment, but SF_6 was not present in the field

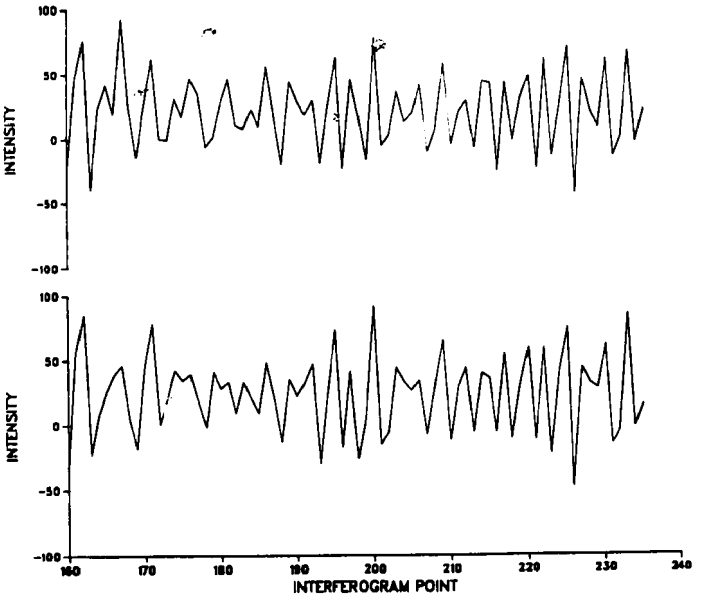

Figure 2. Segments (points 160-235) of two interferograms collected by the remote sensor. SF_6 was present when the lower interferogram was collected.

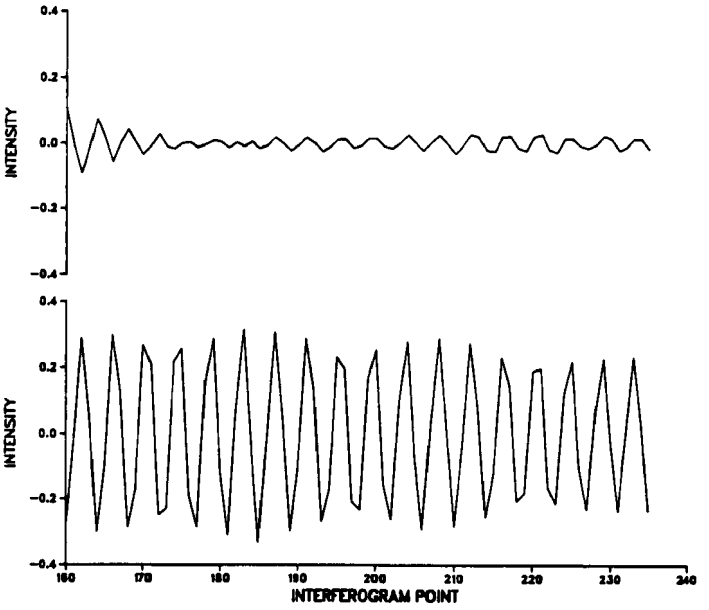

Figure 3. Interferogram segments from Figure 2 after application of the bandpass filter. The SF_6 information is now clearly seen in the lower plot.

of view of the spectrometer. No discernible difference can be seen in the two interferograms to indicate the presence of SF_6 information in the lower plot. Figure 3 displays the same interferogram segments after application of an interferogram-domain digital filter developed to approximate the frequency response in Figure 1. By suppressing frequencies other than those associated with the targeted spectral band, the filtering operation produces a signal that can be used to detect the presence of the analyte. The 76-point sinusoidal signals in Figure 3 form the test data used in this work in the development of an automated detection scheme for passive FTIR remote sensors.

DIGITAL FILTER DESIGN STRATEGIES

The design of a practical digital filter for use in the manner described above requires that the h(k) values in eq. 1 be generated such that the convolution integral can be approximated accurately. Additionally, the approximation must be truncated to a finite number of terms. The most common approach to this approximation takes the form of

$$x'_t = h_0 x_t + h_1 x_{t-1} + \ldots + h_k x_{t-k} \qquad (2)$$

where x'_t is point t in the filtered interferogram, the h_k are as defined above, and the x_{t-k} are points in the raw (i.e. unfiltered) interferogram. Since the impulse response function has been truncated to a finite number of terms, filters of this type are termed finite impulse response (FIR) digital filters.

The most widely used approach to the generation of FIR filter coefficients was developed by McClellan and Parks (2). In this method, the Remez-Exchange algorithm is used to generate a series approximation to the frequency response function of the filter. The h_k are then computed directly from this series approximation.

Recently, we have introduced a design strategy for FIR filters based on regression analysis (3). This approach is based on two considerations. First, some of the terms in eq. 2 are undoubtedly more significant than others in obtaining a good approximation to the convolution integral. Therefore, it may be possible to delete some terms without a significant loss in filter performance. Given that eq. 2 is a linear model, standard regression analysis techniques can be used to assess the significance of the individual terms. In this computation, a set of interferograms collected by the remote sensor is used to build the regression models.

Second, a better approximation to the convolution integral may be obtained by utilizing a different set of filter coefficients for each interferogram point. For example, interferogram points 160 and 161 would be filtered with different filter coefficients. Analogously, the filter for use in application to a 100-point interferogram segment would contain 100 sets of filter coefficients.

We have termed these filters FIR matrix (FIRM) filters, as the filter format defines a two-dimensional matrix of filter coefficients. By tailoring each filter to an individual point, smaller sets of filter coefficients can be used at each point, thereby saving computation time. In testing, FIRM filters outperformed conventional FIR filters with twice the number of coefficients.

For the work reported here, a FIRM filter was generated for points 160-235 based on a set of 2429 interferograms collected by the FTIR remote sensor. Both SF_6-containing (429) and non-SF_6 interferograms (2000) were present. The filter was generated to approximate the frequency response shown in Figure 1. The region of points 160-235 was selected as the point at which the information due to the Gaussian frequency response function has effectively damped to zero. Across this point range, the Gaussian signal decreases from 0.2% to 0.0005% of its maximum value.

In the filter calculation, a stepwise multiple linear regression procedure was used to select statistically significant terms from the region of t-0 to t-100 in eq. 2. To be included in the final model, terms had to meet a significance level of 99.99%, based on the F distribution. The resulting filter averaged 37 coefficients per point, while the average value of R^2 for the regression calculations was 93.2%. This filter was used in the generation of Figure 3.

INTERFEROGRAM ANALYSIS BY PATTERN RECOGNITION

The filtered interferogram segments in Figure 3 are easily differentiated. However, as the analyte band decreases in intensity to the limit of detection, the corresponding filtered interferogram segments are indistinguishable from those arising solely from background noise. If a decision is to be made regarding the presence of the analyte, a procedure must be devised for distinguishing interferogram segments exhibiting weak analyte signals from those exhibiting only noise.

Pattern recognition techniques are numerical algorithms for use in classifying data objects ("patterns") into categories or classes. These methods have been used in a variety of applications in chemistry (4-6). In the present example, interferograms belong to one of two dis-

tinct categories: (1) SF_6-active or (2) SF_6-inactive. The patterns in this case are the 76-point filtered interferogram segments. These interferogram segments can be considered as points in a 76-dimensional vector space. If the points corresponding to the given categories cluster together in the data space, pattern recognition techniques can be used to assign unclassified points to the appropriate categories.

Two issues are paramount in developing a successful pattern recognition analysis scheme. First, a representative set of example data must be obtained for use in developing the data classification algorithm. This "training set" of data must, to the degree possible, encompass the range of patterns to which the analysis will be exposed. Second, the appropriate pattern recognition algorithm must be selected. A knowledge of the data space must be gained in order to make the proper selection. Both of these issues are addressed below for the case of the filtered interferogram data.

OPTIMAL SELECTION OF TRAINING SET MEMBERS

When initially forming a training set, it is desirable to select a variety of patterns from a pool of candidate patterns that is as large as possible. A training set comprised of a large number of patterns is not necessarily the same as one comprised of a large variety of patterns, however. Many of the available patterns may effectively be duplicates. The intelligent selection of training set members involves maximizing pattern diversity while minimizing the inclusion of duplicate patterns.

This type of optimized selection of training set members becomes increasingly complicated as the number of candidate patterns increases and as the dimensionality of the patterns themselves increases. In the present example, 31 different data sets were collected, consisting of approximately 14,700 interferograms. Standard techniques for deducing pattern similarity such as the calculation of all pairwise distances between patterns are computationally cumbersome with data sets of this size. To address this problem, we have developed an algorithm which provides an automated way to select optimal training sets which have the same characteristics as the starting pool of candidate patterns.

The intelligent selection of patterns for use in the training set requires some type of distance calculation to quantify the relationships among the data points. Performing this calculation with the 76-dimensional data is undesirable, however, due to the high computational cost. The selection process can be greatly simplified by reducing the dimensionality of the patterns. This can be accomplished through the use of principal components analysis (7,8). For n-dimensional patterns, an optimal p-dimensional representation can be formed simply from the projections of the n-dimensional patterns onto the first p principal components. To insure the accuracy of any subsequent interpoint distance calculations, p is typically chosen to span a large fraction (e.g. 95%) of the data variance.

Patterns for the training sets were chosen by use of an algorithm which divides a p-dimensional principal components space into smaller p-dimensional volumes. One pattern is then selected from each of the smaller volumes, thus providing equitable, global sampling of all patterns in the principal components space. For ease of conceptualization, this global sampling strategy is illustrated in three dimensions in Figure 4. The total number of smaller volumes, blocks in this case, as well as the shape of the blocks, is determined by the number of specified divisions along each principal component. The number of divisions is termed the mesh size. Each of the smaller volumes may contain several patterns, as shown in the expanded view of one of the blocks in Figure 4. To insure that the pattern selected from that block is the most different from patterns selected from neighboring blocks, the pattern closest to the center of each block is chosen. The center of the block in the expanded view is indicated by a solid dot. Applying this procedure to all blocks results in a smaller set of selected patterns

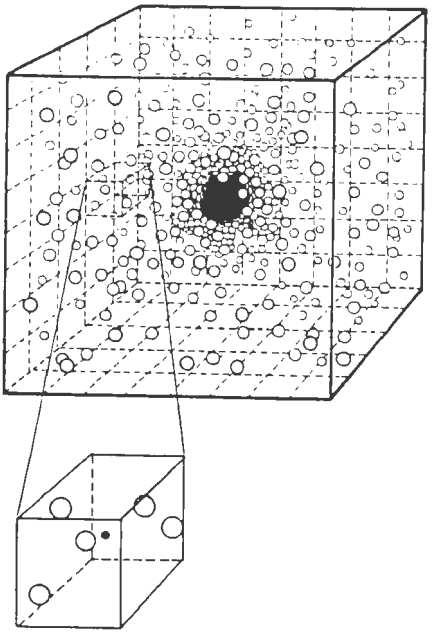

Figure 4. Conceptual depiction of the division of a three-dimensional principal components space into smaller three-dimensional volumes. Patterns are selected from each of the smaller volumes.

which preserves the overall distribution of patterns in the full data set. For the filtered interferogram data, the spread of patterns for the two data classes is different. For this reason, the principal components analysis and pattern selection were performed individually for the two data classes.

After the number of blocks and their dimensions are defined, each block is assigned a unique number from 1 to the total number of blocks, N_b. N_b is defined as

$$N_b = \prod_{j=1}^{p} m_j \qquad (3)$$

where m_j is the selected mesh size for the j^{th} principal component and p is the number of principal components being used. The relative location of each pattern is thus defined by determining its block number. Since the block numbers are positive integers, the real principal components coordinate values of each pattern are also converted to positive whole numbers. Coordinates along the j^{th} principal component are transformed as

$$c_j' = m_j[(c_j - c_{j,min})/(c_{j,max} - c_{j,min})] \qquad (4)$$

where c_j' is the transformed coordinate, c_j is the original coordinate, m_j is the mesh size defined above, and $c_{j,min}$ and $c_{j,max}$ are the minimum and maximum coordinates along the j^{th} principal component. The computed c_j' values are then rounded to the nearest integers, thereby creating a new set of coordinates for each pattern. The transformed integer coordinates are designated as c_j''. The block number, B, of any pattern can then be computed directly as

$$B = c_1'' + \sum_{i=2}^{p} [(c_i'' - 1) \prod_{j=1}^{i-1} m_j] \qquad (5)$$

where c_1'' is the integer coordinate value of the pattern along the first principal component, c_i'' is the integer coordinate value along the i^{th} principal component, and p and m_j are as defined above. After computing the block number for a given pattern, the center of the block and the distance to the pattern are computed using the c_j'. This distance is used later to select the pattern which is closest to the center of the block. The patterns are then sorted by increasing block number, and the total number of occupied blocks is calculated. The final set of optimum patterns is selected by sampling each of the occupied blocks.

This procedure was used to reduce the set of 14,700 interferograms to 4000. Of the 4000 filtered interferogram segments chosen to form the training set, 2000 contained SF_6 signals, while 2000 contained no SF_6 information. Six principal components were used in the selection of the non-SF_6 patterns, while three principal components were used in the selection of the SF_6-active patterns. This training set was used in the development of a pattern recognition scheme for the automated detection of SF_6 signals in the filtered interferogram data.

PIECEWISE LINEAR DISCRIMINANT TECHNIQUES FOR THE AUTOMATED DETECTION OF SF_6

The selection of an appropriate pattern recognition technique for the SF_6 detection problem is keyed by an investigation of the manner in which the SF_6 and non-SF_6 data classes cluster in the 76-dimensional space. Principal components analysis can be used to explore these relationships visually. Figure 5 is a plot of the projections of the 4000 training set patterns onto the first three principal components of the data. SF_6-active interferogram segments are indicated by open circles, while non-SF_6 interferograms are indicated by solid triangles. All of the non-SF_6 points are clustered at the center of the plot. To provide a better view of the interface between the data classes, Figure 6 is an expanded view of the boxed region in Figure 5. It is clear from an inspection of Figure 6 that the data classes merge at the limit of detection of SF_6.

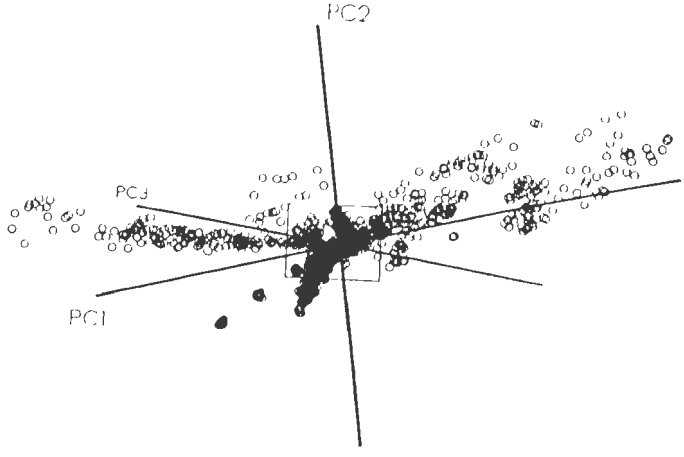

Figure 5. Principal components plot depicting the relationships among the 4000 patterns in the training set. SF_6-active patterns are depicted as open circles. The non-SF_6 patterns (solid triangles) are all located in the boxed region.

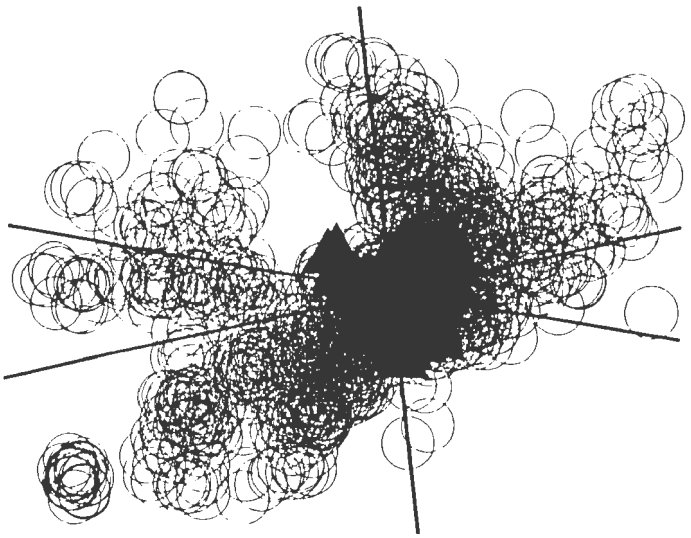

Figure 6. Expanded view of the boxed region in Figure 5. The SF_6-active patterns are again indicated as open circles, while the non-SF_6 patterns are indicated as solid triangles.

Consideration of the class distributions in Figures 5 and 6 suggests that piecewise linear discriminant analysis (9,10) is the pattern recognition method of choice for the filtered interferogram data. This technique is based on the construction of boundaries or separating surfaces between the data classes. The separating surfaces are termed discriminants, as they define boundaries in the data space that allow the classes to be discriminated. The piecewise linear discriminant consists of multiple linear surfaces which collectively form a piecewise approximation of a nonlinear separating surface. The need for a nonlinear discriminant is clearly motivated in Figures 5 and 6 by the circular distribution of the SF_6-active points around the non-SF_6 points.

Each linear surface comprising the piecewise linear discriminant is defined by the locus of points orthogonal to an n-dimensional vector termed a weight vector or discriminant, where n is the dimensionality of the pattern data (76 in the present example). Each weight vector, $\mathbf{w}$, is calculated such that

$$\mathbf{w}^T\mathbf{x}_a > 0 \qquad (6)$$

$$\mathbf{w}^T\mathbf{x}_n \leq 0 \qquad (7)$$

where $\mathbf{x}_a$ represents a SF_6-active pattern, and $\mathbf{x}_n$ represents a non-SF_6 pattern. The dot products in eqs. 6 and 7 are termed discriminant scores. The individual weight vectors comprising the piecewise linear discriminant are calculated sequentially, with each discriminant separating a portion of the patterns in the training set.

The algorithm used for this work calculates discriminants that have a pure-class subset on one side of the discriminant and a mixture of the two classes on the other side. A discriminant of this type is termed "single-sided". After a single-sided discriminant has been calculated, those patterns on the pure-class or single-side of the discriminant are removed from the calculation, and another discriminant is computed in the same manner. The result is a set of discriminants in which each discriminant separates a different pure-class subset. Collectively, the set of discriminants defines a separating surface.

To classify an unknown pattern, each discriminant is applied to the pattern, producing one of two possible results: (1) the pattern falls on the pure-class side of the discriminant; or (2) the pattern falls on the mixed-class side of the discriminant. The first discriminant which classifies the pattern onto the pure-class side determines the class of the pattern. The last discriminant determines the class if the unknown pattern is never classified on the pure-class side.

A multi-step procedure was devised to calculate and optimize the set of discriminants comprising the piecewise linear separating surface. The keys to this algorithm are the use of Simplex optimization techniques (11) to position each discriminant and a novel discriminant recalculation procedure to perform a collective optimization of the discriminants.

The Simplex algorithm computes a new weight vector $\mathbf{w}$ by moving the previous $\mathbf{w}$ in an optimal direction in the data space. The algorithm consists of a set of rules which governs this movement based on a numerical response function that reflects the performance of the weight vector. For the current work, many variations of response functions were implemented and evaluated. To be effective, the response function must encode several characteristics related to the performance of each weight vector, including the number of patterns separated, and whether the discriminant is single-sided. In addition, the response function should define a continuous surface along which the optimization can travel. The response function, R, used in this work is defined as

$$R = [1.0 - \underline{s}^{1/f}]\ S \qquad (8)$$

$$S = (N_s/N_t)^a\ N_s \qquad (9)$$

$$f = 2\,[\log(N_S)+1] \qquad (10)$$

S is termed the single-sided response, where N_S is the number of SF_6-active patterns separated, N_t is the total number of patterns placed on the single-side of the discriminant, and a is an exponent that penalizes discriminants that are not single-sided. Appropriate values of a have been determined empirically to be in the range of 10-200, depending on the magnitude of N_S. For a single-sided discriminant, S is equal to the number of SF_6-active patterns separated by the discriminant (i.e. $(N_S/N_t)^a = 1.0$). R is made a continuous function by the use of $\underline{s}$, the standard deviation of the discriminant scores for the non-SF_6 patterns. A smaller standard deviation value produces a larger (i.e. more optimum) value of the response function. It was hypothesized that by minimizing the variation of the non-SF_6 discriminant scores, the resultant discriminant would be more nearly aligned with the interface between the two data classes. For the data used here, the value of the standard deviation is typically on the order of 10^{-5}, and consequently must be scaled to reduce its influence on R. The scaling factor, f, is used for this purpose. Thus, the value of R can be interpreted as the value of S (i.e. number of SF_6-active patterns) that has been penalized based on the degree of variation among the discriminant scores for the non-SF_6 patterns.

The Simplex optimization described above is an effective technique for optimizing each weight vector. However, optimizing each weight vector individually may not produce the optimum piecewise linear discriminant, since the discriminant consists of a set of weight vectors. To address this problem, a collective optimization algorithm was developed for this study. The procedure used here is motivated by considering that the calculation of the initial set of weight vectors is hierarchical in nature. The calculation of each weight vector is influenced by the performance of weight vectors that have been previously computed. Each of these vectors is computed such that it separates as many of the remaining patterns as possible. In order to effect a collective optimization, a method must be developed to allow subsequent weight vectors to influence the calculation of previous weight vectors.

The recalculation is performed identically to the single weight vector calculation described above, but the data set of patterns is altered to reflect the presence of other vectors in the set. Prior to recalculating a given weight vector, those patterns classified by later weight vectors are removed from the data set. This simple procedure allows the earlier weight vectors to be repositioned based on the classification performance of the later weight vectors.

Employing the 4000-member training set, a piecewise linear discriminant was computed consisting of eight weight vectors. The Simplex optimization algorithm was used to optimize each of the vectors, and the recalculation procedure was applied to optimize the set of weight vectors collectively. The recalculated discriminant classified 3945 of the 4000 patterns correctly (98.6%).

To evaluate the prediction performance of the discriminants, two data sets were employed that were not represented among the 4000 interferograms in the original data set. The two data sets each contained 1000 interferograms. The application of a piecewise linear discriminant to a set of unknown patterns is performed by computing the discriminant score for each pattern. In a graphical representation, the results can be displayed as a plot of the discriminant scores vs. pattern number. Since multiple weight vectors are used, there are multiple discriminant scores that could be plotted. For the purposes of this analysis, the largest discriminant scores obtained by applying all weight vectors to each pattern were used. For SF_6-active patterns, the signal is then maximized, and for non-SF_6 patterns, the plotted values then reflect the distance from the pattern to the nonlinear separating surface.

Figures 7 and 8 show the resulting plots of discriminant scores for the two prediction data sets. The discriminant scores greater than zero in the plots correspond to detections of SF_6. An inspection of the figures and plots of transformed spectra indicate that the detections are highly accurate. The rate of false alarms is less than 1%. These results suggest that the combination of an intelligent training set selection algorithm along with the calculation of an optimized piecewise linear discriminant produces a sensitive, effective detection scheme for passive FTIR data.

CONCLUSION

The results presented here confirm that a short interferogram segment can be used for the reliable detection of target analytes from passive FTIR data. The combination of digital filtering and pattern recognition techniques allows this detection algorithm to be implemented. This achievement makes possible the design of a new generation of passive FTIR sensors based on the "short-scan" interferometer concept.

These results also introduce two new general-purpose algorithms for use in pattern recognition analyses. The training set selection algorithm described here can be used to select

training sets for use with any pattern recognition method. Results obtained in testing this algorithm indicate clearly that the method outperforms pattern selection strategies based on random sampling of a pool of candidate patterns.

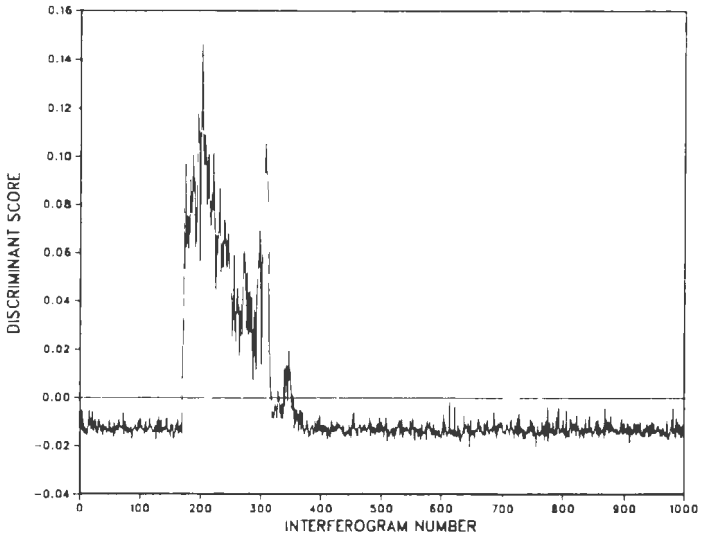

Figure 7. Plot of discriminant scores for the first prediction data set. None of these interferograms were included in the calculation of the piecewise linear discriminant.

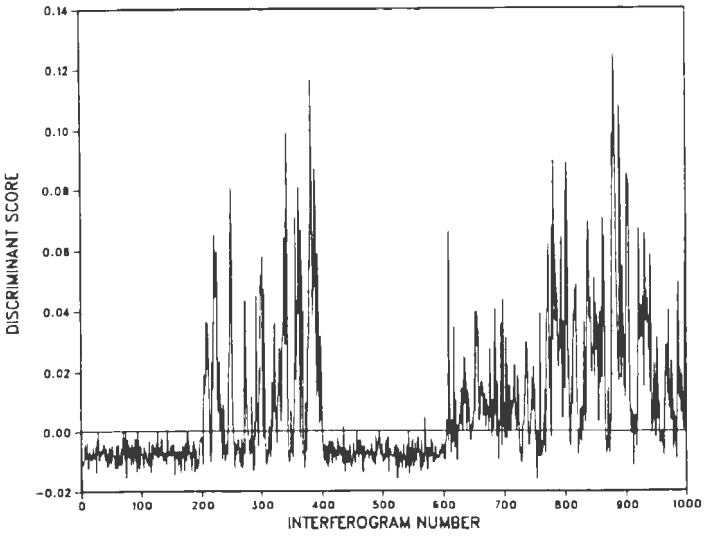

Figure 8. Plot of discriminant scores for the second prediction data set. None of these interferograms were included in the calculation of the piecewise linear discriminant.

The multi-step procedure described above for optimizing the placement of piecewise linear discriminants is also a general approach that is not limited to the remote sensing application used here. The techniques developed in this work are applicable to any pattern recognition problem in which the interface between the data classes is complex. The optimized discriminants are particularly suited to problems in which it is important that the discriminants define the limit of detection of a species.

Work is continuing in our laboratory on the overall problem of collective optimization of the weight vectors comprising a piecewise linear discriminant. We are currently exploring the possibility of operating the simplex optimization with a response function based on the performance of all weight vectors simultaneously.

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DISCUSSION

DONALD GURKA: Can you visualize a digital filter analog to the Hadamard, to eliminate the multichannel disadvantage on the transparent spectral component? For example, use a series of digital filters which would only let through the channels of information that you want to transform.

GARY SMALL: It's a nice idea. The problem would come in the construction of the filters that would have many, very narrow individual band passes. The problem that you get in the design of filters is that the narrower you want the band pass, the more difficult it is to actually implement the filter that will work in the time domain. The problem that you would come into would be having to have either many individual filters, or to have a very complex filter that would have multiple band passes. So, I think the key question would really be going back to the electrical engineering techniques that one uses in designing filters to see whether that would be viable. Our experience is that if you really want very narrow band passes, it's a difficult problem in filter design. That might be too tough, actually.

DONALD GURKA: So, the answer is yes, but it won't be easy?

GARY SMALL: The answer is it's conceptually a nice idea. I think implementing it would be difficult.

REMOTE VAPOR SENSING USING A MOBILE FTIR SENSOR

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(A) Introduction

The remote-passive detection of hazardous chemical vapors is an important application for both the military and civilian communities interested in environmental issues. Remote Fourier Transform Infrared [FTIR] Spectrometers are capable of detecting absorptions and emissions of low-concentration chemical vapor clouds using an ambient temperature atmospheric background. For many pollution-monitoring problems FTIR spectroscopy represents the only viable approach for the detection of many environmental pollutants.

Remote FTIR technology, developed to detect chemical warfare agents, is directly applicable for compliance assurance for many of the chemicals listed in the U.S. Clean Air Act. FTIR spectrometers have the potential to monitor stack emissions, hazardous components in wood smoke, auto emissions, and industrial releases. By using a FTIR one can detect vapor concentrations from chemical leaks or spills. With advanced warning provided by an FTIR, residents located in a surrounding area might be given enough time to safely evacuate. In these applications an FTIR would be mounted on an emergency response team helicopter to give an identification of a particular chemical species.

An infrared remote chemical sensor consists of a sensor and signal processor that operate in parallel to give an indication of the presence of a pollutant. The sensor detects the signatures of all chemical vapors and backgrounds, while the signal processing algorithms discriminate between the spectral features associated with the pollutant and background emissions. The typical instrumentation required for remote infrared chemical vapor sensing consists of a two wave number resolution interferometer with a specialized set of collimating optics. The signal processor detects a chemical cloud in a fixed-site application by measuring the background radiant emission profile as a function of time. When a target cloud moves into the field of an interferometer a specific change in the background radiant emission profile is detected.

Recently, a number of new applications using a remote chemical sensor have been developed using interferometers operating from helicopters, aircraft, and earth-orbiting satellites. The remote sensing problem for these cases is severely complicated because the background emission profile changes rapidly with respect to time. When operating in a rapidly moving scenario, the change in emission profile versus time cannot be

used for detection of the presence of a vapor cloud. This change in the radiant background can be an order of magnitude greater than the spectral emission profile of the vapor cloud. In order to remove the changing background spectral features a signal processing technique is needed.

The collection of data from mobile FTIR applications is further complicated by the extreme data-processing requirements in which an interferometer may collect up to 30 two wave number scans per second. For many pollution monitoring applications, size, power, cost, and weight limitations require that a low-powered signal-board computer be used for real-time data analysis. A recent development in the signal processing hardware area is the advent of the Digital Signal Processing (DSP) chip. Current DSPs are capable of processing up to 33 million floating point instructions per second. Remote sensors operating in mobile environments can benefit from the high computational throughput of single-board computers using DSP technology.

(B) THE BACKGROUND OF THE PROBLEM

One can consider the radiance incident on a remote sensor as combinations of energy from the background, the target vapor cloud of interest, and the intervening atmospheric gases. One can describe an integral equation consisting of infinitesimal layers of atmosphere. In this case, a radiance emission source will be absorbed in the layer by both the target cloud and the intervening atmospheric constituents. The radiance measured at the detector is given by the following equation, where

$$(1) \quad N = \int_0^x \{ K_T(\lambda) N_x(\lambda) - K_T(\lambda) N'(\lambda) + K_A N_x(\lambda) - K_A N'(\lambda) \} dx$$

where k_T and k_A are the extinction coefficients of the target gas and the atmosphere. N_x is the radiance of a blackbody at the temperature on the infinitesimal layer. N' is the radiance incident on the infinitesimal layer, traveling to the sensor, and x is the length variable that is integrated for the length of the target cloud and intervening atmosphere.

Assuming homogeneous atmospheric and target cloud species, the integration of equation (1) gives the power incident on a passive sensor as shown in reference [1],

$$(2) \quad P = [T_A T_T N_{BG} + (1 - T_A T_T) N_T A \Omega$$

where T_A is the atmospheric transmittance, T_T is the target cloud transmittance, N_{BG} is the radiance of the background, N_T is the radiance of a blackbody at the ambient temperature, A is the collector area, and Ω is the solid angle of acceptance of the sensor. The atmospheric cloud transmittance is

$$(3) \quad T_T = e^{-K_A R}$$

where R is the distance of the intervening atmosphere. The target cloud transmittance is

$$(4) \quad T_T = e^{-K_T L} = e^{-\alpha C L}$$

where $\alpha (m^2/mg)$ is the absorptivity of the target cloud, C is the concentration of the target cloud (mg/m^2), and L is the length of the target cloud (m).

The remote detection of a target cloud is dependent on the fact that N_{BG} and N_T will differ by up to a few percent. In equation (2) it is seen that if $N_{BG} = N_T$ then equation (2) collapses to $P = N_T A$ and the incoming radiation contains no information about the spectral properties of the intervening atmospheric gases or the target cloud. For field measurements the difference in radiance level required for detection of a vapor is generally converted into a temperature measurement. The temperature associated with a difference in radiance levels can be determined by knowing the optical wavelength and using Plank's equation. In this case the difference in temperatures of the target cloud and background is required for a detection to occur. Temperature differences required for detection using current state-of-the-art instrumentation are 0.1 centigrade for concentrations of between

1 to 20 ppm-m. The exact detection level is dependent on the absorptivity of each compound.

(C) SIGNAL PROCESSING OF REMOTE SENSING DATA FOR DETECTION AND ALARM

(1) BACKGROUND

Signal processing of remote sensing data is required to extract background spectral features from those of a vapor target cloud. It has been shown that digital filtering used in either the frequency or the interferogram space can be used to extract spectral background features.[2,3,4] Signal processing algorithms used in the interferogram space have advantages with application to detection and alarm algorithms for remote sensors. First, the signal processing algorithm does not require a conversion into the frequency domain by a Fast Fourier Transformation (FFT). This reduces the number of computations required for a detection algorithm. It also reduces some resolution degradation caused by the apodization function of the FFT in the transformed spectrum. Second, the broad band spectral background features are somewhat separated by point number in the interferogram space. In the time domain, the central fringe of an interferogram is at the zero retardation of the moving mirror of the interferometer and contains information from all spectral wavelengths. For remote sensing data the central fringe contains a disproportionate contribution of the broad-band blackbody radiation curve.[5,6] As one moves further out into the ends of the interferogram, the broad spectral components constructively interfere with each other more than the narrow band spectral features. The effect is a severe damping of the contribution of the broad spectral components. Signal processing in the interferogram domain can take advantage of this effect for remote sensing by processing only short interferogram segments located adjacent to the center-burst of the interferogram. Digital filters used away from the center-burst are not required to operate over the entire 16-bit dynamic range of the data. Because of these reasons, digital filters can be used more efficiently for signal detection algorithms in the interferogram space than in the frequency domain.

(2) FINITE IMPULSE RESPONSE FILTERS

The most commonly used digital filter for signal processing applications is known as the finite-impulse response (FIR) filter. The basic form of the equation is shown in the following equation.

$$(3) \qquad Y = \sum_{i=1}^{N} b_i \, X^{i-n}$$

where Y is the filtered data point resulting from the application of the filter, X is the input raw data values, and b_i are the filter coefficients.

The purpose of an FIR filter used for signal detection in a remote sensing interferogram is to generate narrow bandpass responses to eliminate the background information. One of the most widely used techniques for generating coefficients for an FIR filter is the process known as the Remez Exchange procedure. In this method, the filter coefficients, b, are generated through the use of the attenuation approximation theorem. In this theorem, if the approximation error of the frequency response outside of a passband response is uniformly distributed, the resulting narrow bandpass filter response error will be minimized.

The Remez Exchange procedure must satisfy the condition where the response is defined as P, where,

$$(4) \qquad P(e^{jw}) = \sum_{n=0}^{M} b_n \cos(wn)$$

A weighted error function is defined as the difference to the true response from that of P where,

$$(5) \qquad E(e^{jw}) = W(e^{jw}) \, [\, D - P(e^{jw}) \,] \, .$$

In this equation W is the passband to stopband weighing function, and D is the actual real frequency response of the function.

The alternation theorem states that for any selected set of extremal frequencies, w, the alternation condition must be satisfied where,

$$(6) \qquad E(e^{-jw}) = -E(e^{jw}i+1).$$

The Remez procedure is based on the fact that an iterative solution can be developed in a convergence procedure between equations (5) and (6). When the correct values of b are generated, then value of $E(e^{-jw})$ in the two equations will converge.

Generating narrow bandpass digital filters to extract out the signal of interest has been applied to the analysis of collected remote sensing interferograms that contain a spectral absorptions of the simulant Sulfur Hexafluoride (SF_6). In this example a narrow bandpass digital filter using 40 coefficients was developed that had a center frequency corresponding to 940 wave numbers. At the modulation frequency of the interferometer this spectral frequency corresponded to a bandpass of 50 Hz with a center frequency of 2450 Hz. Figure 1 shows two short segment interferograms collected from an interferometer mounted on a UH-1 Army helicopter travelling at 120 knots and 1000 feet altitude. The bottom interferogram was collected when the interferometer was travelling past the target cloud of SF_6. Figure 2 shows the results after filtering the segment with the 40-term digital filter. The bottom interferogram segment shows the fundamental frequency in which the SF_6 was present. It should be noted that the digital filter strategy can detect either the absorption or emission case. The result of a case of the target cloud being warmer than the background is that the resulting filter output will be 180 degrees out-of-phase from the absorption case.

The result of collecting successive interferogram segments while moving is shown in figure 3. In this figure a magnitude response of the output for the 40-term digital filter is shown as a function of time. During this run an interferometer was mounted on a UH-1 helicopter and flown around a source of SF_6. As the helicopter passed by the target cloud (three times) the instrument alarmed to make a detection. The x-axis in this figure corresponds to approximately three minutes of collected data. The target cloud was released at the beginning of the data run. During each helicopter pass the response of the digital filter became weaker due to the fact that the target cloud was dispersing in a 10 mile per hour cross wind.

(3) INFINITE IMPULSE RESPONSE FILTER

Infinite impulse response (IIR) digital filters are generally feedback loop filters in which additional filter coefficients are used. The basic form of the equation is shown in the following equation.

$$(9) Y_N = \sum_{i=1}^{N} a_i \, Y_{i-N} + \sum_{j=1}^{M} b_i \, X_{j-M}$$

The coefficients, b, are identical to the FIR case. The only difference is in the feedback response which is a weighted sum of the past output values. The weighted sum of present and past input values are added to the feedback response. The major advantage in using a narrow band IIR filter for an interferogram is that the number of coefficients is reduced making it a highly efficient filter. This effect can be illustrated in figure 4. The attenuation response in this figure shows that the IIR case has a better attenuation than for the FIR case. The two filters compared are on a logarithmic scale and have roughly equivalent numbers of computations for an interferogram segment. The major disadvantage of IIR filters are that they can be unstable over large dynamic ranges and can have phase non-linearities. A practical problem in the implementation of narrow-bandpass IIR digital filters is the required interferogram segment length for feedback response to stabilize and the output result to become constant. This

requirement is currently being studied in order to develop alternate methods for implementation of IIR filters for analyzing short interferogram segments.

(D) INSTRUMENTATION FOR REMOTE SENSING

Instrumentation currently being used for the mobile-remote detection of chemical vapors consists of an interferometer, an infrared detector, an analog signal module, and a digital signal processing module. The interferometer and detector collect the infrared background spectral radiance and convert it into an analog signal. The analog signal processing module filters and amplifies the detector signal. The analog module has a 16-bit analog-to-digital convertor to convert the signal to digital form. The digital signal processing module can analyze the data using a wide variety of signal processing techniques.

The interferometer constructed for the U.S. Army CRDEC by the Midac Corporation, Costa Mesa, California occupies 0.3 cu feet, weighs approximaely 15 pounds, and uses only 28 watts at 12 volts. The interferometer consists of a linear drive mechanical mechanism capable of collecting two wave number spectra at speeds of up to 11 scans per second. The interferometer has a Helium-Neon 10 milliwatt laser to provide a reference signal for the analog-to-digital convertor. The mechanical mechanism is controlled by two small electronic servo cards in which one card contains the analog electronics and the second card contains the digital electronics. The infrared detector used in the interferometer was purchased from Judson Electronics, Costa Mesa, California, and is a 2 mm square Mercury Cadmium Teluride (MCT) infrared detector. A narrow band detector is used in this application since the atmospheric transparent spectral window for remote sensing is only from 8 to 12 microns. A Zinc Selenide (ZeSe) beamsplitter allows the instrument to give a measured noise equivalent spectral radiance (NESR) of approximately 1.5×10^{-8} Watts/cm^2 * sr * cm^{-1}.

(E) DIGITAL SIGNAL PROCESSING HARDWARE FOR REMOTE SENSING

The requirement to perform real-time data analysis for the mobile chemical sensor can easily surpass that of today's conventional microprocessors. This is particularly true when applications demand several of the time series analytical methods. Conventional processors are designed to perform a wide variety of functions, resulting in lackluster performance during multiplication and summing operations. To overcome this shortcoming, many microcomputer users purchase an optional numerics coprocessor.

The coprocessors are microcomputers that have been optimized to perform a variety of mathematical functions. These functions include integer and floating point arithmetic as well as some algebraic functions. Coprocessors can increase the performance of a microcomputer dramatically; however, even the slowest of the DSP chips can outperform the processor-coprocessor combination by a factor of ten for common functions required for signal processing applications.

DSP processors are much faster than conventional processors because of differences in the chip design architecture. To perform the multitude of functions required by the desktop microcomputer, the internal architecture of the general-purpose processor is not tailored to any particular application. Most microprocessors use a single-bus architecture in which both program instructions and data flow across the same set of data lines. This architecture, known as von Neumann architecture, can result in a data bottleneck caused by the path of flow on the data bus.

The size of the general purpose registers can also have a serious effect on computational performance. Intel's 8088 and 80286 processors have only 16-bit-wide registers, while the 80386 possesses 32-bit registers. To perform math operations, the microprocessor breaks the numbers into manageable portions and performs a series of software operations to obtain the desired result. This process requires

many machine cycles to complete. Numeric processors reduce the number of required cycles by employing larger registers. The Intel 8087 numeric processor has 80-bit-wide internal registers; however, it still requires multiple cycles to perform even the simplest mathematical computation.

DSP chips are distinguished from the general-purpose processor-coprocessor by their ability to perform instructions in a single cycle. Internal architecture of a DSP is optimized to perform single-cycle computations that allow faster performance of the sum-of-product calculations required by many digital signal-processing algorithms. The performance is obtained through the use of hardware multipliers-accumulators, Harvard architecture, or pipelining.

Hardware multipliers and adders of the DSP eliminate the software overhead required by conventional processors in mathematical operations. These units allow the DSP to perform operations in a single cycle and insure sufficient register width for accurate results. These multipliers and accumulators are arranged to optimize the multiplication followed by addition type operations.

To take advantage of the high speed advantage of the multiplier, the DSP must insure a steady flow of data into it. To achieve this, many different techniques are employed; however, most manufacturers use some variation of the Harvard architecture. Unlike the von Neumann approach, the Harvard architecture uses separate program and data memories, each having its own bus or buses. In a digital filtering operation, this architecture allows the data and a corresponding coefficient to be fetched from memory along separate buses and loaded into the multiplier simultaneously while an instruction is fetched on the program bus.

Pipelining is another scheme used to insure an adequate flow of data to the multiplier-accumulator. In a pipelined architecture, each instruction is composed of several steps such as FETCH, DECODE, MULTIPLY, and ADD. Each subsequent instruction is likewise divided; however, it always follows one step behind the previous instruction in the pipeline. In other words, while the first instruction is decoding the instruction fetched one cycle before, the second instruction is being fetched from memory. While requiring multiple cycles to complete an entire instruction, once the pipeline is filled, a result is obtained every cycle.

The general-purpose DSP is a single-chip integrated circuit designed to allow the greatest flexibility as well as provide good overall throughput. These integrated circuits range from 16-bit to 32-bit floating point architectures and are capable of real-time signal processing on signals of up to 200 KHz. Commonly offered features include zero overhead looping, bit reversed addressing, and external interfaces to serial and parallel devices. Numerous combinations of on-board and off-board memory are also available from several manufacturers. The general-purpose DSP architectures make them ideal for a wide range of applications.

The general-purpose DSP can be programmed to perform any of the digital signal processing algorithms much like a conventional microprocessor. They are generally programmed in their native assembly code; however, many of the DSP chips have a high level language compiler available. The use of a high level language makes software conversion from the microprocessor-based systems much easier.

Popular DSP chips include Texas Instrument's 320 family (32010, 32020, 320C25, and the 32030), the AT & T DSP32C, the Motorola 56001, and the Analog Device ADSP2100. Development boards for the popular IBM PC/XT/AT/compatibles are often available from either the manufacturer or a third-party source. These boards are either used for the development of stand-alone design or as a high speed digital signal processing coprocessor for a host computer. Assemblers, compilers, simulators, and debuggers are often included with many of the development boards.

The Remote Sensing Group at U.S. Army Chemical Research, Development and Engineering Center (CRDEC) has selected the AT & T DSP32C as the target processor. The DSP32C is a CMOS 32-bit floating-point processor based on a piplined, von Neumann architecture. This 25-MIPS (million instructions per second) device contains twenty-one 16-bit fixed-point registers for use in control, address, and logic functions and, in addition, four 40-bit accumulators to perform 32-bit floating-point mathematical operations. On-chip memory includes 2 K of read-only memory and 4 K of random access memory. The DSP has an off-chip memory capability of 16 MB. The DSP32C also supports serial I/O and a parallel I/O channel designed for easy interfacing to either an 8-bit or a 16-bit microprocessor.

(F) CONCLUSIONS

Infrared interferometer hardware, signal processing computer hardware, and the application of new mathematical algorithms have rapidly advanced the remote sensing technology during the last four years. Lightweight, small interferometers exist that can withstand severe mechanical vibrations while operating on rapidly moving helicopter platforms. Signal processing algorithms are available which can extract infrared background information in order to give an automatic alarm indication for the presence of a particular chemical vapor species. Finally, digital signal processing hardware has been constructed which allows infrared remote sensors to process data in real-time. This advance eliminates the need to collect data for later analysis in a laboratory.

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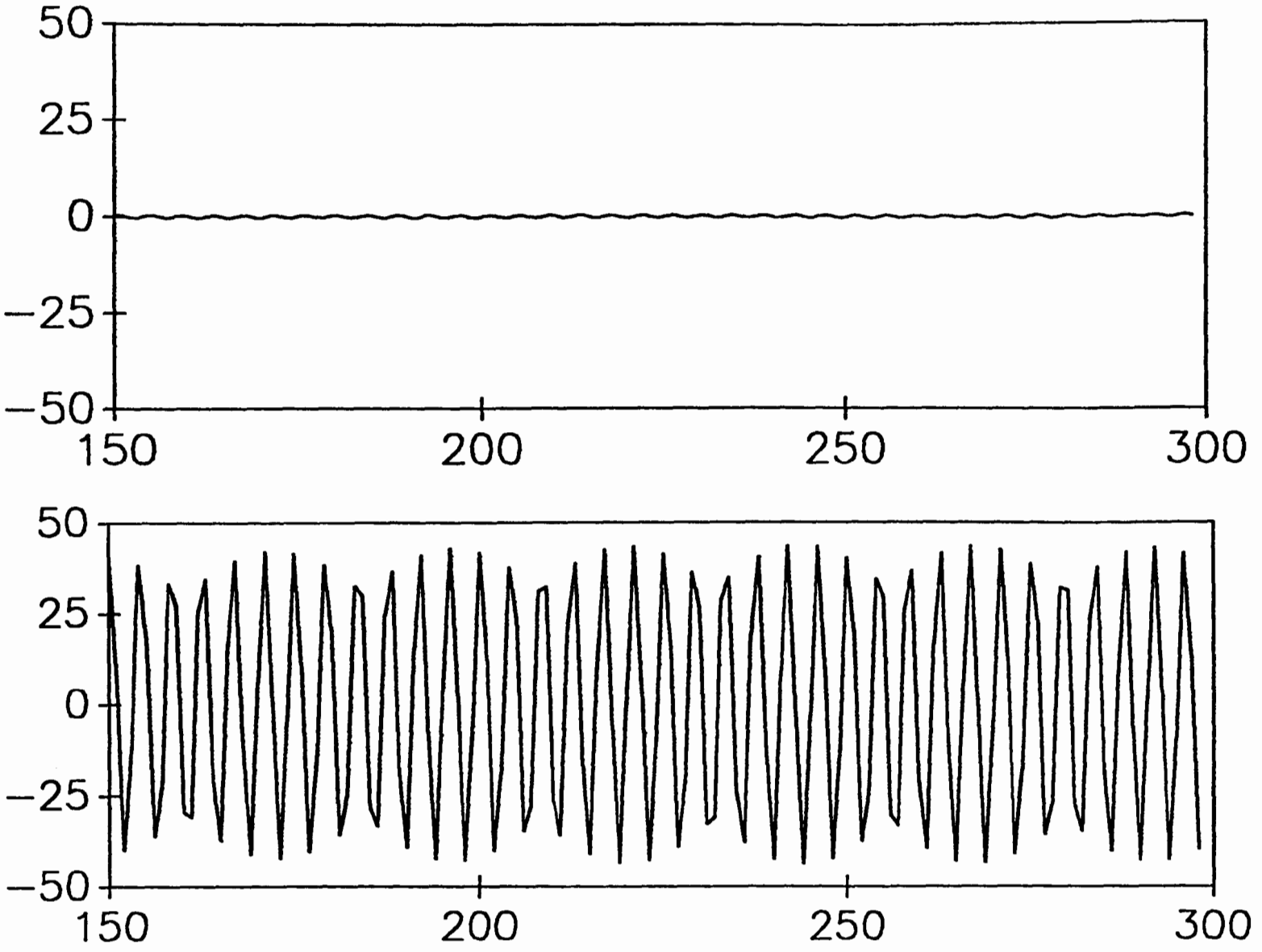

Figure 1

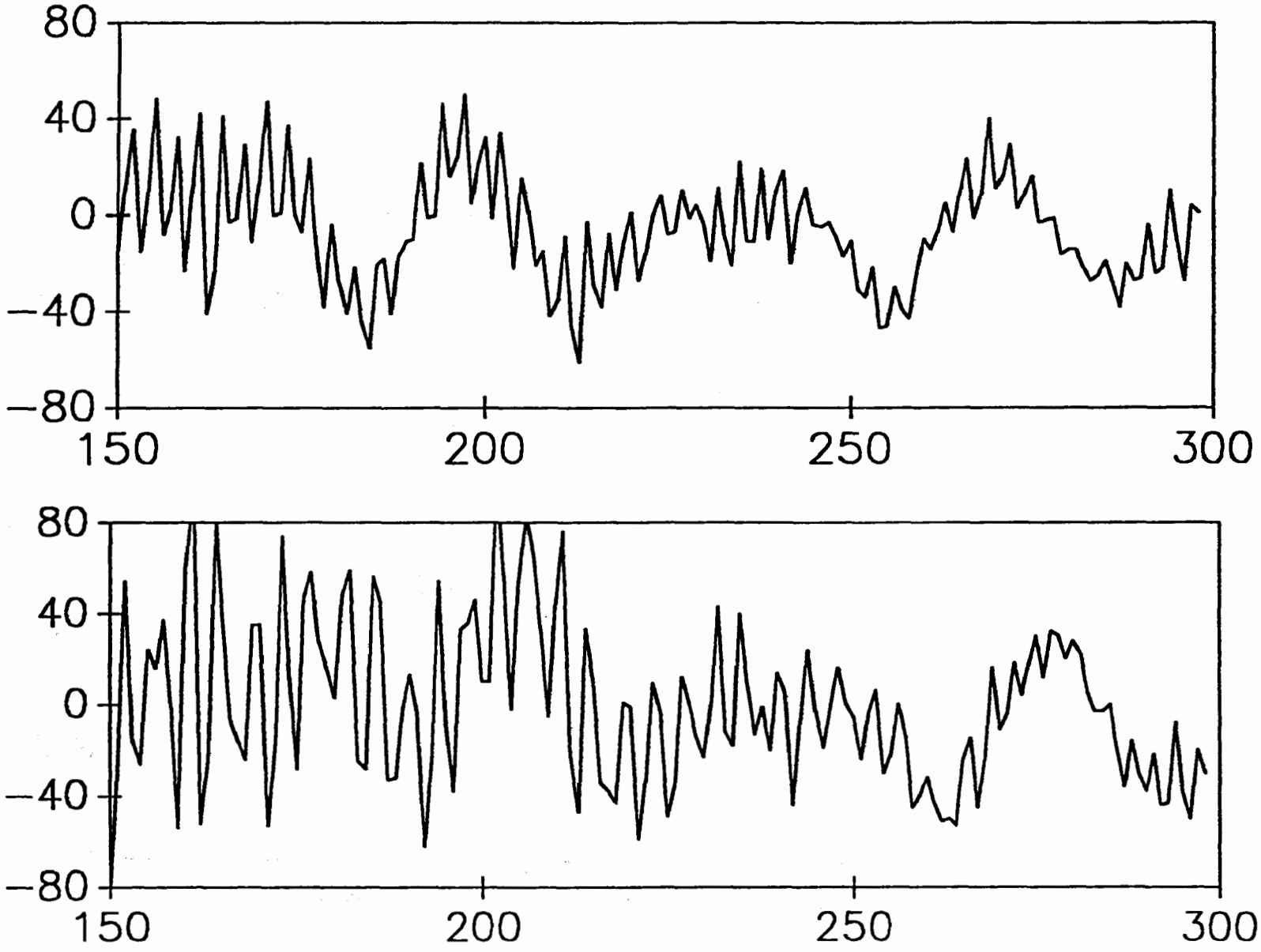

Figure 2

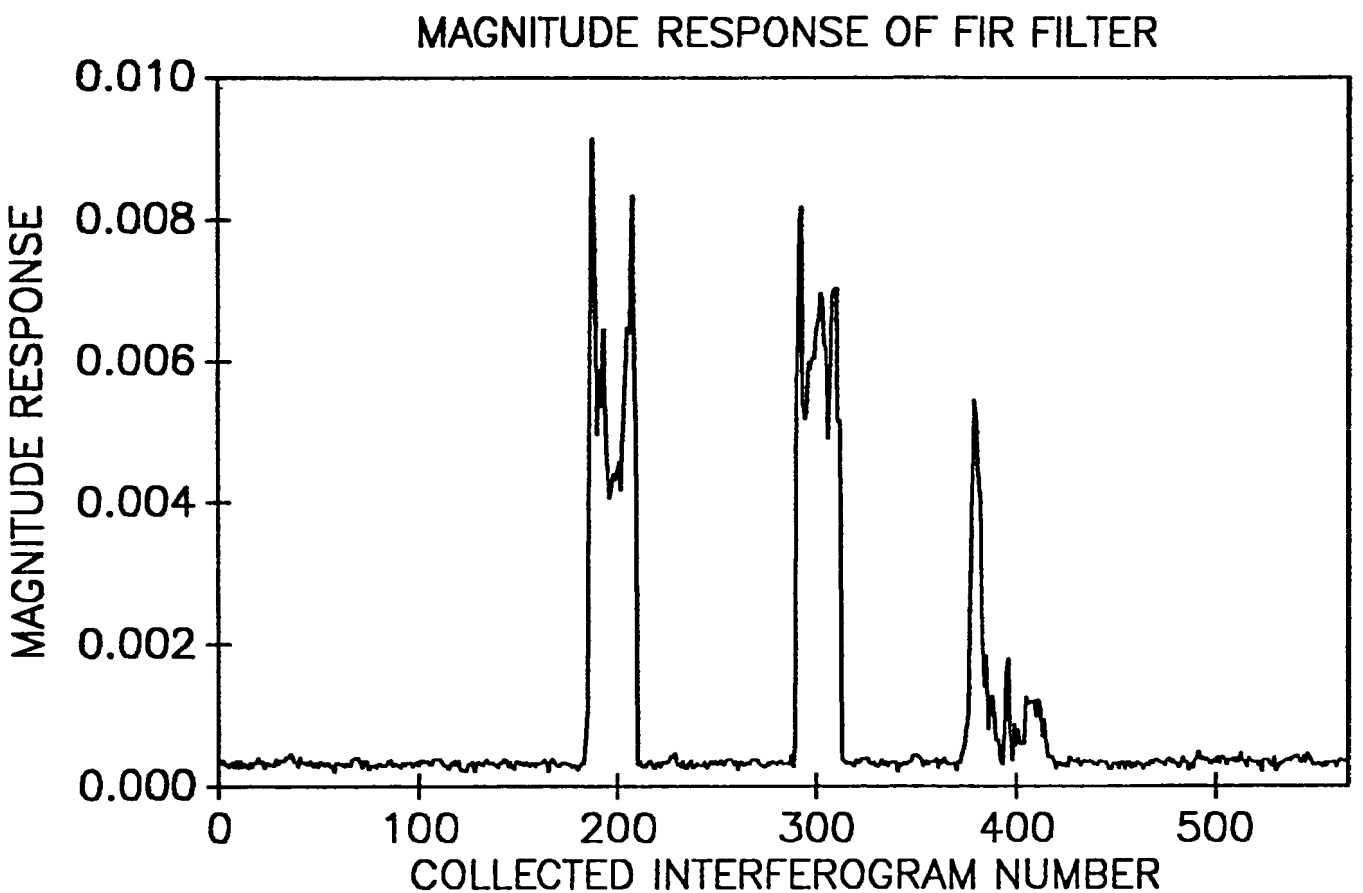
MAGNITUDE RESPONSE OF FIR FILTER
MAGNITUDE RESPONSE
0.010
0.008
0.006
0.004
0.002
0.000
0
100
200
300
400
500
COLLECTED INTERFEROGRAM NUMBER

Figure 3

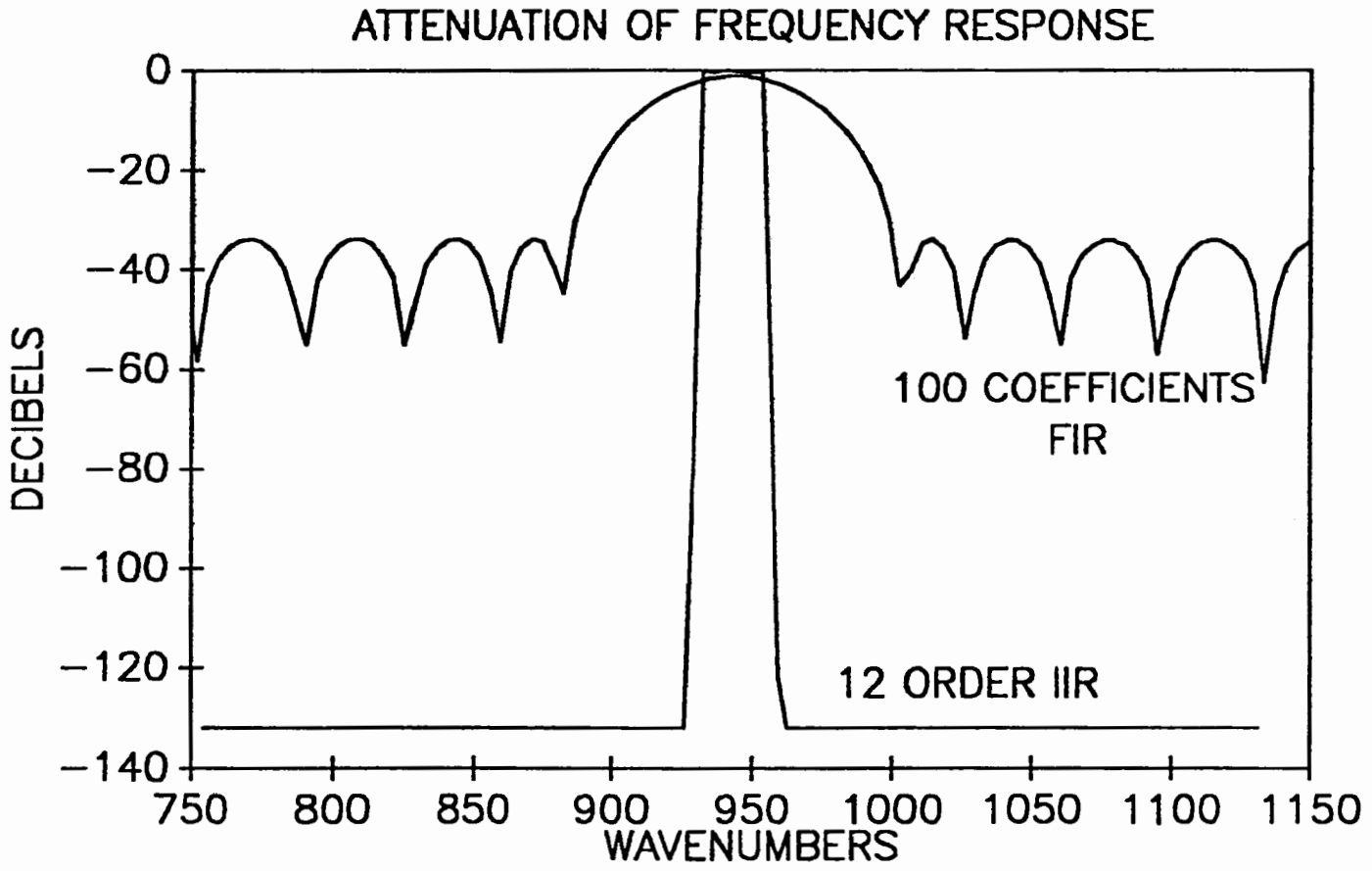
ATTENUATION OF FREQUENCY RESPONSE
0
-20
-40
-60
-80
-100
-120
-140
DECIBELS
100 COEFFICIENTS
FIR
12 ORDER IIR
750
800
850
900
950
1000
1050
1100
1150
WAVENUMBERS

Figure 4

DISCUSSION

DONALD GURKA: Can you tell us something about the range and payload of your drone?

JOHN DiTILLO: Right now, the payload is about 25 pounds, and that includes everything, the video cameras, the interferometer, the gas, the whole bit. Just the electronic portion or the sensor portion of it has to be limited to about 25 pounds. It just happens that the specification for the aircraft the contractor had. You can build them as large as you want, and the military drones that are under development have very large payload capacities. This just happened to be the one that we fell upon. A little bit about the aircraft: it flies at about 100 knots with the gas on board, it can fly for about an hour, and it has autopilot capabilities so you can send it out on a pre-planned mission and have it fly lazy eights or whatever over a specific area. Some of the efforts we have this year are to tie a global positioning system into that, so you can not only get video information back, which isn't very realistic from a military standpoint, particularly if you look at the scenario we have now in Iraq where the ground features aren't very distinct. Video is not going to tell you a whole lot. So, we think it would be a much better idea if you actually had grid coordinates as well as a response out of the algorithm. So, there's some more effort that's going into the aircraft itself as far as its capabilities, but that just happened to be what was available at the time.

TOM PRITCHETT: I'm familiar with calibrating the active FTIR units. How do you calibrate a passive unit?

JOHN DiTILLO: I don't know that much about the optical end of things. The XM-21 had an internal black body calibration that it went through on start up. Beyond that I don't know that much about it.

CHIP MILLER: Seems like from the days of show pair, low pair days, I remember problems with confusing silicates and absorption of silicates with the phosphoryl absorption of the organophosphonates that you're interested in. Is that still considered a problem, especially with regard with the desert scenario and the silica?

JOHN DiTILLO: That's the montmorillinite and kaolin problem. A lot of time and effort was spent on that problem. That was a serious problem early on. As you can imagine in a military scenario, false alarms can be devastating. And through years and years of testing and refinement of the algorithm, the XM-21 is virtually fool proof. The instrument has been trained to eliminate a lot of those early problems with dust or compounds that are similar to nerve agents and pesticides. Just from a military standpoint, if a unit were to get a false alarm out of an XM-21, the first thing they would do is go into mob gear. As soon as a unit does that, their fighting efficiency goes down to about 10%. So, you can imagine if your enemy knows that it hasn't hit you with agent, and it's looking across the field and you're in mob gear, you can imagine what kind of ramifications that's going to have. So, the army goes through great pains to eliminate any kind of false alarms due to dusts and dirts and burning tires, and that type of stuff. And the instrument has been trained to eliminate those problems.

USE OF WIND DATA TO COMPARE POINT-SAMPLE AMBIENT AIR VOC CONCENTRATIONS WITH THOSE OBTAINED BY OPEN-PATH FT-IR

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ABSTRACT

The technique of open-path FT-IR spectrometry is being used increasingly to measure VOCs in ambient air. Since the FT-IR technique produces a path-integrated concentration and most other techniques produce point concentrations, some method of interconversion is often desirable. In the case of a plume generated by a single point source, a solution to the interconversion problem can be found through the use of wind data. A quantitative relationship was developed between wind direction frequency and concentration. This relationship was used to predict path-integrated concentrations, given point concentrations. The same principle was used to predict point concentrations, given path-integrated concentrations.

The interconversion technique involved the use of one-minute means of wind direction as inputs to a Gaussian dispersion model. The one-minute concentration-to-emission rate (C/Q) ratios produced by the model were integrated over the sampling period of the test to yield a C/Q ratio that was based on the wind directional frequency distribution, rather than on the overall mean wind direction. These integrated C/Q ratios for selected points were used to develop predictive methods for both point concentrations and path-integrated concentrations; this process is described in detail within the body of the paper.

The interconversion technique was tested, using data from simulated field tests during which VOC releases were made. The VOC plumes generated were monitored along a line normal to the projected plume centerline, using the FT-IR technique and also by collecting whole-air samples in evacuated stainless steel samplers for subsequent GC/FID analysis. During the final test set, no FT-IR measurements were made; an observed path-integrated concentration was produced by using the mean of concentrations from point samples collected five meters apart along the path, thus providing an evaluation of the technique free of any bias that might exist between the two analytical methods.

Correlations between the observed concentrations for the point samples and the corresponding integrated C/Q ratios were assessed for each test and found to be significant at the 0.1 level in most cases. Although a bias between the two analytical methods was seen, the predicted path-integrated concentrations were strongly correlated with the observed values. For the test set in which only point samples were collected, excellent agreement between the predicted and observed path-integrated concentrations was seen. The predictive method for point concentrations did a good job of predicting both the location and the magnitude of the highest concentrations from each test, and reflected the general shape of the concentration-versus-crosswind curve well.

INTRODUCTION

The technique of open-path Fourier transform infrared (FT-IR) spectrometry is being used increasingly to measure volatile organic compounds (VOCs) in ambient air. Depending on the circumstances (nature of the source, receptors affected, etc.) this technique may complement, or in some cases replace, the collection of multiple whole-air samples with subsequent laboratory analysis.

The FT-IR technique produces a concentration integrated over the length of the path from source to detector for a given compound, whereas the whole-air method produces a concentration for only those points sampled. In order to use the data produced by the two techniques optimally, some method of interconversion is desirable.

Solution of the interconversion problem would be difficult in many cases. However, in the case of a plume generated by a single point source with relatively constant emission characteristics, a solution can be found through the use of wind data. The location and movement of the plume centerline (and therefore the maximum concentrations) are determined by the wind direction. Thus, the concentration of plume-derived compounds found in point samples should be primarily a function of the amount of time that the wind blew from the source toward those points during the sampling period.

If a quantitative relationship between wind direction frequency and concentration can be derived, that relationship can be used to calculate the concentration at any point along the path from the IR source to the detector. The mean of those values for points closely and evenly spaced along the path should then provide an approximate path-integrated concentration. The same principle can be applied to the conversion of path-integrated concentrations to point concentrations.

APPROACH

Sampling and Analysis Framework Overview

Plumes consisting of both single compounds and mixtures were generated from a stack two meters above the ground. Point samples were collected downwind from the source along a line normal to the projected plume centerline for subsequent analysis. During the first three of the four test sets performed, the plume was also monitored along the same path using an open-path FT-IR spectrometric method developed at Kansas State University (1).

During the fourth test set, point samples were collected at five-meter intervals along the path; no FT-IR measurements were made. This closely-spaced network of point samplers provided a more detailed characterization of the concentration-versus-crosswind distance curve. It also provided an observed path-integrated concentration based on the mean of concentrations from those samples, allowing further evaluation of the interconversion technique free of any bias that may exist between the two analytical methods.

Wind data collected during the sampling period were then used in conjunction with a Gaussian dispersion model to determine a calculated concentration-to-emission rate ratio (C/Q) for selected points along the path for each minute of the test. The C/Q values for each point were then summed over the sampling period of the test to produce an integrated C/Q (or C/Q*) for each point.

The above data and calculated values were then used in the following ways, to test the validity and usefulness of the conversion technique:

1) Correlations between the observed concentrations for the point samples and the corresponding C/Q* values were performed for each test.

2) The observed point concentrations and the calculated C/Q* values were used to predict a path-integrated concentration. This value was then compared to the observed path-integrated concentration for the same time period.

3) Using the observed path-integrated concentration and the wind data, an equation was developed to predict concentrations at selected points. These predicted values were then compared to observed concentrations present in samples collected at those points.

Individual Test Runs

Four sets of field tests were performed, one on each of the following dates: February 24, 1989; October 20, 1989; April 25, 1990; and October 22, 1990. VOC releases were made from a stack two meters above the ground in an open field near Lawrence, Kansas. During the first three test sets, the general spatial relationship of the VOC source and the sampling devices was as shown in Figure 1. Specific parameters (distances, number of point samples collected, etc.), in addition to the field deployment used in the fourth test set, are described in the succeeding paragraphs.

Figure 1

On February 24, 1989, a 20-minute release of toluene was made. The release was monitored along a line normal to the projected centerline of the VOC plume 50 meters from the source, using the open-path FT-IR methodology developed at Kansas State (1) and also by collecting whole-air samples in evacuated stainless steel samplers for subsequent GC analysis. Sampling and analysis of whole-air samples followed protocols developed at the University of Kansas

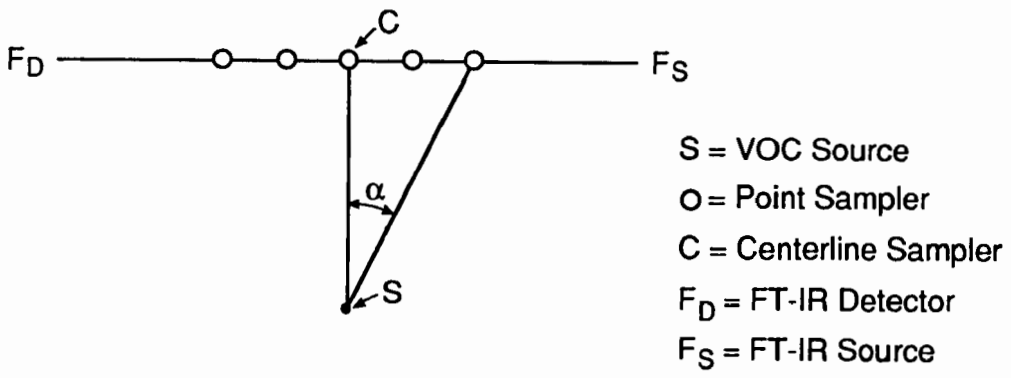


Figure 1. Sampling Network

(2). Nine whole-air samplers were deployed at ground level along the path, with α = 30x. The FT-IR path length was 120 meters.

On October 20, 1989, six 30-minute releases were made. Only 1,1,1-trichloroethane was released during the first three of these tests. During the final three tests, various mixtures of the following six compounds were released: n-pentane, methylene chloride, methyl ethyl ketone, tert-butyl alcohol, 1,1,1-trichloroethane, and toluene. The releases were again monitored along a line normal to the projected plume centerline 50 meters from the source, using both the FT-IR and whole-air techniques. Five whole-air samples were collected at ground level during each test, with α = 30x. The FT-IR path length was 100 meters. During the final two tests of this set, the wind had shifted approximately 30 degrees, making it questionable whether the plume centerline was within the sampling network. Data from those tests are not reported.

On April 25, 1990, ten 12-minute releases were made. Mixtures of the following five compounds were released during the first nine tests: methylene chloride, methyl ethyl ketone, tert-butyl alcohol, 1,1,1-trichloroethane, and toluene. Only 1,1,1-trichloroethane was released during the final test. The plumes were again monitored along a line normal to the projected plume centerline, this time 40 meters from the source, using both the FT-IR and whole-air techniques. A minimum of five whole-air samplers were deployed along the path during each test at one meter above the ground, with α = 20x during Tests 1-3 and α = 30x during Tests 4-10. The IR path length was 50 meters during Tests 1-3, 200 meters during Tests 4-6, and 100 meters during Tests 7-10.

On October 22, 1990, three 12-minute releases were made and again monitored along a line normal to the projected plume centerline 40 meters from the source. Fifteen whole-air samplers were collected at ground level along the path at five-meter intervals in each of the the three tests, as shown in Figure 2. No FT-IR measurements were made. Only toluene and 1,1,1-trichloroethane were released.

The network of samplers was shifted five meters to the left for Test 3 to account for what was perceived to be a slight wind shift. Samplers were thus arrayed from 40 meters left to 30 meters right of the projected centerline during this test.

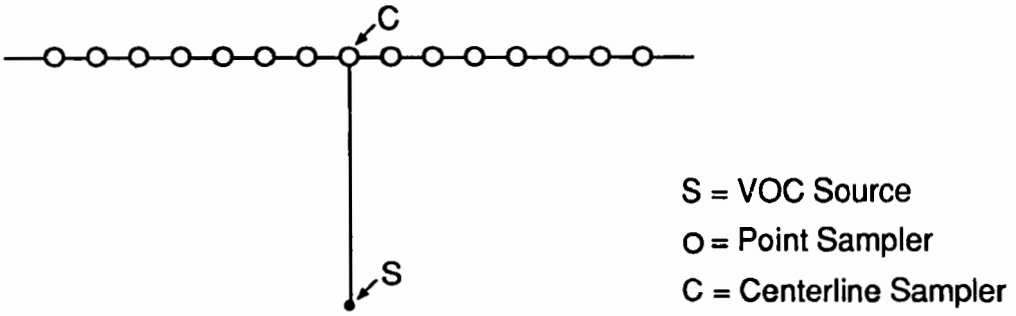


Figure 2. Sampling Network, 10/22/90

The following meteorological data were collected during all releases: one-minute means of temperature and relative humidity, and one-minute means and standard deviations of wind direction and wind speed.

EXPLANATION OF METHOD

Determination of C/Q Values

An algorithm was written to calculate integrated concentration-to-emission rate ratios (C/Q*) for selected points. As it is now written, the algorithm can produce a C/Q* value for up to ten points per execution. The following inputs are required:

- wind direction means for each minute of the test
- wind speed means for each minute of the test
- overall standard deviation of wind direction for the test
- location of the centerline point (distance and direction from the source)
- location of the remaining points selected (distance left or right of the centerline point)

Inputs were used in conjunction with a dispersion model to produce C/Q* ratios for selected points, in the following manner:

1) For each minute of the test, x- and y-coordinates were determined (with the source as the origin and the mean wind direction for that minute providing the direction of the x-axis) for each of the selected points. Each of the points was assumed to be on a line perpendicular to the line from the source to the centerline point and the appropriate trigonometry was then performed. An example for one such point is shown in Figure 3.

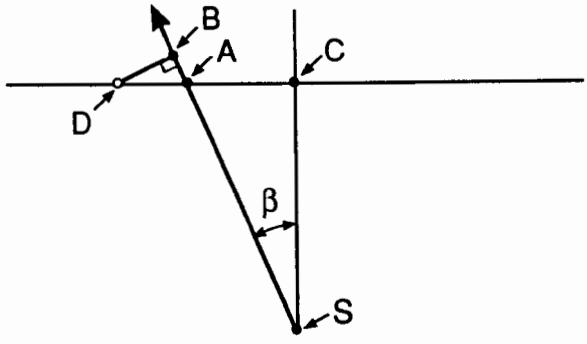
2) The standard deviation of the wind direction was then used to determine the stability class. Based on that class, and on the x-coordinate for a given point, a value for σ_y and σ_z was determined for each point (3). An example of this process is shown below, using the point discussed in part 1 and assuming a directional standard deviation of 10 degrees and a wind speed of 5 m/sec.

- direction standard deviation of 10° indicates stability class D
- for that stability class,

$$\sigma_y = 0.08 \times (1 + 0.0001x)^{-1/2}$$

$$= 0.08(55.5m)(1 + 0.0001(55.5m))^{-1/2}$$
$$= 4.43m$$

$$\sigma_z = 0.06 \times (1 + 0.0015x)^{-1/2} = 3.20m$$



Observations

S = VOC source

C = centerline point

D = designated point

$\overline{SC}$ = 50 meters

$\overline{DC}$ = 25 meters
network centerline direction = 180°

meanwind direction (→) = 160°
β = 180° - 160° = 20°

Trigonometry

$\overline{DA} = \overline{DC} - \overline{AC} = \overline{DC} - \overline{SC} \tan\beta$

$\overline{SA} = \overline{SC}/\cos\beta$

$\overline{AB} = \overline{DA} \sin\beta = (\overline{DC} - \overline{SC} \tan\beta) \sin\beta$

$x = \overline{SB} = \overline{SA} + \overline{SB}$

$= \overline{SC}/\cos\beta + (\overline{DC} - \overline{SC} \tan\beta) \sin B$
$= 55.5$ meters

$y = \overline{DB} = \overline{DA} \cos\alpha = 6.4$ meters

Figure 3. Determination of x- and y- coordinates

3) These values for σ_y and σ_z are then used in the dispersion equation to calculate C/Q, as shown below, also for the point discussed in parts 1 and 2.

$$C/Q = \frac{1}{2\pi\sigma_y\sigma_z u} e^{-y^2/2\sigma_y^2}$$

$$= \frac{1}{2\pi(4.43)(3.22)(5)} e^{-(6.4)^2/2(4.43)^2}$$

$$= 7.907 \times 10^{-4}$$

4) The C/Q values for each point were summed over the sampling period for that test, which yielded an integrated C/Q (or C/Q*) for each point. C/Q* values for the seven points at which point samples were collected during Test 10 on April 25, 1990 are as follows:

Location	C/Q*
30°L	3.206×10^{-4}
20°L	2.020×10^{-2}
10°L	4.888×10^{-2}
centerline	4.112×10^{-2}
10°R	4.016×10^{-3}
20°R	8.565×10^{-6}
30°R	2.840×10^{-11}

Correlation of Observed Point Concentrations with C/Q* Values

Correlations between observed concentrations from point samples and corresponding C/Q* values were assessed. This operation produced a correlation coefficient (r) and an associated probability (p). The latter value represents the probability that a correlation coefficient of this magnitude could occur if there were no relationship between wind directional frequency and concentration. For Test 10 on April 25, 1990, the following concentrations of 1,1,1-trichloroethane were found in the point samples:

Location	Concentration (ppb)
30°L	215
20°L	1056
10°L	1163
centerline	1188
10°R	175
20°R	46
30°R	0.0

These concentrations produce a correlation coefficient of 0.968 with the corresponding C/Q* values for the same test (shown in part 4 of the preceding section), with a probability of <0.001.

Prediction of Path-Integrated Concentrations

The observed point concentrations and the calculated C/Q* ratios were used to produce a predicted path-integrated concentration for each test, in the following manner:

1) A linear regression was performed, with the model-derived C/Q* values used as the independent variable and the observed concentrations in point samples the dependent variable, yielding a functional relationship between wind direction frequency and concentration. A regression equation of this form ($y = ax + b$) normally contains a non-zero intercept value, which can produce relatively high predicted concentrations corresponding to extremely low C/Q* values (an unrealistic situation), or even negative concentrations if the intercept is negative.

   Two solutions to this problem were attempted. The first was to constrain the regression line to pass through the origin (intercept = 0). This solution eliminates the problems caused by the intercept, although it does not produce as good a fit between predicted and observed values. The second solution was to perform a log-log regression. The equation produced generally yielded a slightly better fit than the zero-intercept method, while still allowing predicted concentrations to asymptotically approach zero for decreasing values of C/Q*. Shown below are regression equations produced from the 4/25/90 (Test 10) data, using both methods described in this paragraph. Also shown are F-ratios, indicating the significance of the regression, and predicted versus observed values.

   Zero-Intercept Method

   C = 33804 (C/Q*)
   F = 88.0 (p <0.001)

Location	Observed C	Predicted C
30°L	215	11
20°L	1056	683
10°L	1163	1652
centerline	1188	1390
10°R	175	136
20°R	46	0.3
30°R	0.0	0.0

Log-Log Method

$$\ln C = 0.392\ (\ln(C/Q^*)+8.28$$
$$F = 280 \quad (p < 0.001)$$

Location	Observed C	Predicted C
30°L	215	168
20°L	1056	852
10°L	1163	1204
centerline	1188	1124
10°R	175	452
20°R	46	41
30°R	0.0	0.3

2) Once the regression equation was derived, it was used to predict concentrations at evenly spaced points along the path. Predicted concentrations (based on a log-log regression) for the 4/25/90 test are as follows:

Location	Concentration	Location	Concentration
50m L	0.0	50m R	0.0
45m L	0.0	45m R	0.0
40m L	0.2	40m R	0.0
35m L	2	35m R	0.0
30m L	17	30m R	0.0
25m L	97	25m R	0.1
20m L	359	20m R	2
15m L	818	15m R	34
10m L	1146	10m R	219
5m L	1236	5m R	658
centerline	1129		

3) The mean of the predicted concentrations for evenly spaced points produced a predicted path-integrated concentration. The predicted and observed path-integrated concentrations are shown below for the 4/25/90 test.

observed path-integrated concentration = 185 ppb

predicted path-integrated concentration = 272 ppb

Prediction of Point Concentrations

The observed path-integrated concentration and wind data collected for the same time period were used to produce predicted concentrations for selected points along the path in the following manner:

1) Wind data and a dispersion model were used to produce C/Q* values for evenly spaced points along the path, as outlined earlier.

2) A conversion factor was determined, based on the observed path-integrated concentration and the mean of C/Q* values for evenly spaced points along the path, using the following equations:

$$PIC = F \times \left[\sum_{i=1}^{n} (C/Q^*)_i\right]/n$$

and $(C_{pt})_i = F \times (C/Q^*)_i$,

where F = conversion factor
PIC = path-integrated concentration
$(C/Q^*)_i$ = integrated C/Q for the ith point
n = total number of evenly spaced points
and $(C_{pt})_i$ = predicted concentration at the ith point.

Based on the data collected during Test 10 on 4/25/90,

$$F = 185/7.955 \times 10^{-3}$$
$$F = 23255.8$$

3) The conversion factor was used in conjunction with C/Q* values to predict concentrations for selected points, which were then compared with observed concentrations from samples collected at those points. For the centerline point on 4/25/90 (Test 10), the predicted 1,1,1-trichloroethane concentration is as follows:

$$C_{pt} = 23255.8 \times 4.112 \times 10^{-2}$$
$$C_{pt} = 956 \text{ ppb}$$

Shown below are 1,1,1-trichloroethane concentrations predicted for all points at which samples were collected during the 4/25/90 test. Also shown are the observed concentrations for those points.

	Concentration (ppb)	
Location	Predicted	Observed
30°L	8	215
20°L	470	1056
10°L	1137	1163
centerline	956	1188
10°R	93	175
20°R	0.2	46
30°R	0.0	0.0

RESULTS, DISCUSSION

Correlation of Observed Point Concentrations with C/Q* Values

Table 1 shows correlations (and associated probabilities) between observed point concentrations and corresponding C/Q* values for each test. For releases that consisted of mixtures of two or more compounds, only 1,1,1-trichloroethane (1,1,1-TCA) and toluene concentrations were used in the analysis.

In all but three tests, the correlation coefficients produced were associated with probabilities of less than 0.1. In at least one of those three cases, Test 3 on 10/20/89, it appears that additional valid data points would improve the correlation. These statistics would support the belief that there is a strong relationship between wind direction frequency and concentration.

Predicted Versus Observed Path-Integrated Concentrations

Table 2 shows observed path-integrated concentrations for all field tests. Again, only results for 1,1,1-trichloroethane and toluene are reported. Also shown are the corresponding predicted path-integrated concentrations, based on observed point concentrations and wind data. The values reported are those produced using log-log regression of concentration against C/Q*. At the time of this writing, FT-IR data was not available for 2/24/89.

It should be noted that observed path-integrated concentrations reported for the test set of 10/22/90 were produced by using the mean of concentrations from point samples collected five meters apart along the path. Values of predicted path-integrated concentration for this data set were produced using log-log regression of concentration against C/Q* for the following five of the fifteen points at which samples were collected: the projected centerline point, points 10 meters left and right of that point, and points 20 meters left and right of that point.
Excellent agreement is seen in the observed and predicted values from the 10/22/90 test set, with the largest percent difference being 2.5%. Values shown for the 10/20/89 and 4/25/90 test sets indicate the possibility of a bias between the two analytical methods, especially in the analysis of 1,1,1-trichloroethane, making an evaluation of the prediction technique more difficult in this case. In order to gain some

Table 1. Correlation of Concentrations with C/Q* Values

Date	Test	Stability Class	Number of Valid Data Points	Correlation Coef. and Probability 1,1,1-TCA vs C/Q*	Toluene vs C/Q*
2/24/89	1	C	9	NR	r = 0.889 p<0.01
10/20/89	1	B	5	r = 0.900 p<0.05	NR
10/20/89	2	B	4	r = 0.970 p<0.05	NR
10/20/89	3	B	4	r = 0.885 p<0.2	NR
10/20/89	4	B	5	r = 0.868 p<0.1	r = 0.858 p<0.1
4/25/90	1	D	5	r = 0.946 p<0.02	r = 0.940 p<0.02
4/25/90	2	D	5	r = 0.943 p<0.02	r = 0.944 p<0.02
4/25/90	3	C	5	r = 0.968 p<0.01	r = 0.982 p<0.01
4/25/90	4	C	5	r = 0.853 p<0.1	r = 0.895 p<0.05
4/25/90	5	C	5	r = 0.878 p<0.1	r = 0.887 p<0.05
4/25/90	6	D	5	r = 0.960 p<0.01	r = 0.916 p<0.05
4/25/90	7	D	5	r = 0.898 p<0.05	r = 0.910 p<0.05
4/25/90	8	C	5	r = 0.663 p<0.4	r = 0.675 p<0.4
4/25/90	9	C	5	r = 0.739 p<0.2	r = 0.759 p<0.2
4/25/90	10	D	7	r = 0.968 p<0.001	NR
10/22/90	1	B	15	r = 0.942 p<0.001	r = 0.942 p<0.001
10/22/90	2	B	15	r = 0.968 p<0.001	r = 0.969 p<0.001
10/22/90	3	C	15	r = 0.948 p<0.001	r = 0.954 p<0.001

NR - Compound not released during this test

Table 2. Predicted vs Observed Path-Integrated Concentrations

Date	Test	1,1,1-TCA Conc. (ppb) Observed	1,1,1-TCA Conc. (ppb) Predicted	Toluene Conc. (ppb) Observed	Toluene Conc. (ppb) Predicted
2/24/89	1	NR		NA	235
10/20/89	1	185	284	NR	
10/20/89	2	181	297	NR	
10/20/89	3	199	307	NR	
10/20/89	4	78	106	NA	64
4/25/90	1	56	85	35	31
4/25/90	2	138	197	85	142
4/25/90	3	38	44	233	204
4/25/90	4	16	37	20	12
4/25/90	5	34	62	30	45
4/25/90	6	7	10	42	55
4/25/90	7	36	71	18	28
4/25/90	8	75	107	116	76
4/25/90	9	18	25	146	118
4/25/90	10	185	272	NR	
10/22/90	1	334	340	333	341
10/22/90	2	277	280	284	279
10/22/90	3	282	278	288	282

NR - Compound not released during this test
NA - FT-IR data not available

insight into the performance of the technique, correlations between observed and predicted values were assessed for the 4/25/90 test set. For 1,1,1-trichloroethane, the correlation coefficient was 0.994, with an associated probability of much less than 0.001. For toluene, the correlation coefficient produced was 0.915, with an associated probability of less than 0.001. These results indicate that the technique presented for predicting path-integrated concentrations is potentially a sound one and warrants further study.

Predicted vs. Observed Point Concentrations

Table 3 (on following pages) shows observed concentrations for all point samples collected in the four test sets.

Also shown are the corresponding predicted concentrations for the points, based on observed path-integrated concentrations and wind data. At the time of this writing, FT-IR data was not available for 2/24/89.

As seen in Table 3, the technique presented for predicting point concentrations does a reasonably good job of predicting the general shape of the concentration-versus-crosswind distance curve, although concentrations 15 or more degrees from the centerline are generally predicted less accurately than are those nearer the centerline. Given the bias present between the two analytical methods, both the location and the magnitude of the highest concentrations from each test are predicted quite accurately.

CONCLUSIONS

The following conclusions are warranted, based on the data presented:

1) The use of one-minute means of wind direction as inputs to a Gaussian dispersion model produce concentration-to-emission rate ratios that are strongly correlated with observed concentrations.

2) The predicted path-integrated concentrations show good agreement with the observed values, given the bias seen between the two analytical methods.

3) The predicted point concentrations reflect the general shape of the concentration-versus-crosswind distance curve well. The location and the relative magnitude of the highest concentrations from each test are predicted accurately.

4) The principles underlying the interconversion methods are sound, and the methods themselves warrant further testing and development.

Table 3. Predicted vs Observed Point Concentrations

Sample Location	1,1,1-TCA Conc. Obs.	1,1,1-TCA Conc. Pred.	Toluene Conc. Obs.	Toluene Conc. Pred.
2/24/89 - Test 1				
30° L			214	
20° L			891	
10° L			1009	
5° L			718	
centerline		NR	364	NA
5° R			351	
10° R			333	
20° R			114	
30° R			28	
10/20/89 - Test 1				
30° L	67	206		
15° L	711	336		
centerline	966	405		NR
15° R	749	304		
30° R	65	34		
10/20/89 - Test 2				
30° L	223	181		
15° L	884	376		
centerline	X	386		NR
15° R	283	232		
30° R	47	88		
10/20/89 - Test 3				
30° L	X	236		
15° L	925	372		
centerline	1043	410		NR
15° R	241	294		
30° R	43	68		
10/20/89 - Test 4				
30° L	48	65	27	
15° L	272	98	149	
centerline	278	141	148	NA
15° R	297	176	158	
30° R	20	57	11	
4/25/90 - Test 1				
20° L	33	6	12	4
10° L	182	170	65	106
centerline	295	191	106	119
10° R	134	63	50	39
20° R	44	0.8	19	0.5
4/25/90 - Test 2				
20° L	78	8	68	5
10° L	525	286	357	176
centerline	737	715	502	440
10° R	277	73	193	45
20° R	28	0.1	23	0.1
4/25/90 - Test 3				
20° L	29	8	117	48
10° L	88	71	374	438
centerline	123	135	613	830
10° R	83	63	396	387
20° R	16	14	79	84
4/25/90 - Test 4				
30° L	130	3	26	4
15° L	150	34	57	42
centerline	346	179	111	224
15° R	90	83	34	103
30° R	17	0.3	8	0.4
4/25/90 - Test 5				
30° L	179	21	149	19
15° L	439	220	293	194
centerline	381	325	284	286
15° R	130	82	100	73
30° R	4	0.2	13	0.2
4/25/90 - Test 6				
30° L	20	0.0	102	0.0
15° L	66	27	402	161
centerline	116	93	561	559
15° R	18	7	94	41
30° R	2	0.0	16	0.0
4/25/90 - Test 7				
30° L	37	0.8	22	0.4
15° L	310	67	118	34
centerline	329	161	130	81
15° R	22	2	12	1
30° R	6	0.0	7	0.0
4/25/90 - Test 8				
30° L	39	5	31	8
15° L	746	243	494	376
centerline	308	385	211	595
15° R	111	88	73	136
30° R	12	0.9	3	1
4/25/90 - Test 9				
30° L	96	24	463	195
15° L	95	106	478	855
centerline	49	37	228	301
15° R	5	0.6	23	5
30° R	4	0.0	21	0.0

Table 3. Predicted vs Observed Point Concentrations (cont'd)

Sample Location	1,1,1-TCA Conc. Obs.	1,1,1-TCA Conc. Pred.	Toluene Conc. Obs.	Toluene Conc. Pred.
4/25/90 - Test 10				
30° L	215	8		
20° L	1056	470		
10° L	1163	1137		
centerline	1188	956	NR	
10° R	175	93		
20° R	46	0.2		
30° R	0.0	0.0		
10/22/90 - Test 1				
35m L	6.1	5.7	5.7	5.7
30m L	21	21	22	21
25m L	61	68	63	68
20m L	144	194	148	193
15m L	479	458	486	457
10m L	909	818	920	816
5m L	789	1027	785	1024
centerline	691	911	686	909
5m R	607	650	591	648
10m R	574	429	575	428
15m R	482	249	470	248
20m R	232	116	224	116
25m R	8.0	43	9.9	43
30m R	2.8	13	2.8	13
35m R	1.8	3.4	4.5	3.4
10/22/90 - Test 2				
35m L	1.2	5.5	1.3	5.6
30m L	17	24	19	25
25m L	24	85	28	87
20m L	89	228	90	234
15m L	342	448	358	459
10m L	641	620	643	636
5m L	690	619	725	635
centerline	610	520	592	533
5m R	479	456	506	468
10m R	553	416	561	427
15m R	333	335	344	343
20m R	229	217	237	222
25m R	80	113	83	116
30m R	25	49	27	50
35m R	42	18	44	18
10/22/90 - Test 3				
40m L	0.6	0.0	0.5	0.0
35m L	1.7	0.0	0.6	0.0
30m L	1.5	0.0	0.7	0.0
25m L	1.5	0.1	1.0	0.0
20m L	33	2.0	34	2.0
15m L	59	32	61	33
10m L	189	200	198	204
5m L	395	527	420	538
centerline	740	900	768	919
5m R	826	1127	846	1151
10m R	778	777	787	793
15m R	621	404	627	412
20m R	391	188	379	192
25m R	122	56	123	57
30m R	64	9.8	66	10

NR - Compound not released during this test
NA - FT-IR data not available
X - Whole-air sampling error, no data

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DISCUSSION

DONALD GURKA: How certain are we that there is no physical gradient across the plume? That is, we're not looking at part gas and part aerosol?

RAY CARTER: We have found that, based on the studies that we've done over a five-year period, the plume is well dispersed as it comes out of the stack. It is in fine liquid droplets as it comes out of the stack, but the droplets are so dispersed that they vaporize almost immediately. We have data from other tests that would support this.

DONALD GURKA: I guess my point is that the physical gradiant might have a differential effect on the open path concentration approach versus the canister concentration approach.

RAY CARTER: I think I see your point, and there did seem to be a bias between the two methods. And that is one good possibility if it is not all in vapor state. We believe that it is, but since there is a bias it's still worth looking into.

TOM PRITCHETT: Since in essence you're doing a controlled release of essentially a known emission rate, and in the case of your long path, open path monitoring, you're calculating emission rate versus concentration ratio. Have you used the open path monitoring to calculate an experimental emission rate and compared that against the generation rate of vapors? And also, use, let's say, the transect method of data reduction on the canister data, to also calculate an emission rate and see which one of those methods was giving you an experimental emission rate that was closest to your generation rate?

RAY CARTER: We did not have real good control on the FTIR methodology. It was primarily done by the people from Kansas State, and so we haven't really done anything with their data. I think your point is a good one, though. We could use our data and the method that you suggest to see if we accurately predict the emission rate that we did measure.

TOM PRITCHETT: Just as a follow up to that, if you looked at both the canister data and the open-path monitoring data, since you have a consistent bias, you might be able to resolve who's causing the bias by checking the two experimental emission rates versus your generation rate.

RAY CARTER: Yes, I would agree with that. And if we can obtain all of data from Kansas State that would be a good test to undertake.

ERNIE TUAZON: Would it be better to use a dye compound, like something that is more evenly distributed in the atmosphere which can be measured by the FTIR while it's doing its measurements, and also being sampled by your canister? Like a compound as simple as methane in the air — it's almost relatively constant. Even nitrous oxide or carbon dioxide. This will be in the data already. You will have sampled it, and the FTIR will have measured it already. So, if you're looking for that bias then, part of your answer may lie there.

RAY CARTER: You're suggesting using compounds that do naturally exist? Then you would not have the gradient across the path?

ERNIE TUAZON: That's correct, this is not a test of your model, but it tells you which one is producing a lower reading in that general direction.

RAY CARTER: Yes, since our main purpose was to test this model, then we preferred to actually have a gradient across the path, but I see your point. That would be another good method of determining which is the biased method. That was not really our intent. When we discovered that there was a bias, the reason we did the fourth test set was to try to test the method independent of the bias.

ERNIE TUAZON: I am aware of that. Also, one thing that might also affect your comparison is the way you sample with the FTIR. There is a dead time between FTIR measurements if you're calculating right after you collect the interferograms. In other words, there will be segments of interferograms being collected and then dead time while you're calculating, and then you again collect interferograms. In the canister, you're continuously sampling while that's occurring, aren't you?

RAY CARTER: I'm not sure I understand your question, but if I do, I believe that was taken care of by the sequencing of the sampling. We attempted to cooperate as much as possible with the people doing the FTIR measurements, merely adjusted our sampling to fit whatever schedule they preferred.

DONALD GURKA: Yes, it seems to me that the RTP Group with, I think that's Bill McClenny, also saw this negative bias, but it seems to me that the bias was within the combined experimental error. Is that correct?

BILL McCLENNY: The tests that we did were in the Delaware Site Program. And the tests there were done with a plume that was originating from a nearby industrial plant, and consisted of two primary emissions, paradichlorobenzene and chlorobenzene. All tests that we did were by moving a canister along the path next to the path of the augus — the line of sight for the beam. We had the system set up with a source receiver at one end and a retroreflector at the other end. We were carrying the canisters back and forth between those two locations. By moving over a period of one-half hour, we get an integrated canister sample, or a sample that's integrated over time. And then the spectra from the Fourier Transform System, were co-added over the same period of time. The two were compared. The comparison was based on a common standard, i.e., the GC/MS standard that was used to look at the paradichlorobenzene and the chlorobenzene, also used for the FTIR System. By using a common standard we had a common basis on which to compare, and we compared those measurements directly. And those measurements were very close with paradichlorobenzene, even though we were depending on a plume that was dispersing from a point source over which we had no control. But, in our case we had to locate it at the right position, which was an inconvenience. So, this type of comparison in which you have a control source has advantages. For us, we were in the field. We had to locate downwind of the source, and so our efficiency of taking these comparisons was reduced because we had to wait for the right experimental conditions.

DONALD GURKA: But, the negative bias was within the combined experimental error for the chemistry of these compounds?

BILL McCLENNY: We didn't have any bias that was discernable for the paradichlorobenzene. But, we were dealing with concentrations that varied from 150 ppb down to about 11 ppb. And over that range, because paradichlorobenzene has a very high absorption coefficient, we can see it easily with the FTIR system, and therefore we had, I think, a good comparison.

REMOTE DETECTION OF ORGANICS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY*

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ABSTRACT

Fourier transform infrared (FTIR) spectroscopy is an ideal technique for remote detection of organic emissions. There is an atmospheric window in the 1200 to 800 cm^{-1} region, which corresponds to the "fingerprint" region for organic molecules. Virtually all organic molecules have a unique absorption/emission pattern in the fingerprint region. A remote-passive FTIR relies on ambient emission of infrared energy from organics to obtain spectra. The instrumentation consists of inlet optics, an interferometer, a mercury cadmium telluride (MCT) detector, and an on-board computer. The transportable unit measures 40 cm by 50 cm and has been used to collect data while mounted on a helicopter or ground vehicle. Through the use of this FTIR combined with least squares software, it is possible to analyze qualitatively and quantitatively for organic vapors from either the air or ground.

The data presented will include quantitative releases of common organics present in incinerator stacks, hazardous wastes, and illegal laboratories. Data will be presented for pure compounds, mixtures, and target analytes in the presence of interfering compounds. The sensitivity, reproducibility, and the potential of the technique will be discussed.

INTRODUCTION

The emission of organic vapors is a concern for environmental, health, safety, and regulatory reasons. Sources of organic vapors include industrial leaks, incinerator emissions, motor vehicle exhausts, evaporation from contaminated areas, leaking storage tanks, petroleum refineries, and even illegal drug laboratories.

The EPA-certified procedures for organic emissions consist of sampling a fixed amount of air through a sampling apparatus such as a volatile organic sampling train (VOST), which traps the organics. The sample is then transported for gas chromatographic (GC) or gas chromatographic/mass spectroscopic (GC/MS) laboratory analysis. Results are available in a period of weeks or months. The entire procedure is costly and time consuming. Also, the GC or GC/MS analysis is a one-time procedure. If the concentration of organics is outside the acceptable instrumentation limits, the sample cannot be reanalyzed.

Remote-passive FTIR offers the potential to detect, identify, and monitor emissions in real time in the field. FTIR spectroscopy is ideal for remote detection. There is an atmospheric window in the 1200 to 800 cm^{-1} region, which corresponds to the "fingerprint" region for organic molecules. Virtually all organic molecules have a unique absorption/emission pattern in the fingerprint region. Through the use of FTIR combined with classical least squares (CLS) or partial least squares (PLS) software, it is possible to analyze qualitatively and quantitatively for organic emissions from either the air or ground.

The FTIR consists of infrared optics, interferometer, MCT detector, on-board computer, and external data collection system. The remote FTIR used to collect the data presented in this report was designed by the U.S. Army and is designated as the XM21. It is extremely rugged and can collect data mounted on a helicopter or tank or ground mounted. It can be programmed for target analytes and will set off an alarm as soon as they are detected.

The instrumentation emits no energy but detects the natural emissions of organics due to the difference in temperature of the organic molecule from the background. For example, organics emitted from an incinerator will be thermally warm relative to the sky or ground near the stack. A solvent exiting from an open window or exhaust pipe will be warmer or colder than the building from which it is emitted. On a sunny day when the background is warmer than the solvent vapor, a standard transmittance spectrum is obtained. During the evening when the background is cooler than the solvent vapor, an emission spectrum is obtained.

This paper will focus on two potential applications for remote FTIR spectroscopy: (1) the monitoring of incinerator emissions and (2) the detection of solvents emitted from a building, such as an illegal drug laboratory or production facility in which solvents are used.

EXPERIMENTAL

1. Method

In a typical experiment, the distances from the target (brick wall, blackbody, field release) to the FTIR were accurately measured. A series of releases of single components and mixtures was performed using a vaporizer designed at this facility. The vaporizer was capable of converting a liquid flow to vapor, which was released in front of the appropriate background. The flow from the vaporizer was determined using a hot wire anemometer. The design of the vaporizer is described elsewhere.[1]

2. Concentration Units

Data are reported in concentration-pathlength units of ppm-m. For example, a concentration-pathlength release of 1 ppm-m is equivalent to a release of 1 ppm over a width of 1 m. Our release width was 10 cm, the width of the vaporizer. Hence, when we release 10 ppm over a width of 10 cm (0.1 m), the pathlength concentration is 1 ppm-m. A 1 ppm-m release is equivalent to a concentration of 1 ppm emitted from a stack 1 m in diameter while the remote FTIR is collecting data across the plume. The parts per million level for the data presented herein was determined by converting the liquid flow to cubic centimeters of vapor and dividing by the cubic meters of air released.

RESULTS AND DISCUSSION

Data are presented for three pure liquids, methanol (MEOH), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4), to determine their detection levels under laboratory conditions. The liquids were released in front of a blackbody that was maintained at 40°C. The liquids represent common laboratory solvents, two of which ($CHCl_3$ and CCl_4) are also principal organic hazardous components (POHCs) monitored in incinerator emissions.

1. Analysis of Pure Components

Methanol data were collected at flows corresponding to concentrations of 3.7, 7.6, 13.9, 27.2, and 34 ppm-m. The IR spectra for the data are presented in Fig. 1. The quantitative results are presented in Table 1.

Table 1. Quantitative Data for MEOH Using a Blackbody Background. Concentration-pathlength units are ppm-m.

Conc.	Detected 2 std	Detected 3 std
34.0	STD	STD
27.2	27.7	27.6
13.9	15.7	STD
7.6	9.9	8.8
3.7	STD	STD

Agreement is excellent for the 27.2 ppm-m sample, with deviation less than 2%. The deviation was less than 13% for the 13.9 ppm-m sample. However, when only two standards were used, the error for the 7.6 ppm-m sample was 30%. This error decreased to 16% when a third calibration standard was used.

Both $CHCl_3$ and CCl_4 are of special interest because they are monitored during an incinerator trial burn. Monitoring them in real time enables the determination of on-stream destruction removal efficiency (DRE). On-stream DRE determination would eliminate the need for a trial burn.

$CHCl_3$ and CCl_4 are strong infrared absorbers in the 800-700 wavenumber region. This is beyond the optimum region for the detector in the XM21. Hence, the sensitivity of the instrument is lower for detecting these two components than would be the case with a detector optimized in this region.

Analysis of $CHCl_3$ consisted of five different flows corresponding to concentration pathlengths of 2.87, 5.12, 6.49, 7.85, and 8.87 ppm-m. The first and last values were used for the calibration curve. The IR spectra obtained are shown in Fig. 2. All absorbances in the region 830-720 wavenumbers were used in quantitation. The quantitative results are shown in Table 2.

Table 2. Remote Detection of Chloroform Using a Blackbody Background. Concentration-pathlength units are ppm-m.

Conc.	Detected	% Error
5.12	4.85	5.3%
6.49	6.15	5.2
7.85	7.10	9.6

The relative intensity of the two peaks associated with chloroform are clearly seen. The absorbance in the 1220 wavenumber region was not used for the data calculations shown in Table 1. With a two-point calibration curve, the percent error was within 10%. The intensity of the 2.89 ppm-m absorption is sufficiently strong to demonstrate sensitivity in the high parts per billion concentration range.

Data for CCl_4 showed similar sensitivity. Five different flows of liquids were analyzed, which correspond to concentration pathlengths of 3.47, 4.33, 5.77, 6.92, and 8.36 ppm-m. The first and last values were used for the calibration curve. The IR spectra obtained are shown in Fig. 3. All absorbances in the region 810-784 wavenumbers were used in quantitation. The quantitative results are shown in Table 3.

Table 3. Remote Detection of Carbon Tetrachloride Using a Blackbody Background. Concentration-pathlength units are ppm-m.

Conc.	Detected	% Error
4.33	3.92	9.5%
5.77	6.28	8.8
6.92	7.58	9.5

The quantitative data are accurate to within 10%, as were the chloroform data. The detection levels are similar. The absorption of CCl_4 is much sharper than that for $CHCl_3$. The relatively low resolution of the instrumentation gives the CCl_4 its sharp features. At 2 wavenumber resolution, the fine structure of most organic absorbances becomes evident. At 4 wavenumber resolution, the fine structure is lost, and the absorption degrades to a curve or straight lines. The 4 wavenumber resolution of the equipment employed in this preliminary study limits the ability of the software to identify and align peak absorbances by their fine structure. The absorbance in the 780-760 region is background carbon dioxide. This absorbance is also present in, and overlaps with, chloroform. Higher resolution data would show the carbon dioxide as sharp bands superimposed on the chloroform absorbance.

The laboratory work with $CHCl_3$ and CCl4 demonstrated the potential of FTIR for remote detection of organics. The next phase consisted of determining the efficiency of the instrumentation in the field. An experiment was set up to detect MEOH released in front of a brick wall. This experiment simulates the detection of organics emitted from production facilities or illegal drug laboratories. Data collection is made more difficult because the temperature of the brick wall and, hence, the intensity of infrared energy being emitted are changing during the day.

Data collected for MEOH are presented. The three MEOH flows used correspond to concentrations of 8.2, 18.3, and 27.8 ppm-m. The spectra for these three concentration ranges are shown in Fig. 4. Because the brick wall was cooler than the released vapor emission, spectra were obtained. The concentration of the second sample was calculated to be 22.5 ppm-m, or approximately 23% above the actual value.

2. Analysis of Mixtures

A critical issue in demonstrating the potential of remote FTIR is the ability of the instrumentation to function in complex environments. The technique must be able to identify and quantify components in mixtures under difficult and changing backgrounds. Usually, components in mixtures absorb infrared radiation at different energies. The difference was readily observed in a simple experiment in which 10 µL of MEOH and 5 µL of ethyl ether were injected into an evacuated 10 cm cell placed in front of a blackbody background. The spectral data are presented in Fig. 5.

a. Laboratory Release

Qualitative and quantitative data were obtained for a mixture of $CHCl_3$ and CCl_4. These two analytes have partially overlapping absorbance peaks. This work simulates monitoring two POHCs being emitted from an incinerator. The blackbody temperature initially was set at 41°C and allowed to slowly increase to 44°C by the end of the measurements. This changing background better simulates background conditions found in an actual remote situation, where data collection begins in the morning and as the day progresses the temperature increases.

Data were collected at six concentrations: 0.40, 0.81, 1.45, 2.02, 3.03, 4.04 for $CHCl_3$ and 0.34, 0.68, 1.23, 1.71, 2.56, 3.41 for CCl_4. $CHCl_3$ and CCl_4 were mixed 50:50 by weight. The lowest concentration level (<0.5 ppm-m for each analyte) was below threshold detection level and is not replotted. The IR spectra of the other five solutions are shown in Fig. 6. The quantitative data are shown in Table 4. The 820-784 wavenumber region was analyzed for CCl_4 and the 784-720 wavenumber region was used for $CHCl_3$.

Table 4. Remote Detection of a Mixture of $CHCl_3$ and CCl_4. Concentration-pathlength units are ppm-m.

Conc.	$CHCl_3$ Detected	Error	Conc.	CCl_4 Detected	Error
0.40	0.70	75%	0.34	0.59	74%
1.45	1.17	19	1.23	1.00	19
3.03	3.06	1	2.56	2.58	1

The second, fourth, and sixth samples were used as calibration standards. The software was able to identify the $CHCl_3$ and CCl_4 and quantify their concentrations with the calibration curve. The large deviation for the lowest level is not unexpected. One cannot visually identify $CHCl_3$ and CCl_4 in this spectrum. The capability of the software to identify the analyte under these conditions is encouraging. The steadily increasing background temperature did not result in a degradation of the data.

The absorbances of $CHCl_3$ and CCl_4 only partially overlap. It is necessary to study a system in which the absorbances of both components completely overlap. A diethyl malonate (DEM) and MEOH mixture was studied at six different flows. First, three flows were studied, which contained a low concentration of DEM in MEOH: 0.67, 0.98, 1.12 ppm-m DEM in 6.06, 8.82, and 9.72 MEOH, respectively. This was immediately followed by three more flows, which contained only MEOH: 5.93, 9.88, and 19.69 ppm-m. The objective was to determine if the totally overlapped DEM could be identified and quantified in the first three mixtures and not misidentified (false positive) in the last three flows. Figure 7 shows the IR spectra of pure DEM, pure MEOH, and the mixture of both components collected remotely. One cannot visibly detect the presence of DEM in the spectra of the mixture. The quantitative data are presented in Table 5. The 1090-1000 wavenumber region was analyzed for DEM, and the 1100-975 wavenumber region was used for MEOH.

Table 5. Remote Detection of a Mixture of MEOH and DEM. Concentration-pathlength units are ppm-m.

Conc.	MEOH Detected	Error	Conc.	DEM Detected	Error
8.82	8.30	5.9%	0.98	0.91	7.1%
5.93	7.11	19.9	0	ND	-
19.69	16.46	16.4	0	0.17	

The first, third, and fifth samples were used as standards. The software was able to correctly quantify the low-concentration DEM sample. The first pure MEOH sample was also correctly identified, although the quantitative data showed significantly more error. The highest concentration MEOH sample, 19.69 ppm-m, showed a low concentration of DEM present (false positive). However, the concentration detected was below the threshold detection level of DEM.

b. Field Release

Field data were obtained at Aberdeen Proving Ground. The XM21 was placed approximately 500 ft (~200 m) from the region where SF_6 was released. The angle of view, low sky background, is the most difficult to work with because of the infinite pathlength and greater amount of atmospheric pollutants.

A methanol-DEM mixture was released while an SF_6 release was in progress. The methanol peaks were observed as emissions because they were released at 42°C, which was above ambient temperature. The SF_6 was observed as an absorbance spectrum because it was released from a pressurized tank and the gas was below ambient temperature.

The spectral data are presented in Fig. 8, and the quantitative data are presented in Table 6. The spectral data show the steadily increasing concentration of the methanol-DEM spectral features and the reduction of the SF_6 absorption as the gas disperses. The primary band for DEM is completely overlapped by the MEOH emission (Fig. 8). The secondary bands at 1200-1150 wavenumbers are readily observed.

Table 6. Methanol-DEM Release with SF_6 Dispersion in Low Sky Background. All concentrations are in ppm-m.

MEOH		
Conc. Released	Detected	% Error
4.6	STD	
11.7	8.2	29.9
17.4	STD	-
23.5	25.5	9.4

DEM		
Conc. Released	Detected	% Error
2.2	STD	-
5.8	3.9	32.8
8.5	STD	-
11.6	12.5	7.8

The quantitative data in Table 6 were obtained using only two standards. The percent error was approximately the same as that obtained for pure methanol. However, the analysis was more difficult because only the spectral range of 1125-975 wavenumbers was used. The DEM and methanol completely overlap in this region. No pure components were entered into the calibration file. Hence, these data indicate that the analysis of mixtures is no more difficult than the analysis of pure components.

SUMMARY AND CONCLUSION

This study has demonstrated that remote infrared detection is a precise and reliable technique for monitoring organic emissions. The equipment is capable of detecting SF_6 releases at 500 ft (~200 m) and low concentrations of pure components and mixtures released in the environment. Quantitation was within 30% for these releases. Mixtures were no more difficult to analyze than pure components.

Several areas still must be addressed. The limitation of the PLS software is the large number of spectra required to reduce quantitation error. For the data presented here, it was not possible to obtain the number of spectra that would reduce the quantitation error. The classical least squares method requires fewer library data and should improve data quality. We hope to expand this work to include advanced signal processing using digital filtering in the time domain so that variations in background and the need for calibration spectra are eliminated. A limitation of the existing equipment is the lack of front-end optics, which are required for analysis at distances of 1 km.

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*Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38 and the Chemical Research Development and Engineering Center.

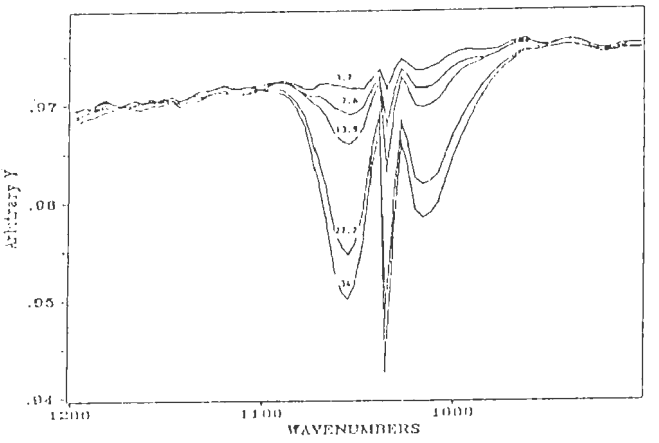


Fig. 1. Remote IR Spectra of MEOH Obtained Using a Blackbody Background. Concentrations of MEOH were 3.7, 7.6, 13.9, 27.2, and 31 ppm-m.

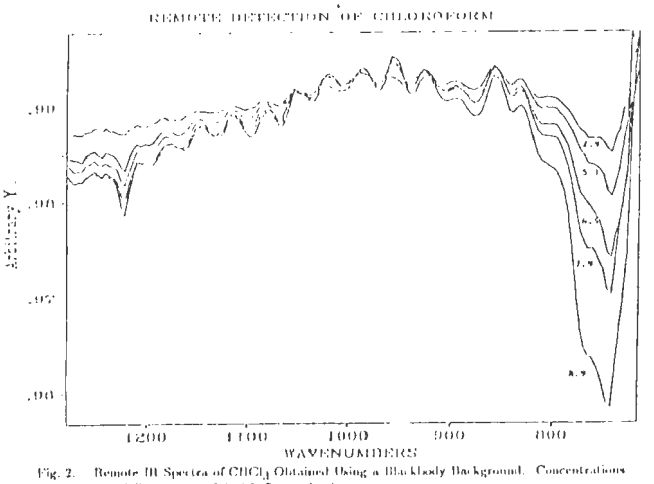
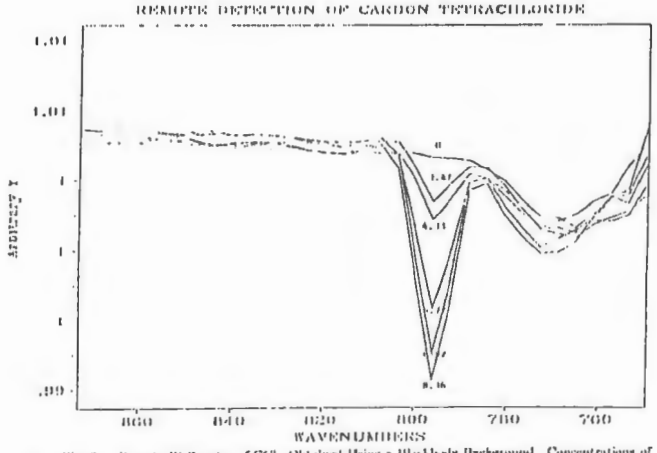
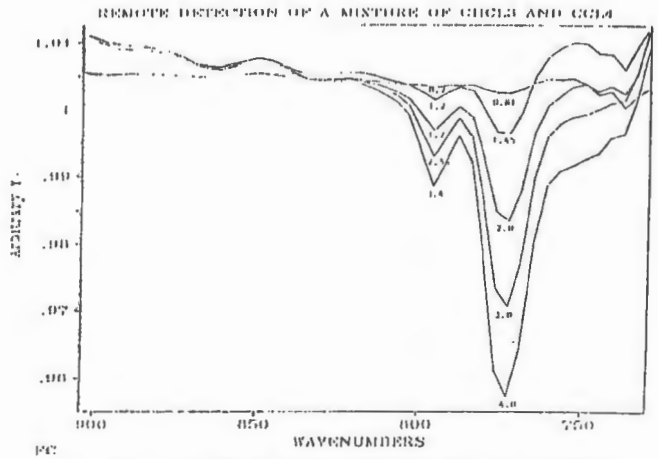


Fig. 2. Remote IR Spectra of $CHCl_3$ Obtained Using a Blackbody Background. Concentrations of $CHCl_3$ were 2.9, 5.1, 6.5, 7.9, and 8.9 ppm-m.



CA Fig. 3. Remote IR Spectra of CCl_4 Obtained Using a Blacktasty Background. Concentrations of CCl_4 were 3.5, 4.3, 5.3, 6.9, and 8.1 ppm-m.



FC Fig. 6. Remote Detection of a Mixture of $CHCl_3$ and CCl_4 at Five Concentrations.

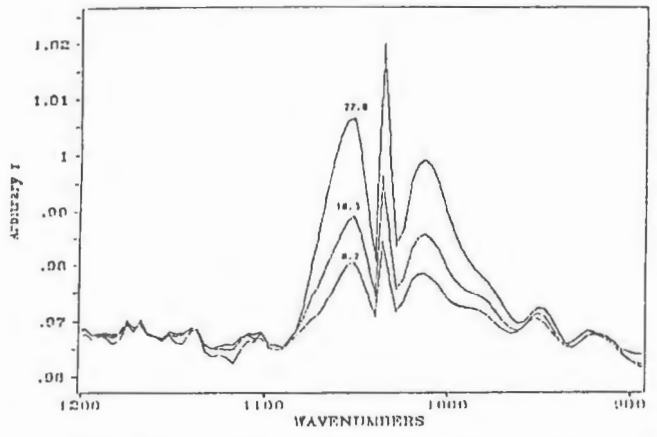


Fig. 4. Remote IR Spectra of MEOH Obtained Using a Brick-Wall Background. Concentrations of MEOH were 3.2, 13.3, and 27.8 ppm-m.

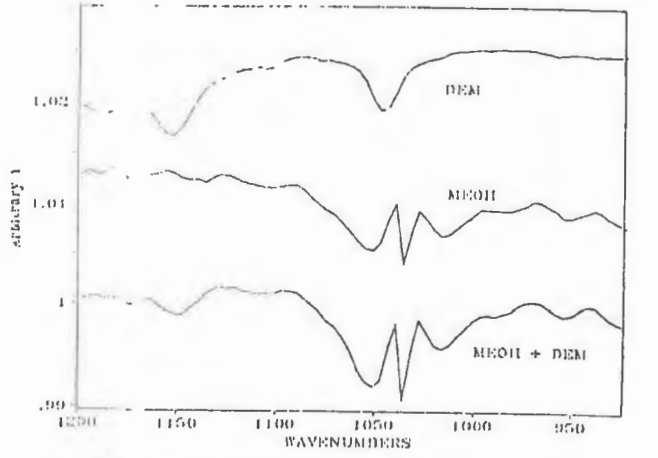


Fig. 7. Remote Detection of Pure MEOH, DEM, and a Mixture of DEM and MEOH.

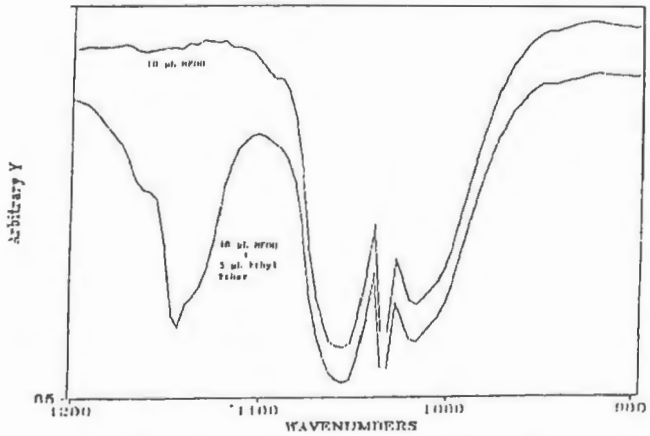


Fig. 5. Comparison of Remote IR Spectrum Containing 10 μL of MEOH and a Spectrum of the MEOH with a 5 μL Aliquot of Ethyl Ether Added to a 10 cm Cell with a Blacktasty Background.

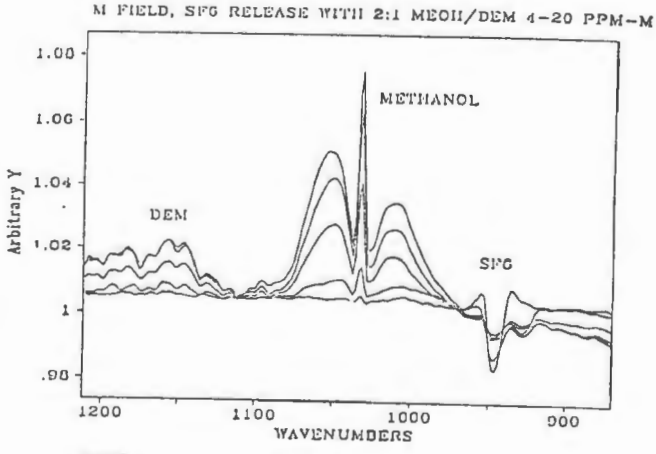


Fig. 8. MEOH-DEM Release with Low Sky Background during and after an SF_6 Release 200 m from the Instrumentation.

DISCUSSION

EMILE HYMAN: Can you comment on the potential for stack emission monitoring?

JACK DEMIRGIAN: We think there is tremendous potential for stack emission monitoring, and that's one reason we ran carbon tetrachloroform as an early set. We are currently collecting, with the DOE Program, regular on-stream incineration monitoring data. Once we get that data we will be giving it to Kroutil so that he can calculate the coordinates for it. And then we can start to test this technique on incinerations. There is a municipal incinerator on-site or near on-site, at the Aberdeen Proving Ground. We have already collected some data there, before some of the signal processing work was completed, and we will be analyzing that data. We will be definitively moving, and hopefully we'll be presenting some on-stream incineration monitoring data at the incineration conference this May. Hopefully, after that we will present the remote equivalent of the on-stream monitoring. So, stay tuned.

EMILE HYMAN: How about SO_x and NO_x and that kind of thing?

JACK DEMIRGIAN: Again, SOx and most of the NO_x absorb out of the detector window for this particular detector. SO_x and NO_x are a little more difficult because they're between CO_2 and water in their absorption region. And so the digital filter has to be done to eliminate water, or certainly reduce the effect of water. This is not undoable. The technology is right there now. The new plateau I discussed by Kroutil and Ditillo and Small, gives the potential to do that. I think it's just more a function of time and staff than it is technologically difficult. Right now the emphasis has been on organics as opposed to the SO_x and NO_x. There are several good SO_x and NO_x monitors and we don't really want to compete. We want to open up new areas. The new Clean Air Act has opened up a lot of areas in which I think this remote passive technique will fill the bill. And I think FTIR is right now about the only technique available that can do some of the requirements of the new Clean Air Act.

DONALD GURKA: Those who know me know me to be skeptic. You said no false positives and no false negatives? That suggests that the systems that you looked at thus far are simple. Is that your conclusion?

JACK DEMIRGIAN: Yes, well, first off, keep in mind that the sophisticated algorithms have just been developed this past September. What we have been doing now is with conventional techniques. You're absolutely right. The first system we worked with were pure components. Then we worked with two component mixtures. We've worked with two component mixtures now with some varying background. In this year we are funded to go ahead with more complex backgrounds and more complex mixtures. In fact, we have ordered the equipment so that we can now make multi-component mixtures and better characterize the complex mixtures that would put more of the false positives and false negatives to the test, but your point is quite well taken. We presented data with one and two component mixtures. The fact that we've chosen a difficult two component mixture is a good sign of things to come. Had we failed miserably with the methanol DEN, then I think you would have a very valid statement. I think when we had succeeded with the very difficult methanol DEN case we have justified going on to more complex mixtures. Again, the quantitative remote passive as we're doing now is very new. And I guess if I'm here at the next conference, you'll know that it worked.

DONALD GURKA: Can you visualize slanting this approach to all false positives or all false negatives? Can you adjust your approach so that you screen out only negatives or you screen out only positives?

JACK DEMIRGIAN: That's an interesting question. And I think that the key on doing the false positives and false negatives is probably going to reside with Kroutil's ability to digitally filter these things out. They have specific expertise in filtering out false negatives, and they have a very great interest in filtering out false positives. In order to do that properly with very complex mixtures, it is better to ask Ditillo or Kroutil, because that's their specific expertise.

ERNIE TUAZON: You allude to methanol being a simple system. It isn't. Underneath methanol, if you look at it very closely, there would be interferences by ammonia. So, if you are in an area where there's fertilizer or a factory, or even ammonia producing cows are around, it will be an interference. Also, CO_2 is an interference. These are the so-called lacing lines of CO_2 that you don't see in the laboratory, but at long parts you will see them. It's underneath those. Also, if you are in the Los Angeles atmosphere, ozone will be an interference. So, it's not a simple one as far as that is concerned, anyway.

JACK DEMIRGIAN: We specifically addressed the CO_2 by collecting chloroform data which totally enveloped the CO_2. The Army has been working on the ozone problem for quite a bit of time, and that's within their coordinate system to filter out. Now, I don't think we have done ammonia yet or high concentrations of...

ERNIE TUAZON: No, I don't mean that. I mean just in analyzing that particular band that you see, there are a lot of interferences underneath that.

JACK DEMIRGIAN: Yes, ammonia itself has relatively sharp bands and the algorithm is able to discern a sharp band versus a smooth band. And I can show you some data. If we get into the THAMA data where we're looking for explosives which are nitrates, they absorb smack in the middle of the water region. So, if you've got an interference, it's water in the soil samples. And we've spiked the soil samples with 10% water, and looked at ppm explosives. Even with the very sharp water bands versus the relatively broad explosive bands it does not affect the algorithms' ability to quantify. We were very satisfied with these results. A lot of the atmospheric gases that are small molecules have very sharp bands, and the organics have much broader bands and that makes quantitation and identification a good deal easier. So, as I said, methanol was relatively straight forward. Most of the atmospheric gases are not going to be as big a problem. I would guess in an application such as treaty verification where you have someone deliberately trying to fool your system and put out components that are very, very similar, that might be a tougher test. But, atmospheric is not as bad as you would think.

INTERPRETATION OF PPM-METER DATA FROM LONG-PATH OPTICAL MONITORING SYSTEMS AS THEY WOULD BE USED AT SUPERFUND HAZARDOUS WASTES SITES

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Recently, several groups have been evaluating the use of long-path optical monitoring systems such as remote sensing UV and remote sensing FTIR. Because of the potential power of this field analytical technique, several of the more active groups have been attempting to compare the results from the long-path systems to Summa canister results. While these comparisons have generally demonstrated that the two techniques are indeed comparable, they generally have not addressed how the long-path (or path-integrated) data could be interpreted to meet the site manager's needs. Unfortunately, many in the air toxics field are not familiar with the downwind dispersion equations which can be used in conjunction with path-integrated concentrations to define the emission source to downwind receptor relationship. Instead, most are usually used to interpreting only average concentration data from single locations.

The fundamentals of downwind transport illustrate how ppm-meter data can be interpreted in three of the most appropriate applications of long-path optical monitoring: assessing of the baseline air emissions from an inactive site, assessing the air impact of future cleanup operations during pilot scale testing and fenceline monitoring during actual cleanup operations. In all cases, the path integrated data can be used to predict "worst-case" air concentrations for the surrounding area — even for areas not covered by the original monitoring study.

DISCUSSION

DONALD GURKA: My question is on regulatory aspects that are driven by the technological state of the art. As far as emissions go, the state of the art is usually or always point sampling approaches. The question is, are there any gaps in the point sampling approaches which are covered by open path IR, thus that open path IR in that situation is now the state of the art?

TOM PRITCHETT: There are two types of regulatory approaches. There are air toxics people who work with point monitoring. Those point monitoring techniques assume either a time averaged, a long term exposure average concentration, or they assume a maximum concentration. Well, the point monitoring approach is not a trivial matter to ensure that you're taking your point monitoring sample at the maximum point in the plume. You have to know where that maximum is before you take your sample. I've actually been out with a mobile mass spec and was driving down the highway and watched a regulatory agency take a measurement, a grab sample, that they're going to use to slam on a company. Well, I drove another 50 yards down the road and found the plume from the facility, which they were actually trying to go after. They were taking a sample in the upwind plume. So you've got to be very, very careful when you're doing point monitoring to determine regulatory compliance. You can very easily miss the maximum plume.

At this time, if you're trying to regulate a particular emission source based upon a long-term average point monitoring concentration, there is a major gap in guidance in how to interpret that data. Particularly, what do you do with nondetects. Do you use a source receptor relationship and treat the upwind nondetects as zeros, or do you use detection limits? That's particularly important for risk assessment because the one-to-two order of magnitude difference between the instrument detection limits and the concentration of concern tends to mask its risk.

The other type of regulatory situation is the one that is used in the Clean Air Act. They regulate in terms of emission rates, grams per second. You cannot exceed so many grams per second. I don't know what approach they're going to take in the Clean Air Act, but I think ultimately they're going to have to go to grams per second. To calculate an emission rate using point monitoring techniques under simple gauging conditions takes anywhere from seven to ten Summa canisters, and that's to get one reading which you then have to do in triplicate. So, that's 21 to 30 samples just to get one measurement you feel that you can use as an emission rate.

With open path monitoring you can do that in probably about three minutes. You may very well be driven not so much by the detection limit — how many spectra you have to co-add to get your detection limit, as much as how many spectra must you require before you have the gauging conditions which you're using to interpret the data.

TOM PRITCHETT: The answer is that there's a lot of gaps in point monitoring techniques which make it not as ideal for, let's say, health assessment purposes related to specific source, and for determining emission rates related to a given source that I think open path monitoring can solve.

GARY ROBERTSON: Tom, while I was listening to you I noticed that you were doing most of your measurements perpendicular to the plume. It looked to me that if you took those measurements at various angles to the plume, you could get a lot of information about defining the plume and perhaps even the shape of the plume.

TOM PRITCHETT: Under the straight gauging condition, if you're near perpendicular, say within about 30 degrees perpendicular, you can use the meteorological data to define the plume. It's a lot easier, believe it or not, to define the plume using your meteorological conditions, as was shown by the Kansas State study, than it is to try to multiplex by burying the angle that you're shining the beam. It's also logistically a lot easier to have one beam set up and just filter out the data where you're essentially perpendicular, than it is to sit there and continuously move your beam to try to get your multiplex beam orientation.

CLIFF DAHM: I wanted to explore a couple of things. One is you talk about meteorological measurements and conditions. What do you recommend routinely be measured meteorologically, for example at a fence line? And secondarily, I also want to know, whether, on any of these studies that you've been talking about, if there's been vertical structure determined at some of the plumes that you've been monitoring?

TOM PRITCHETT: In answer to the first question, you typically look for wind speed, wind direction and sigma theta to calculate the stability class. And in answer to the second question, looking at the vertical component of the plume, no, we haven't. Again, we're looking downwind of small point sources. The one thing we have done in that relationship is we actually used controlled releases. Let me go back to one of my questions here; look at the bottom equation, equation 5. If you have a controlled release, and you're measuring the path of concentration, and you know wind speed, the only thing that's unknown is sigma θ. What we've done is used controlled releases at different distances to see whether or not the sigma θ's were, consistent with the predicted sigma θ's of the Clifford Path — I guess it was Clifford that measured it or Pascal. But anyhow, we found very, very good agreement for that stability class of the sigma θ's. So, in essence we have not directly measured vertical dispersion, but we've shown that the vertical dispersions being used in the gauging equations were experimentally confirmed.

AWARDS CEREMONY

The sponsors of Second International Symposium — Field Screening Methods for Hazardous Wastes and Toxic Chemicals were pleased to include an awards program. Mr. John Koutsandreas, Florida State University and the Symposium Executive Secretary organized the program and assembled the review panel that evaluated nearly 60 platform presentations and over 60 poster session papers. The members of the awards committee included:

Mr. Robert Booth, former director of U.S. EPA's Cincinnati EMSL
Dr. Steven Levine, University of Michigan, School of Public Health
Dr. David Nelson, Vice President, Perkin-Elmer Corporation
Dr. Roy Herndon, Director, Chemical, Biological and Toxicology Research, Florida State University
Dr. Michael Dellarco, U.S. EPA, Office of Research and Development
Dr. Russell McAllister, U.S. EPA, Office of Solid Waste and Emergency Response
Dr. Joseph Leonelli, Associate Director, Applied Electromagnetic and Optics Lab, SRI International
Mr. David Bottrell, Department of Energy, Office of Technology Development
Dr. Richard Tinlin, Geraghty & Miller, Inc.

The Symposium organizers and sponsors are grateful to this awards committee for their time and effort expended in evaluating the presentations.

The panel judged the two best private sector (i.e., non-Federal) papers and the two best Federal papers and awarded U.S. EPA engraved plaques to:

Private Sector
Susan Eberlein for "Space Technology for Application to Terrestrial Hazardous Materials Analysis and Acquisition"

Hui Wang for "Comparison of Aqueous Headspace Air Standard Versus Summa Canister Air Standard for Volatile Organic Compound Field Screening"

Federal
Donald Smith for "A Study of the Calibration of a Portable Energy Dispersive X-Ray Fluorescence Spectrometer"

Tom Spittler for "The Use of Field Gas Chromatography to Protect Groundwater Supplies"

U.S. EPA engraved plaques were awarded to the two best poster presentations as determined by the Awards Committee. They were:

"A Field-Portable Supercritical Fluid Extractor for Characterizing Semivolatile Organic Compounds in Waste and Soil Samples" B.W. Wright and J.S. Fruchter

"Real Time Detection of Biological Aerosols" P.J. Stopa, M.T. Good, W. Zulich, D.W. Sickenburger, E.W. Sarver, R.A. Mackey

Mr. Larry Cottran from Hewlett Packard presented two eagle trophies, donated by Hewlett Packard, for overall outstanding technical contribution and quality of presentation. Hewlett Packard pays considerable attention to these two critical elements: improving quality and increasing technical contributions. The winners were:

For best technical contribution:

Fred Milanovich for "A Fiber Optic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons"

For best presentation:

Steven Levine for "Fourier Transform Infrared Spectrophotometry for Monitoring of Contaminant Gases and Vapors in the Workplace Air"

Certificates were also presented that recognized the most outstanding paper in each of the ten platform sessions. They were:

Session 1 CHEMICAL SENSORS

Fred Milanovich for "A Fiber Optic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons"

Session 2 ION MOBILITY SPECTROMETRY

Suzanne Ehart Bell for "Hand-Held GC-Ion Mobility Spectrometry for On-Site Analysis of Complex Organic Mixtures in Air or Vapors over Waste Sites"

Session 3 ROBOTICS

Susan Eberlein for "Space Technology for Application to Terrestrial Hazardous Materials Analysis and Acquisition"

Session 4 QA AND STUDY DESIGN

John Mateo for "A Quality Assurance Sampling Plan for Emergency Response (QASPER)"

Session 5 AIR PATHWAY MONITORING AT SUPERFUND SITES

Steven Levine for "High Speed Gas Chromatography for Air Monitoring"

Session 6 FIELD MOBILE GC/MS TECHNIQUES

Mary Cisper for "Field Measurement of Volatile Organic Compounds by Ion Trap Mass Spectrometry"

Session 7 PORTABLE GAS CHROMATOGRAPHY

Hui Wang for "Comparison of Aqueous Headspace Air Standard Versus Summa Canister Air Standard for Volatile Organic Compound Field Screening"

Session 8 FIELD SCREENING METHODS FOR WORKER SAFETY

Gerald Moore for "Improvements in the Monitoring of PPM Level Organic Vapors with Field Portable Instruments"

Session 9 X-RAY FLUORESCENCE

Donald Smith for "A Study of the Calibration of Field Portable X-Ray Fluorescence Instruments"

Session 10 FOURIER TRANSFORM INFRARED SPECTROMETRY & OTHER SPECTROSCOPY METHODS

Gary Small for "Pattern Recognition Methods for FTIR Remote Sensing"

CONCLUDING REMARKS BY SYMPOSIUM CHAIRPERSON, DR. LLEWELLYN WILLIAMS

As I lay in bed this morning, I looked back over the week as each of my senses awakened. First came my sense of touch, and I felt that the Symposium was a success. and I was touched by the quality of the papers and of the posters. And I was almost "touched" by a number of technology developers looking for Federal funds. And I recall the pain of stabbing my upper lip with a toothpick holding two Swedish meatballs.

Next came my hearing. I heard a broad range of useful information from the bureaucrats. I heard of breakthroughs and research advances from our researchers and technology developers. Fortunately, I heard few complaints about the papers. And I heard the sound of two thousand Swedish meatballs being poured into a silver chafing dish.

Next to return was my sight. I saw a lit entry way and a table full of awards. I saw dim images on the screen during the Plenary Session. I saw colorful exhibits and the sharp graphics of poster and platform sessions. And I saw two thousand Swedish meatballs being poured into a silver chafing dish.

The next of my senses to return was that of smell. I detected the sweet smell of success that could be attributed to the enthusiasm and energies of you, the participants. I smelled the various emergency deodorizing measures used on Wednesday morning when the shower water didn't work in the hotel. And I smelled the odor of over two thousand Swedish meatballs simmering in a silver chafing dish.

The last sense to return was my taste. I recall the good taste displayed by the exhibitors during our reception period. I can taste a consistently good coffee that was provided on our breaks. And I fear I'll continue to taste the Swedish meatballs for days to come.

The results of all of this sensory input was a series of visions. The first is a vision of us all returning to Las Vegas two years from now to do it all again. The second vision is of the widespread acceptance of field methods and the data derived therefrom. And finally the vision of fifty large Lutheran women feverishly molding Swedish meatballs.

At this time, as unprepared as I am, someone asked for another poem.

Now that you have seen it all and will set upon your way,
We'd love to get your feedback as we plan for number tres.
How'd you like the balance and the papers and the rest?
What things would you change?
What did you like the best?
Thanks to all the many folks who made this whole thing happen,
And bailed out the Chairman every time they caught him napping.
And thanks for sponsor monies, and support from all the brass.
It helped us build a program that was nothing but first class.
My special thanks to Eric and JoAnn, and yes, to Kouts,
For pulling things together so give your horns some toots.
And if we had success in our attempts to make it work,
It was your participation here that really made it perk.
So, looking to the future I suspect we'll meet again,
As we catch up on developments in monitoring, and then
We'll see if the technologies have made it to the play off
Can bear the fruit, and stand the test, and over time will pay off.

Ladies and gentlemen, thank you very much.

CALIBRATION OF FIBER OPTIC CHEMICAL SENSORS

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Fiber optic chemical sensors to be used for monitoring environmental pollutants have been extensively researched for at least ten years. Although excellent research results have been presented, few if any systems have met the quality assurance requirements such that they are now in production and available for general use. Many fiber optic sensors for monitoring physical parameters as temperature, microstrain, and accoustics are available. Sensors for monitoring chemical processes have been used successfully.

Sensors that meet QA/QC manufacturing requirements are usually the result of careful modeling. For the past several years a part of our research activity has been related to the formulation of appropriate models for FOCS. Our studies have shown that the chemistries of the materials placed on the distal end of the fiber are adequately modeled. The deficiencies appear to be related to the physics and engineering of the optics, lack of quality control during the manufacturing process, and/or lack of sufficient information being collected to assure reliable information in the presence of interferents.

Optical fibers are used as:

(1) Carriers of optical signals - photons travel simultaneously in many directions.

(2) Sensor/Carriers - Optical properties of the fiber provide the sensing medium.

(3) Components of integrated diagnostic systems.

Photons pass down the core of a fiber in several ways. In addition to the rays passing down the center of the fiber some of the photons are reflected at the boundary between the core and the cladding. The cone that includes rays that pass through the fiber is shown in Figure 1A. Energy can be lost to the cladding when a bend occurs in the fiber as shown in Figure 1B. To avoid loss due to microbends and to protect the fiber from stress, the clad fiber is bundled into a protective cable shown in Figure 1C.

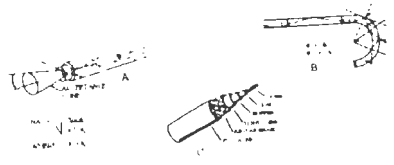

Figure 1. Light Transmission Through Fibers

The communication industry has spent millions of dollars on obtaining high purity silica core, selection and application of the cladding, and cabling of the fiber. Some of the problems that must be overcome are shown on Figure 2.

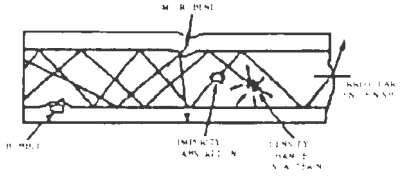

Figure 2. Sources of Energy Loss in Fibers

Our recommendation for quality sensors are:

(1) Use the purist high quality fiber
(2) The cladding for high quality fiber is added to the core while the fiber is still in the inert atmosphere of the drawing furnance. Do not attempt to change the cladding except doing the manufacturing process.
(3) If possible use only cabled or rigidly supported fiber.
(4) Standardize the sensor using a sufficient number of measurement parameters such that all meaningful variance is represented. It is not necessary to quantitate all sources of variances, but a measurement parameter must be included.

Figure 3 shows a test chamber that we have used successfully for determining the required number of measurement parameters and standardizing our sensors.

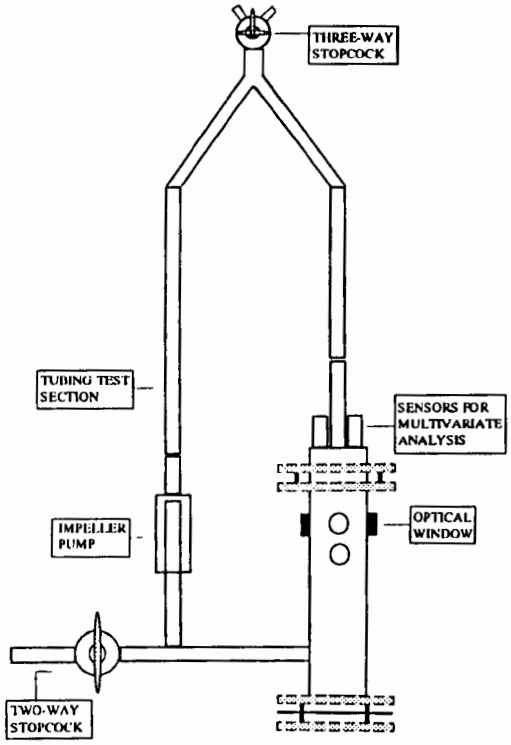

Figure 3. Inline Multivariate Analysis Flow Apparatus

GAS-CHROMATOGRAPHIC ANALYSIS OF SOIL-GAS SAMPLES AT A GASOLINE-SPILL

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ABSTRACT

The U.S. Geological Survey is studying remediation processes at a gasoline-spill site in Galloway Township, New Jersey. A field-laboratory trailer was equipped with a gas chromatograph (GC) configured to analyze soil-gas samples for gasoline hydrocarbons and inorganic gases, such as oxygen, nitrogen, carbon monoxide, and carbon dioxide. This instrument was selected over other analytical options because of its versatility; it can be used to monitor all significant organic and inorganic components of unsaturated-zone gases. Each of two chromatographic columns is equipped with a vapor-sample injection valve fitted with a sample loop. The sample-loop volume determines the injection size. A chromatography data system and a micro-computer are used for data acquisition, processing, and storage.

A thermal-conductivity detector is used in conjunction with a 3.3-meter-long molecular sieve column for analysis of inorganic gases. A flame-ionization detector is used with a 30-meter-long fused silica capillary column with a dimethylpolysiloxane stationary phase for analysis of vapor-phase gasoline hydrocarbons. Inorganic and organic species are identified by retention time and quantified by linear-regression standard-curve analysis.

A method for evaluating hydrocarbon chromatograms that does not require identification of specific peaks was developed. Chromatograms are divided into retention-time increments, each of which contains peaks of compounds that have the same carbon number (number of carbon atoms). A sample can then be described semiquantitatively in terms of the number of compounds of each carbon number, total mass of each carbon number, or percent of mass represented by each carbon number. The method is based on the relation between the carbon number of a compound and its boiling point, and between boiling point and GC retention time. By using this method, retention time can be used to determine the boiling point and most probable carbon number of an unidentified hydrocarbon compound. The margin of error of the method was established by determining the carbon numbers of 167 compounds from their boiling points. Correct carbon-number assignments were made for 131 compounds (78.4 percent), and carbon-number was underestimated for 16 compounds (9.6 percent) and overestimated for 20 compounds (12.0 percent). All over- and underestimates were in error by one carbon atom.

The GC and the data-evaluation methods used are providing excellent soil-gas characterization during this field study. Chromatogram analysis by carbon-number determination can be used in other studies where hydrocarbons are detected but not specifically identified.

SIGNIFICANT PHYSICAL EFFECTS ON SURFACE ACOUSTIC WAVE (SAW) SENSORS*

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Surface acoustic wave (SAW) devices are presently being developed for applications in chemical sensing as well as for polymer characterization. SAW gas and vapor sensors have the potential for miniaturization and high sensitivity to a wide variety of substances. Polymer characterization is applicable to such diverse fields as protective coating design and decontamination of polymers. Research was conducted to better understand the physical mechanisms behind SAW response. Practical problems as to film uniformity, thickness measurement and environmental controls such as temperature and gas flow rates necessary in such measurements were considered.

The effects of elastic properties in comparison to mass loading of polymer coatings on SAW substrates were investigated. A theoretical basis for the effects of vapor-induced swelling or of thermal expansion was established. Compressive tension and its effect on SAW frequencies were found to be simple to describe, if there is no film slippage or polymer flow. The response of quartz-substrate SAW crystals coated with polycarbonate and polyimide (glassy polymers) upon exposure to toluene and methanol was measured and was found consistent with theory in predicting effects of the order of the ratio of coating to substrate elastic constants.

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*For furthur details see: Bartley, D.L. and Dominguez, D.D.: "Elastic Effects of Polymer Coatings on Surface Acoustic Waves," *Anal. Chem.* 62:1649 (1990).

AN EVALUATION OF FIELD PORTABLE XRF SOIL PREPARATION METHODS

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INTRODUCTION

The USEPA Environmental Response Team (ERT) has been using field portable X-ray Fluorescence (XRF) spectrometers to characterize Superfund and hazardous waste sites. An Outokumpu Electronics Inc. (OEI) X-MET 880 XRF spectrometer equipped with a surface probe containing Cm-244 and Am-241 radio-isotopes was selected. Field portable XRFs have enabled the ERT to estimate the extent of metal contamination; support biological "plant stress assessment" studies in tidal wetlands; and, support a health and safety assessment of the extent of contamination and possible human exposure of a network of hiking trails and campsites contaminated by a smelting operation.

BATTERY BREAKAGE SITE

In September, 1989 the ERT deployed a XRF unit to perform an extensive post remedial site lead survey at an abandoned battery reclamation site. Analyses were planned for both surface and subsurface soil samples to determine the extent of lead contamination. The OEI X-MET 880 XRF spectrometer was calibrated with a suite of 18 site specific lead standards by an analytical chemist.

An in-situ analysis method was preferred since it would reduce sample preparation time and the risk of personal exposure to the contaminants. A literature search failed to find any studies demonstrating the correlation of results from an in-situ XRF analysis and the accepted method of preparing soils by drying and sieving. The analyses included 29 in-situ and prepared soil samples in an effort to evaluate the sample preparation methods. Samples that were analyzed by the XRF in-situ method were dried and sieved and reanalyzed by XRF. The paired-difference t-test was used to evaluate the results of both sample preparation methods using a significance level of 5 percent.

PROCEDURE FOR IN-SITU SURFACE SOIL LEAD XRF ANALYSIS

All organic matter and large rocks were removed from the area (8" by 5") to be analyzed. The area was then rendered flat with a stainless steel trowel. The XRF instrument was initiated for a 60 second measuring time for the lead analysis while the surface probe was held flush against the soil surface. The sample area number, location (A) and XRF lead result were logged into a field notebook. The analysis was then repeated selecting a different analysis location (B) within the prepared area. The results of the two analyses were averaged and reported.

PROCEDURE FOR DRIED AND SIEVED SOIL XRF ANALYSIS

The soil within the prepared area was removed to a depth of a quarter inch. Large stones and organic matter were removed prior to drying. The entire sample was dried in an oven and sieved through 10 and 20 mesh stainless steel sieves with a stainless steel spoon. All organic matter and stones were removed and discarded. The sample was homogenized for one minute by dividing the sample into quarters and mixing opposite sides together.

A 31-mm, polyethylene X-ray sample cup was labeled and filled with soil. The cup was sealed with 0.2-mm thick polypropylene, X-ray window film. Prior to XRF analysis, the sample cup was gently tapped against the table top three times to pack the soil evenly against the polypropylene window film. The sample cup was placed directly on the XRF detector window and the instrument initialized for a 60 second lead analysis time. The result of the analysis was reported.

CHEMICAL ANALYSIS PROCEDURE FOR METALS IN SOIL

The XRF sample cup was submitted to the laboratory for chemical atomic absorption (AA) analysis. Approximately 0.5 g of sample, weighed to 0.001 g accuracy, was thoroughly mixed with 10 ml 1:1 nitric acid:water, digested according to SW-846, Method 3050 and analyzed according to Method 7000.

RESULTS OF THE XRF AND AA METHODS ANALYSES

Seven of the 29 samples analyzed had XRF results below the XRF detection limit of 123 mg/kg or quantitation limit (QL) of 410 mg/kg. The XRF and AA results of these samples are presented in Table 1. The AA results show that all of the sample lead concentrations fell below the XRF quantitation limit of 410 mg/kg. The results of both XRF methods were all below the XRF QL except for sample 5469B's XRF in-situ result that was 543 mg/kg lead. This was considered acceptable since priority samples with XRF results at or near the QL would be sent to the lab for AA analysis. A high frequency of false negative XRF results would have caused either XRF method to be questioned.

Three of the 29 samples analyzed had XRF results above the XRF linear calibration range (5300 mg/kg). The XRF and AA results of these samples are presented in Table 2. The AA results show that all of the sample lead concentrations are near the end of the XRF linear calibration range.

Nineteen of the samples had XRF results above the XRF quantitation limit and below the end of the XRF linear calibration range. The XRF and AA results of these samples are presented in Table 3. These 19 samples along with samples 5464B and 5469B from Table 1 (n = 21) were used in a paired-difference t-test analysis.

RESULTS OF THE XRF AND AA METHODS PAIRED-DIFFERENCE T-TEST EVALUATION

The goal of the paired difference t-test is to determine if the mean difference of two populations of paired results, is different from zero at the 5-percent significance level. In other words, the analyst is willing to accept a 1 in 20 chance of saying that the average difference of the two populations is significantly different from zero when in fact it is not. Additionally, the test makes two assumptions. First, that each pair of measurements is independent of the other pairs. Second, that the differences are from a normal distribution. The populations used in this test were normalized with a square root function.

The in-situ and dried & sieved XRF results were analyzed by the paired- difference t-test. The probability value for this test was 0.279 and is greater then 0.05 (which is associated with a 5-percent significance level). Therefore, the average difference of the paired results of the two XRF analytical methods is not significantly different from zero.

The in-situ XRF and AA results were analyzed by the paired-difference t-test. The probability value for this test was 0.671 and is greater then 0.05. Therefore, the average difference of the paired results of the two analytical methods is not significantly different from zero.

The results of this statistical test enabled the project manager to conclude that the two methods of preparation were not significantly different and that the in-situ XRF method and the AA lead analytical methods were not significantly different. In-situ analysis was then performed on 500 surface and sub-

surface samples. Additionally, portable XRF was used to support selection of soil samples for use in a treatability study.

RESULTS OF THE SITE IN-SITU XRF AND AA EXTENT OF CONTAMINATION ANALYSES

Seventy-one of the 500 samples analyzed by in-situ XRF were collected and submitted to the REAC laboratory for AA lead analysis. Twenty-six of these samples had XRF results below the XRF QL of 270 mg/kg (the XRF lead calibration curve was modified using site-specific standards from the method evaluation work that resulted in lower XRF lead detection and quantitation limits and an extended linear calibration range). The XRF and AA results of these samples are presented in Table 4. Four of these samples had AA results above the XRF QL of 270 mg/kg.

Five of the 71 samples had XRF results above the XRF linear calibration range of 12,000 mg/kg lead. The XRF and AA results of these samples are presented in Table 5. All of these samples had AA results above or near the end of the XRF linear calibration range.

Forty of the samples had XRF results above the XRF quantitation limit and below the end of the XRF linear calibration range. The XRF and AA results of these samples are presented in Table 6. These forty samples and the six samples in Table 4 with "J" XRF values (n = 46) were used in a paired-difference t-test analysis. The probability value for this test was 0.872 and is greater then 0.05 (which is associated with a 5-percent significance level). Therefore, the average difference of the paired results of the two lead analytical methods is not significantly different from zero.

CONCLUSIONS

The paired-difference t-test can be used as a decision tool in the evaluation of XRF soil lead analytical methods. It showed that the average difference between these two methods was not significantly different from zero at the 5-percent significance level. At also showed the average difference between the in-situ XRF and the AA lead analytical methods was not significantly different from zero at the 5-percent significance level for both the XRF method development data and the site extent of contamination data.

Additionally, the portable OEI X-MET 880 supported the following:

*Soil lead analysis in a densely wooded area of the site initially assumed to be uncontaminated . Investigation of the area located battery casings mixed with soil under the leaves. XRF lead analysis confirmed that the area was contaminated with high mg/kg levels of lead.

*Selection of soil samples for a treatability study.

*320 XRF surface lead analysis results were used to develop a site contour map.

OTHER XRF APPLICATIONS

In June, 1990, the ERT deployed a XRF unit to perform cadmium and nickel analyses on sediment samples from a tidal wetlands contaminated by a battery manufacturing facility. The biological "plant stress assessment" work plan called for the investigation of a minimum of one plot of vegetation for each anticipated nominal cadmium concentration range. The results of XRF analyses of the plot sediments enabled the project manager to select the appropriate plots. Selected samples were submitted for laboratory AA analysis. The paired-difference t-test evaluated the results of both XRF and AA analytical methods and found the average difference of the paired results of the two cadmium analytical methods was not significantly different from zero (at the 5-percent significance level).

That same month, an XRF unit performed lead and zinc in-situ surface soil analysis in a network of hiking trails and campsites contaminated by a smelting operation for a health and safety assessment of the extent of contamination and possible human exposure. Samples were submitted for AA analysis and the results of both analytical methods were evaluated by the paired-difference t-test.

The average difference of the paired results of the zinc analytical methods (most lead values were below the XRF QL) were significantly different from zero (at the 5-percent significance level). Almost all of the XRF zinc results were higher then the AA analysis. It is suspected that the contamination from the smelter is concentrated in the top layer of the soil and was diluted when the top quarter inch of soil was removed for laboratory AA analysis.

TABLE 1
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU AND DRIED & SIEVED SOIL XRF Pb ANALYSES,
AND AA Pb ANALYSIS IN mg/kg
SAMPLES WITH RESULTS BELOW THE XRF QUANTITATION LEVEL

SAMPLE NO.	IN-SITU XRF	DRIED & SIEVED XRF	AA LAB
5461B	ND	ND	52
5464B	125-J	148-J	160
5469B	543	125-J	190
5470B	ND	ND	80
4281B	190-J	ND	13
4499B	ND	ND	38
4495B	138-J	ND	49

XRF detection limit = 123 mg/kg. XRF quantitation limit = 410 mg/kg.
AA detection limit = 5 mg/kg.
ND denotes not detected.
J denotes the sample concentration is between the detection limit and the quantitation limit.

TABLE 2
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU AND DRIED & SIEVED SOIL XRF Pb ANAYLSES,
AND AA Pb ANALYSIS IN mg/kg
SAMPLES WITH RESULTS ABOVE THE XRF LINEAR CALIBRATION RANGE

SAMPLE NO.	IN-SITU XRF	DRIED & SIEVED XRF	AA LAB
4332B	13800 *	6040 *	5000
4496B	7680 *	6520 *	5300
3319B	6590 *	7210 *	5100

XRF detection limit= 123 mg/kg. XRF quantitattion limit= 410 mg/kg.
AA detection limit= 5 mg/kg.
*- denotes sample conc. is above the XRF linear calibration range (> 5300 mg/kg).

TABLE 3
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU AND DRIED & SIEVED SOIL XRF Pb ANALYSES, AND AA Pb ANALYSIS IN mg/kg
SAMPLES WITH RESULTS ABOVE THE XRF QUANTITATION LIMIT & IN XRF CALIBRATION RANGE

SAMPLE NO.	IN-SITU XRF	DRIED & SIEVED XRF	AA LAB
5460B	1950	2320	1800
5462B	1390	1500	1200
5463B	3180	3080	3200
5465B	838	1080	880
5466B	771	946	820
5467B	540	615	530
5468B	416	1450	950
5471B	1000	2010	1100
4280B	1170	3040	2800
4331B	1030	1310	1300
4498B	532	644	470
5590C	655	716	460
4500B	1730	1990	1600
5489B	2530	680	1000
5490B	1430	2610	1900
5491B	1390	1350	880
5493B	1370	1250	1200
5494B	910	883	700
5492B	1420	1270	1100

XRF detection limit= 123 mg/kg. XRF quantitation limit= 410 mg/kg. AA detection limit= 5 mg/kg.

TABLE 4
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU XRF AND AA Pb ANALYSIS IN mg/kg ON SURFACE AND BORING SOILS
SAMPLES WITH RESULTS BELOW THE XRF QUANTITATION LEVEL

SAMPLE NO.	IN-SITU XRF	AA LAB	SAMPLE NO.	IN-SITU XRF	AA LAB
B2-1	ND	21	B4-3	ND	32
B6-1	ND	15	B8-2	ND	15
B19-2	ND	32	B20-2	ND	120
B20-4	ND	16	B22-2	ND	19
B24-1	ND	90	B25-1	ND	51
B26-2	ND	33	B28-2	ND	100
B29-3	ND	22	B30-4	ND	11
B32-6	ND	25	B34-6	ND	25
B39-0	ND	50	B45-0	ND	54
MW10-2	ND	24	MW11-2	ND	23
B4-1	81 J	98	B42-6	152 J	370
B13-1	176 J	160	B2-2	190 J	790
B39-12	249 J	480	MW9-1	261 J	1400

ND-denotes not detected. XRF detection limit=81 mg/kg AA detection limit=5 mg/kg.
J-denotes concentration is between the detection and quantification limit. XRF quantitation limit= 270 mg/kg.

TABLE 5
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU XRF AND AA Pb ANALYSIS IN mg/kg ON SURFACE AND BORING SOILS
SAMPLES WITH XRF RESULTS ABOVE THE XRF LINEAR CALIBRATION RANGE

SAMPLE NO.	IN-SITU XRF	AA LAB
B13-2A	22500 *	53000
B25-2	69500 *	120000
B28-3	73000 *	11000
B30-2	54900 *	110000
B30-3	15700 *	170000

XRF detection limit= 81 mg/kg. AA detection limit= 5 mg/kg. XRF quantitation limit= 270 mg/kg.
J-denotes concentration is between the detection and quantification limit.
*-denotes sample conc. is above the XRF linear calibration range (>12000 mg/kg).

TABLE 6
BATTERY BREAKAGE SITE
RESULTS OF IN-SITU XRF AND AA Pb ANALYSIS IN mg/kg ON SURFACE AND BORING SOILS
SAMPLES RESULTS ABOVE THE XRF QUANTITATION LIMIT AND IN XRF CALIBRATION RANGE

SAMPLE NO.	IN-SITU XRF	AA LAB	SAMPLE NO.	IN-SITU XRF	AA LAB
B2-4	555	750	B4-2	1010	780
B5-2	412	1600	B6-0	2990	3100
B10-1	1290	2700	B11-0	10700	6700
B11-1	4230	4100	B13-2B	449	290
B14-1	1120	740	B14-2	11700	6100
B15-1	991	570	B17-1	1740	2500
B19-1	862	1400	B20-1	2460	4500
B20-3	648	610	B22-1	744	1300
B26-1	11000	8900	B31-2	4870	3200
B32-0	8390	12000	B34-0	1120	1500
B36-6	3710	2700	B39-18	844	1100
B41-0	10500	11000	B41-6	292	360
B44-30	730	800	MW9-2	945	810
MW11-1	1920	2700	SS165	579	380
SS170	1630	4400	SS173	1040	970
SS175	3080	2600	SS180	3010	2200
SS183	6930	5500	SS189	5060	2100
SS195	2220	1700	SS199	5690	8300
B5-1	301	140	B12-3A	657	140
B18-3	1303	270	B12-2	2797	170

XRF detection limit = 81 mg/kg. XRF quantitation limit = 270 mg/kg. AA detection limit = 5 mg/kg.

DEVELOPMENT OF A FIELD SCREENING TECHNIQUE FOR DIMETHYL MERCURY IN AIR

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Many forms of organic and inorganic mercury are pervasive in the environment; with both natural and industrial sources contributing to the total environmental mercury burden. Mercury can be biologically metabolized to form various organomercurials. One of these, Dimethyl Mercury (DMM) represents a potential health risk via air exposure because of its high volatility and toxicity.

Mercury contaminated soils and sediments are frequently biologically active and have been demonstrated to contain DMM. If left undisturbed, emissions of DMM will be related to the biological generation rate of DMM as well as the emission rate through the soil or sediments as regulated by porosity, temperature, pressure, and other physical-chemical factors. However, when the soils are disturbed, the potential for elevated emissions of DMM increases.

Research conducted by the USEPA's Environmental Response Team (ERT), with the support of Roy F. Weston, Inc. through the Response, Engineering, and Analytical Contract (REAC), has resulted in a potential real-time monitoring technique.

BACKGROUND INFORMATION PROMPTING RESEARCH

The Army Corps of Engineers had been conducting a cleanup of mercury contaminated soils; however, site remediation was suspended due to the potential for DMM emissions and the lack of a real-time air monitoring method.

A preliminary investigation conducted by ERT and Weston/REAC at the request of the Army Corps of Engineering and USEPA Region I, indicated that DMM could be present in the soils, especially in areas where anaerobic activity was prevalent.

REVIEW OF REAL-TIME PORTABLE INSTRUMENTS FOR DETECTING DMM

The criteria established for selecting a real-time instrument for monitoring DMM were quite restrictive. First, the instrument had to be portable and permit operation by non-technical personnel. Second, it had to have real-time or semi-real-time monitoring capabilities.

The third requirement was that it be specific to organomercurials.
A literature review indicated that the primary methods for detecting mercury were atomic adsorption, gas chromatograph, infra-red analyzers, and gold film technology. Atomic Adsorption instruments are generally not portable, require technical expertise to operate and provide only semi-real-time results. Gas chromatography requires technical expertise and provides semi-real-time results. Infra-red analyzers have too many interferences from organic compounds. Gold film detectors are cross-sensitive to sulfide compounds, however, the use of an internal sulfide trapping pre-filter negates this cross-sensitivity. The gold film technology thus appeared to have the greatest potential for the required application, and a gold film mercury vapor analyzer was selected for detailed review.

GOLD FILM TECHNOLOGY

The Arizona Instruments Model 411, Gold Film Mercury Vapor Analyzer was selected as the instrument of choice. The Model 411 was originally developed for monitoring elemental mercury in air, and operates on the principal that mercury will form an amalgam when it contacts a gold film.

The Model 411 detects the presence of mercury by passing a stream of air across a thin gold film. As the mercury in the air contacts the film an amalgam is formed. The amalgamation causes an increase in the electrical resistance of the film proportional to the mass of mercury in the sample. The change in resistance is compared to a sealed reference gold film and processed by a microprocessor to provide a digital read-out in milligrams of mercury per cubic meter (mg/m^3).

To eliminate the necessity of thermally desorbing the gold film after each use, the Model 411 employs a microprocessor which allows the instrument to operate over a wide range of resistances while remaining balanced with the reference film. Heating the film to approximately 250°C, and subsequently passing a stream of mercury free air across the film desorbs the mercury and restores the film to its baseline resistance.

EXPERIMENTS WITH SILVER-COATED CHROMOSORB

Since DMM may be metabolized from elemental mercury, the hypothesis was made that both DMM and elemental mercury might be present during air monitoring. Elemental mercury would interfere with the detection of DMM in monitoring air, therefore a means to remove the elemental mercury from the sample without affecting the DMM concentration was required. Silver-coated Chromosorb was tested for this purpose.

The first test involved monitoring for elemental mercury with the Model 411 using a silver-coated Chromosorb tube pre-scrubber within a test vessel containing elemental mercury in which the vapor pressure had reached equilibrium. Thirty samples of the mercury-saturated air were collected without breakthrough occurring from the silver-coated Chromosorb tube.

The second test of the silver-coated Chromosorb pre-scrubber involved determining if DMM would pass through it. This was accomplished by preparing a DMM standard and measuring the concentration with and without the silver-coated pre-scrubber. As Table 1 indicates, the test results for the analysis with and without the pre-scrubber are essentially the same.

PREPARATION OF DMM STANDARDS

DMM standards are not commercially available , therefore, it was necessary to prepare them in-house in Summa passivated canisters by injecting a measured volume of DMM and methanol solution into the canister. Due to uncertainties in this procedure, DMM standards were confirmed by select ion gas chromatography and mass spectra analysis.

USE OF THE MODEL 411 FOR DETECTION OF DMM

Initial experiments conducted with the Model 411 (configured as per manufacturer's specifications) provided erratic results and an inadequate detection limit for DMM.

The Arizona Instrument's Model 411 was therefore modified as follows:

1.The detector resistance was increased from approximately 60 ohms to approximately 98 ohms.
2.The instrument's sample flow rate was increased from 720 cubic centimeters per minute (cc/m) to 866 cc/m.
3.The sampling duration was doubled from 10 seconds to 20 seconds.

TABLE 1. COMPARISON OF ARIZONA INSTRUMENTS MODEL 411 RESPONSE WITH AND WITHOUT A SILVER-COATED CHROMOSORB PRE-SCRUBBER TO 4.8 ppb-V and 24.6 ppb-V STANDARDS OF DMM

DMM Standard Concentration ppb-V	Date Run	Model 411 Response (unitless) without Pre-Filter	Model 411 Response (unitless) with silver-coated Chromosorb Pre-Filter
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.004	0.003
4.8	7/27/89	0.003	0.003
4.8	7/27/89	0.004	0.003
4.8	7/27/89	0.004	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.001	0.002
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.003	0.002
4.8	8/01/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.003
24.6	7/25/89	0.012	0.016
24.6	7/25/89	0.011	0.012
24.6	7/25/89	0.010	0.009
24.6	7/25/89	0.015	0.011
24.6	7/25/89	0.016	0.011
24.6	7/25/89	0.014	0.011
24.6	7/25/89	0.012	0.011
24.6	7/27/89	0.013	0.013
24.6	7/27/89	0.013	0.011
24.6	7/27/89	0.012	0.011
24.6	7/27/89	0.011	0.011
24.6	7/28/89	0.011	0.009
24.6	7/28/89	0.009	0.009
24.6	7/28/89	0.009	0.008
24.6	7/28/89	0.010	0.008
24.6	7/28/89	0.008	0.008
24.6	8/01/89	0.010	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.010	0.009
24.6	8/03/89	0.009	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.009	0.009

4.A silver-coated Chromosorb tube was utilized as a pre-scrubber to remove elemental mercury.
5.The calibration switches were adjusted to calibrate the instrument to a known concentration of DMM.

SENSOR STATUS DRIFT IN THE MODEL 411

It was observed during method development that the Model 411's sensor status would first increase after the instrument detected DMM, then decrease after a period of time. The sensor status is an indication of the percent gold film saturation. The increase and subsequent downward drift in sensor status was not encountered with elemental mercury. Sensor status drift resulted in the instrument indicating readings lower than actual concentrations and was corrected for by allowing the instrument to balance the Wheatstone bridge between the sample gold film and the reference film prior to monitoring another sample. This was accomplished by drawing four 20-second samples into the instrument through a iodized charcoal filter. The filter effectively adsorbs organic and inorganic mercury resulting in mercury free sweep air. The number of mercury free air sweeps required to permit the instrument to re-establish baseline resistance was determined empirically to be four.

LINEAR RANGE OF THE MODEL 411 FOR THE DETECTION OF DMM

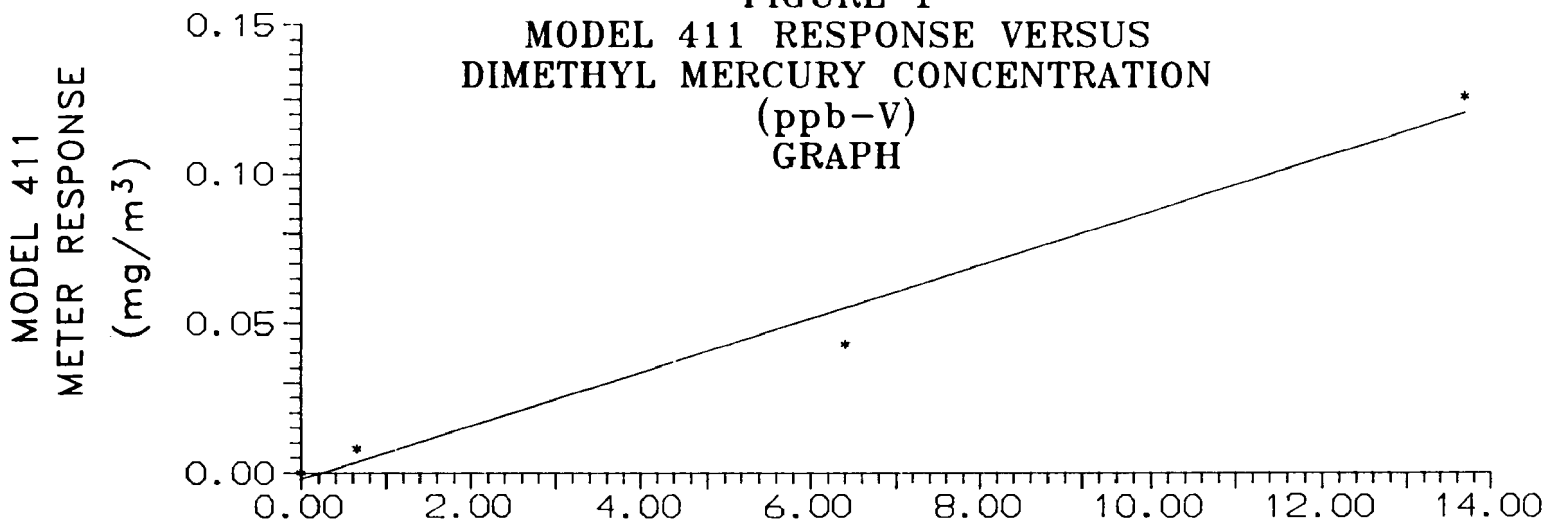
The linear range of the Model 411 for the detection of DMM was determined by diluting a 13.70 ppb-V DMM standard down to approximately one half the Threshold Limit Value (TLV) of 0.01 mg(Hg)/M^3. Dilutions were made to 0, 0.64, 6.40, and 13.70 ppb-V and were validated by GC/MS analysis.

The DMM dilutions were measured with the Model 411 and the data utilized to generate a calibration curve (Figure 1). The calibration curve was found to be linear, with a critical correlation coefficient (R^2) of 0.98. This was deemed an acceptable linear range for this work effort.

DISCUSSION AND CONCLUSIONS

This study indicates that gold film mercury vapor detectors have definite potential in monitoring for DMM. The Model 411 appears promising because of its simplicity, stability and effectiveness as a screening tool. However, as with any screening device, it should not be relied upon exclusively; rather, it should be incorporated into a multi-tiered sampling and monitoring program.

FIGURE 1
MODEL 411 RESPONSE VERSUS DIMETHYL MERCURY CONCENTRATION (ppb-V) GRAPH



Note: 1ppb-V is approximately 0.01 mg/m³ for DMM

DMM CONC. (ppb-V)	METER RESPONSE (mg/m³)
0	0
0.64	0.008
6.40	0.043
13.70	0.126

LINEAR REGRESSION VALUES:

R^2 = 0.98
y Intercept = 0.00220
Standard error of y = 0.010048
Slope = 0.008959
Standard error of x = 0.000911

APPLICABILITY OF THIN-LAYER CHROMATOGRAPHY TO FIELD SCREENING OF NITROGEN-CONTAINING AROMATIC COMPOUNDS

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BACKGROUND

Nitrogen-containing aromatic compounds (NCAC's) are toxic and mutagenic environmental contaminants of widespread occurrence. Often, their presence in soil or sediment is a result of wood preserving activities involving creosote. Previously, we have used thin layer chromatography (TLC) to effect compound class separations of NCAC's from polynuclear aromatic hydrocarbons (PNA's). Prior to the TLC separation, contaminants were extracted from the soil sample and divided into an HCL and neutral fraction. The neutral fraction in particular was subjected to preparatory TLC to isolate neutral NCAC's without interfering polynuclear aromatic hydrocarbons (PNA's).

It seemed feasible to apply TLC to field screening of NCAC's and other compound classes such as PNA's.

EXPERIMENTAL SECTION

TLC

E. Merck silica gel 60 preparative plates were used that were 1 mm thick and 20 X 20 cm size with pre-concentration zone. Aldrich silica gel 60 plates were used with 0.25 mm thickness and 5 X 20 cm in size.
Primary solvent systems were 30:70 methylene chloride:hexane for neutral NCAC's, 30:70:10 methylene chloride:hexane:propanol for the basic NCAC's, and 30:70:10 methylene chloride: hexane:isopropyl ether for combined fractions.

GC/MS

A Finnigan-MAT 4021 was used in the electron ionization mode with source temperature 270°C. The mass range scanned was m/z 50-450 in 1 sec. A 30 m DB-5 column was used and temperature programmed from 60-300°C
at 20°C/min.

RESULTS AND DISCUSSION

Fractionation

Samples were available from Soxhlet, sonication, or supercritical fluid extraction of soils and were analyzed in methylene chloride solution. A fractionation scheme was used to separate NCAC's from PNA's (Fig. 1). This scheme afforded two fractions: the basic compounds called the HCl fraction and the neutral compounds called the neutral fraction. Both fractions were free of interfering PNA's as determined by GC/MS.

The neutral fraction had been subjected to preparative TLC in order to free the cyanoarenes and indole/carbazole derived molecules from interfering PNA's. The R_f range of 0.05-0.32 was scraped (Fig. 2). This region therefore provides screening capability for neutral NCAC's in soil. The HCl fraction could be subjected to TLC determination (Fig. 3) and was free of interfering PNA's as determined by GC/MS.

Validation by GC/MS

Fig. 4 and 5 provide the total ion current chromatograms for the HCl and neutral fractions of NCAC's from a soil heavily contaminated by creosote. Selected compound classes are labeled in order to facilitate comparison of retention behavior and relative amounts of NCAC's present.

Advantages of TLC

TLC offers a low cost, rugged, simple, and efficient method to screen for target compounds such as NCAC's. Greater selectivity can be achieved than that illustrated by incorporation of a third solvent such as isopropyl ether in place of propanol.

A great advantage of the use of TLC is the multiple sample capability. Up to 40 samples could be run on a 20 X 20 cm plate. This is a clear advantage over HPLC methods. By going to greater complexity, automation can be built into the methods. Automatic spotting, densitometry, and multiple development are some of the options available.

CONCLUSION

TLC offers a simple and economical way to do field screening of multiple samples. This technique is by no means limited to NCAC's. Generalization to PNA's and other aromatic compounds is obvious. Non-aromatic compounds can also be determined through the use of visualization reagents or in situ derivatization reagents.

NOTICE

Although the research described in this report has been funded by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

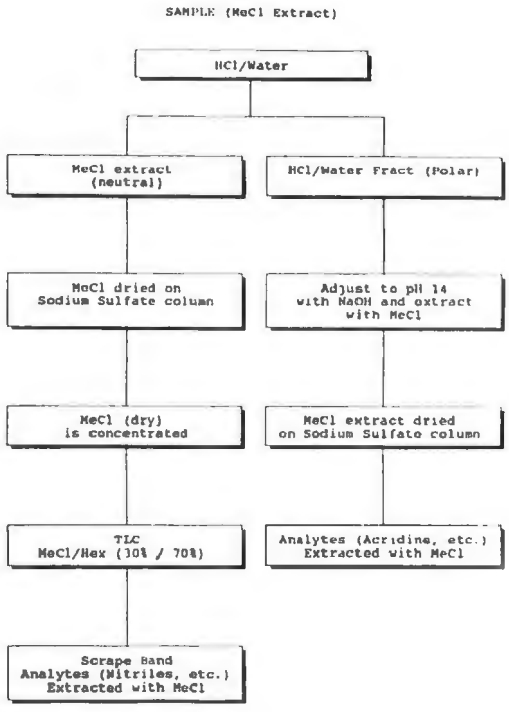

Figure 1. Fractionation scheme to separate NCAC's (both basic and neutral compounds) from PNA's.

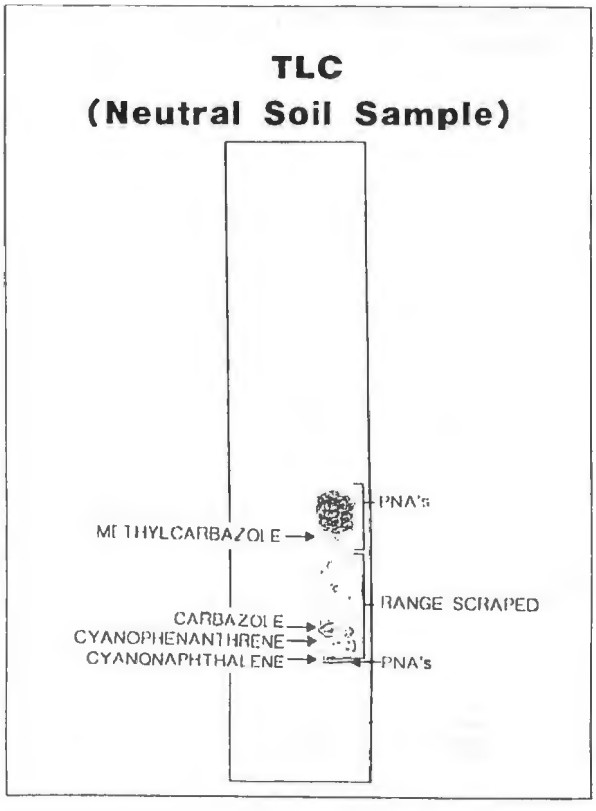

Figure 2. Preparatory TLC isolation of neutral NCAC's in the presence of PNA's; solvent system 70:30 hexane:methylene chloride.

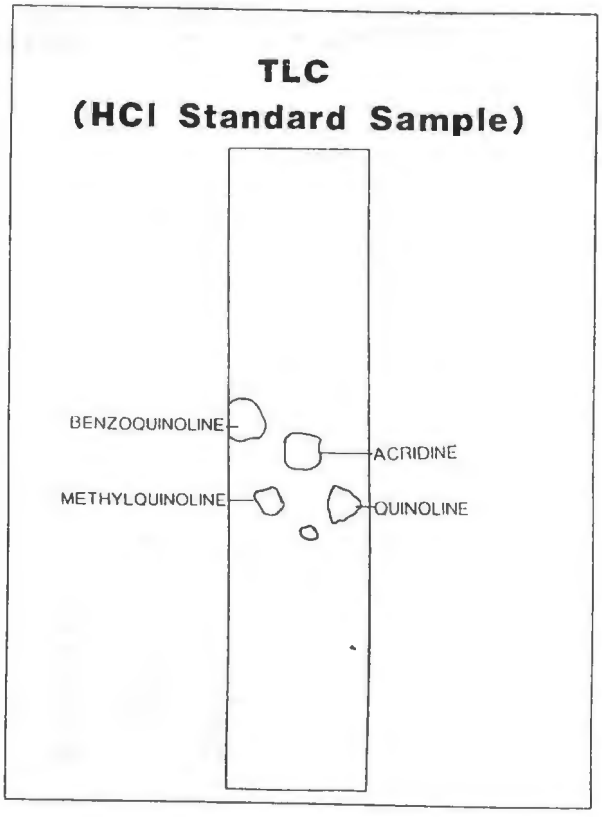

Figure 3. TLC of the HCL fraction (basic NCAC's) illustrated with standards; solvent system 70:30:10 hexane:methylene chloride:propanol.

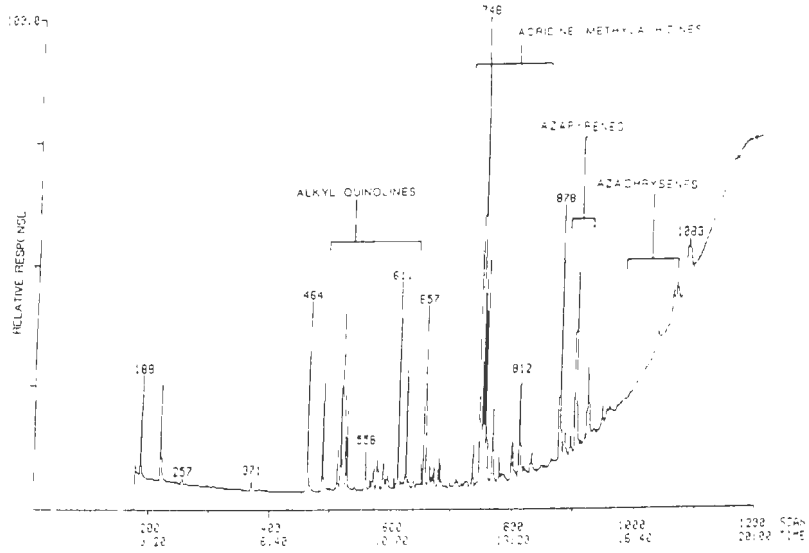

Figure 4. GC/MS total ion trace of the HCL fraction (basic NCAC's), m/z 50-450, electron ionization.

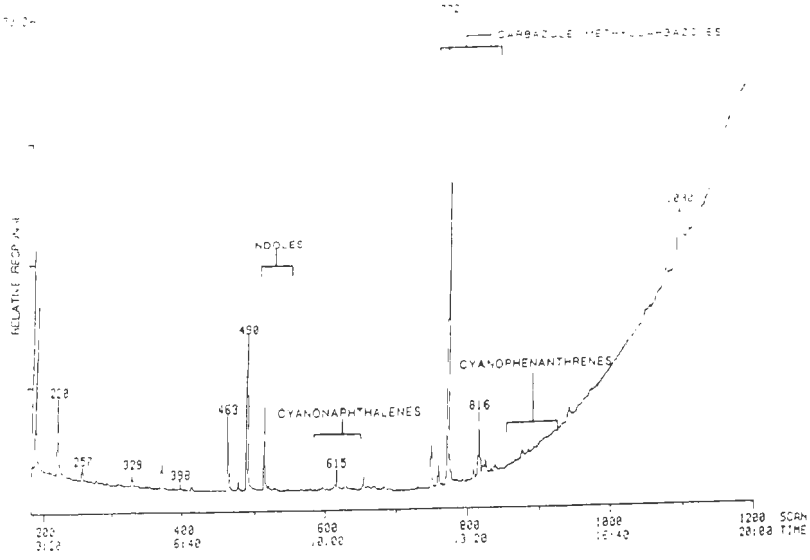

Figure 5. GC/MS total ion trace of the neutral fraction (NCAC's), m/z 50-450, electron ionization.

ASSESSING THE AIR EMISSIONS FROM A CONTAMINATED AQUIFER AT A SUPERFUND SITE

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The Environmental Response Team was asked by Region II to assess the degree, if any, that vapors were migrating from a contaminated aquifer through the vadose zone to the air. If such migration was occurring, the Region also wanted to know what would be the worst case long term average air exposure to the surrounding residents. Even though the emissions may not have been large at any point, the fact that these emissions could be occurring over a large area raised the possibility of an overall significant, long-term air emission problem.

The ERT's sampling approach involved the taking of flux measurements over several transects. The flux measurements were taken using a modified sampling system that would easily switch from purging the system to filling a Tedlar bag without any changes in the flowrates. The results from the portable GC analyses of the Tedlar bag samples were then used to compute flux rates (ug/sec/m^2) at each point.

These flux values were then kriged, and the results were plotted in order to determine the overall area of concern. The intermediate kriging output file was then used to calculate an average flux rate for the area of concern. This average flux rate was then converted to an overall area source emission term (total g/sec) that was then plugged into a long-term exposure air dispersion model in order to estimate the long-term average exposure of the nearby residences. This final set of numbers were given to the Region for a subsequent quantitative risk assessment.

CALCULATION AND USE OF RETENTION INDICES FOR IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS WITH A MICROCHIP GAS CHROMATOGRAPH

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Introduction

A major difficulty in using elution time data for component identification is the high variability of such data with changes in chromatographic conditions. The use of retention indices improves the situation somewhat but a degree of variability remains. Reproducing Kovat's retention indices with different instruments in a laboratory setting can be difficult and such difficulty are increased substantially during field operations.

The Microsensor Technology Inc. model M200 gas chromatograph is a microprocessor controlled instrument constructed from micromachined injector and detector assemblies along with microbore capillary columns. Independent column heaters are capable of controlling the temperature of each column to within 0.1°C over a range of 30° to 180°C. The resulting instrument is not only highly portable but is capable of generating highly reproducible retention data on both a "between days" and a "between instruments" basis.

The dual column capability reduces the likelihood of coincident elution times for different compounds and thereby increases the reliability of component identifications. A software package developed at LSU uses a two tiered standardization technique to provide even more consistent retention data and then uses that data to generate qualitative information.

Discussion

A time series of 220 separate analyses of pentane, hexane and heptane was performed over a period of 4 weeks. Approximately 20 samples per day were run for three one week periods having a 4 day interval between weeks. Variations in retention time were below one percent for the four weeks were on the order of 0.2 percent in any one week. This kind of stability justifies the use of an external retention index standard.

The corresponding retention index data show extremely consistent values over a several week period. Consequently, retention indices may be determined in the laboratory and used in the field without bringing authentic standards of all possible sample components. Variations in Kovat's retention indices over the four week period had standard deviations of less than 0.5 units.

An M200 equipped with an OV-73 column and an OV-1701 column provides multidimensional elution time data . The rather narrow dispersion of compounds about a straight correlation line indicates that the retention indices on these two columns are moderately correlated; a considerable area in the detection space is empty. These two columns do not differ greatly in polarity, thus one might expect such a correlation. As a result the dimensionality of the space is closer to 1.3 than 2. Note however, the substantial increase in resolving power versus that for either of the columns singly (i.e., the projection of the space onto one axis). Using a conservative estimate of a peak capacity of 70 for a typical 100 second chromatogram and a dimensionality of 1.3, this system has a peak capacity of approximately 250. Even with the increased resolving power of two columns,however, an unresolvable pair of compounds is easily found. Such cases could be further minimized by optimizing the choice of which two stationary phases used to obtain the detection space.

Estimation of the retention index from retention time data requires an estimate of the column dead time or gas holdup time. The accuracy of this estimate can substantially bias the resulting retention index values for early eluting compounds. A variation of ±2.5% in the dead time estimate for column temperatures of 40°C results in greater than 10% error in retention index calculations at retention indices of approximately 200. The value of I at which the departure from linearity becomes significant increases with temperature (approximately 100 units per 20° change). Typical variance we have observed in dead time estimates.have been approximately 2.5%.

Significantly, using the elution time of the air peak consistently overestimates the dead time. Comparing the elution times of air and hydrogen suggests that air is actually retained to the extent of 0.1 to 0.2 seconds. This means that using air as to estimate dead time consistently results in a nonlinear function that systematically overestimates retention indices. Consequently, we use an iterative method (1) which estimates t_o by linearizing the log $(t-t_o)$ vs I function. The result a linear function which in essence recalibrates the retention index library to current conditions.

Temperature dependence of retention indices were observed to range from near zero for some nonpolar compounds to approximately 2 units per degree for alcohols. Oxygen containing compounds showed negative correlations with temperature, in contrast with non oxygen containing compounds regardless of polarity. This leads to the possibility of using temperature dependence information as a tool for identifying compound classes, i not specific compounds.

Conclusions

The use of retention index library concept with the M200 should provide a reasonably reliable screening tool for sample component identification. The high degree of reproducibility in retention data for one instrument should make libraries prepared in the laboratory field deployable. Based or our experiences with the M200, there is a good possibility that the 120 component library created at LSU will work with a large proportion of the M200 instruments built to date.

An inherent limitation in the technique presented here is a lack of dimensionality due to the similarity of the two stationary phases used. While the resolving power is quite good as is, improvements can be made by optimizing the choice of stationary phase and/or implementing temperature programming.

Implementation of temperature programming is problematic with the

micro-thermal conductivity detector used in the M200. Baseline drift has been a significant problem. We have recently been successful in obtaining temperature programmed chromatograms with the M200 with thermal conductivity detection. We expect this to result in a tremendous increase in peak capacity and overall range of analytes.

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Determination of PCB's by Enzyme Immunoassay

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ABSTRACT

A competitive inhibition Enzyme ImmunoAssay (EIA) has been developed for the determination of PolyChlorinated Biphenyls (PCB's). The test is capable of analyzing for PCB's in the field in 15 minutes (from prepared sample), using no specialized equipment. The test specificity is restricted to PCB's, with high sensitivity for Aroclor's 1016, 1232, 1242, 1248, 1254, and 1260, and moderate sensitivity for Aroclor 1221. Matrix and solvent interferences are minimal. The test is capable of direct analysis of PCB's at low ppb levels in water. A rapid extraction technique using DMF, DMSO, or methanol gave a mean recovery of 70% of Aroclor 1248 spiked into non-oily soils. Soils spiked with Aroclor 1248 in transformer oil (to a final concentration of 50 ppm) and extracted with DMSO or 4 other solvents showed much lower recoveries, though still adequate to produce a strong test response. These spiked soils were easily distinguished from mock spiked soils (transformer oil only). Semi-quantitative estimates of PCB levels were made using an approximate correction factor based on the oil-DMSO partitioning behavior of Aroclor 1248. Improved soil extraction methods are being developed, but the present rapid extraction and EIA should be suitable for PCB screening of soils in many field and laboratory situations.

METHODS

Reagent Development

The development of the EIA for PCB's followed these steps: 1) PCB derivatives were synthesized for conjugation to proteins; 2) one of these PCB derivatives was conjugated to a carrier protein and the resulting conjugate was used to immunize animals, which then produced antibodies recognizing both the PCB derivative and PCB's; 3) a PCB derivative was conjugated to horseradish peroxidase (HRP) to make a conjugate which can be captured by anti-PCB antibodies; 4) the PCB-HRP conjugate was used to screen and select antibodies; 5) the selected system was optimized for sensitivity and matrix tolerance and characterized for specificity. Also required but at present only partially completed are the following steps: 6) develop sample preparation methods for specific sample types; 7) validate using field samples.

PCB EIA Procedure

The following procedure was used for the analysis of samples containing PCB's: 1) rabbit antibodies which recognize the PCB structure are immobilized on the walls of plastic test tubes or microwell strips; 2) samples or calibrators are added to Assay Diluent in tubes or wells, allowing PCB's to be captured by the immobilized antibodies. PCB's are retained on the solid phase when the rest of the sample is washed away; 3) PCB-enzyme conjugate is added to tubes or wells and bound in the same manner as in step 2. The unbound conjugate is washed away and the amount retained by the immobilized antibody is inversely proportional to the amount of PCB bound in step 2; 4) enzyme substrate and chromogen are added to the tubes or wells for color development by the bound enzyme. The intensity of color is also inversely proportional to the amount of PCB bound in step 2. Therefore, ***more color means less PCB.***

Field Soil Extraction

Soil samples were extracted for analysis by the following procedure: 1) place soil into syringe fitted with plastic frit prefilter in the bottom of the barrel and a 0.2 μM filter. Tap to allow soil to settle, insert plunger and press lightly to tamp surface. Fill to 1.5 mL mark for 2 g soil. Remove plunger and place Luer cap on filter tip; 2) Add 2 mL DMSO or other solvent, re-insert plunger, and shake to break up soil plug. Time one minute from plug breakup; 3) Remove Luer cap and express solvent from syringe. Only a small volume of filtrate is required since the extract will be diluted for EIA. Capture filtrate in clean glass tube or drip one drop (30 μL) directly into Assay Diluent in antibody coated tube (step 2 of EIA procedure).

RESULTS AND DISCUSSION

Matrix and Solvent Tolerance

The EIA interference of methanol extracts of seven PCB-free soils was tested using two EIA formats. The extracts were diluted into Assay Diluent for EIA. The sequential test was performed as described in the EIA Procedure section above. The simultaneous test combined the first and second incubations (sample and PCB-HRP conjugate on antibody-coated tube at the same time). At the end of that incubation, the tubes were washed and the normal procedure was resumed at this point. The sequential test was unaffected (>80% of control) by 1:4 dilutions of extract, while the simultaneous test was strongly affected at 1:10. Similar data were obtained for DMSO extracts of the same soils. Additionally, the sequential assay format tolerated DMSO up to 50% in a similar experimental design.

These data show that the sequential EIA described offers excellent resistance to the effects of concentrated sample extracts, superior to the simultaneous test. This in turn means that extracts of low PCB samples can be assayed with minimal matrix and solvent effects, by increasing the amount added to the test in the sample incubation step.

Assay Precision

Standard solutions of Aroclor 1248 in DMF were diluted 1:100 into Assay Diluent for EIA analysis. The test was performed as described in the EIA Procedure section above. Data were calculated as a percent of the control for each calibrator, then means and standard deviations were calculated for each calibrator. Precision estimates were made based on 14 runs over 11 days. For three calibrators of 0, 7, and 50 ppm, diluted 1:100 (final concentrations of 0, 70, and 500 ppb), the means and standard deviations were respectively 100+/-4, 35+/-2, and 15+/-2; all data are expressed as percent of the mean of all negative control absorbance values. This result shows that the EIA described offers excellent reproducibility.

Test Specificity

The crossreactivity of the test for seven commonly detected Aroclor's was examined. Standard solutions of 200 ppm in methanol (Supelco) were used to make serial dilutions in methanol. These standard solutions were diluted 1:100 into an aqueous diluent for EIA analysis. Figure 1 shows that the test recognizes most of the Aroclor's nearly equally. Based on this 1:100 dilution, the 500 ppb points (final assay concentration) correspond to an initial extract concentration of 50 ppm for soils. Thus, this test will easily detect all seven of these Aroclor's at 50 ppm based on a 1:100 extract dilution.

Specificity was also tested for selected specific congeners in the same manner as for the Aroclor's of Figure 1. The congeners most strongly recognized were 2,2',5,5' tetrachlorobiphenyl, 2,3',4,4',5 pentachlorobiphenyl, and 2,2',4,4',5,5', hexachlorobiphenyl. These data show that the Aroclor specificity reflects the congener specificity. Biphenyl and several chlorinated single ring compounds were also tested for crossreactivity in the EIA. All of these compounds demonstrated less than 0.5% crossreactivity compared to Aroclor 1248: 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, biphenyl, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and

pentachlorophenol. This means that more than 200 ppm of any of these compounds would be required to give the same test response as 1 ppm of Aroclor 1248.

Test Sensitivity

Standard solutions in DMF were diluted 1:100 or 1:250 into reverse osmosis purified water for EIA analysis. The test was performed as described in the EIA Procedure section above. Figure 2 shows a typical standard curve; data points represent the means of two tests run on the same day. Similar results were obtained for repeated runs of Aroclor 1248 diluted in the standard Assay Diluent. These data show that this EIA is capable of direct analysis of PCB's at low ppb levels in water.

Spike Recoveries Using Field Soil Extraction

Soil samples were spiked, extracted, and analyzed by EIA to determine the ability of the test to detect PCB's in soil. Standard solutions in DMF, hexane, or transformer oil were used as noted below.

Spikes of 1 mg/mL Aroclor 1248 in hexane or DMF were made into 2 g samples of 4 PCB-free soils, giving a final PCB concentration of 50 ppm. Soils were extracted using 2 mL of DMF, DMSO, or methanol and recoveries were determined by EIA using 1:100 extract dilutions. Recoveries averaged 70+/-20% for a total of 15 samples. Mock spikes were performed in the same manner, using the same soils and solvents. For sixteen samples, the mean percent of control was 102+/-15% (100% of control means no PCB and no interferences). These data indicate adequate recovery for soil screening and minimal interferences from the soils tested.

Mock spikes were performed in the same manner as above, except the spike material was clean transformer oil in a ratio of 100 µL/2 g soil (5% v/w). For seven samples extracted with DMSO or methanol, the mean percent of control was 77+/-8% (100% of control means no PCB and no interferences). This indicates interferences from the soils tested greater than those non-oily soils described above, but still giving a signal approximately equal to 1 ppm of Aroclor 1248 in the original extract (based on the EIA Procedure step 2 dilution of 1:100). Spikes of 1 mg/mL Aroclor 1248 in transformer oil were made into 2 g samples of 4 PCB-free soils, giving a final PCB concentration of 50 ppm and a 5% v/w ratio of oil to soil. Soils were extracted using 2 mL of DMSO and recoveries were determined by EIA using 1:100 extract dilutions. Recoveries averaged 12+/-3% for a total of 4 samples. These values are similar to those obtained for DMSO extractions of the spiked transformer oil with no soil present. Methanol, DMF, THF, and N-methylpyrrolidone gave slightly less effective extraction from oily soils than DMSO. Significant reductions in recoveries of 50 ppm Aroclor 1248 spikes were observed at a 0.1% v/w ratio of oil to soil.

The extracts of oily spiked soil and oily mock spiked soil described above were analyzed by EIA using extract dilution factors ranging from 1:100 to 1:5. At a dilution factor of 1:20, or 5% extract in PCB Diluent, the mock spike response equated to much less than 7 ppm in the original sample (the color was much higher than the diluted 7 ppm calibrator). At the same dilution, the spiked soil response equated to nearly 50 ppm in the original sample (the color was similar to the diluted 50 ppm calibrator).

Based on the above results, oily soils or suspected oily soils can be analyzed using a direct DMSO or methanol extraction and EIA of an increased concentration of the extract, such as 5%, to partially correct for inefficient partitioning from the oil phase. Using this technique, samples could be confidently screened in the field at the 50 ppm level. Oily soils containing 50 ppm PCB would give a strong EIA response, while oily soils with no PCB's would behave as described for the mock spiked oily soils described above.

CONCLUSIONS

1. The test is capable of analyzing for PCB's in the field in less than 20 minutes (15 minutes from prepared sample), using no specialized equipment.
2. Test specificity is restricted to PCB's.

3. Aroclor's 1248, 1254, and 1260 are recognized best; 1242, 1232, and 1016 are recognized nearly as well; 1221 is recognized significantly less well, but can still be detected easily at 50 ppm.
4. Congener specificity of the test reflects the Aroclor specificity.
5. The test is capable of direct analysis of PCB's at low ppb levels in water.
6. Soils which are not oily can be analyzed using a solvent extraction and direct EIA of the diluted extract.
7. Oily soils can be analyzed using a solvent extraction and direct EIA of an increased volume of the diluted extract to correct for inefficient partitioning from the oil phase.
8. Further work in this area will include improved extraction from oily soils, oil analysis, sediment analysis, biological sample analysis, field testing for the above, and quantitation of PCB's using the strip-well method for lab analysis.

ACKNOWLEDGEMENT

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Figure 1. Crossreactivity for 7 Aroclors

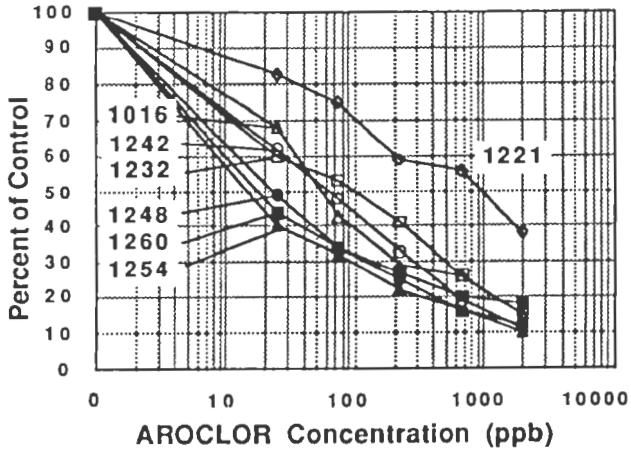
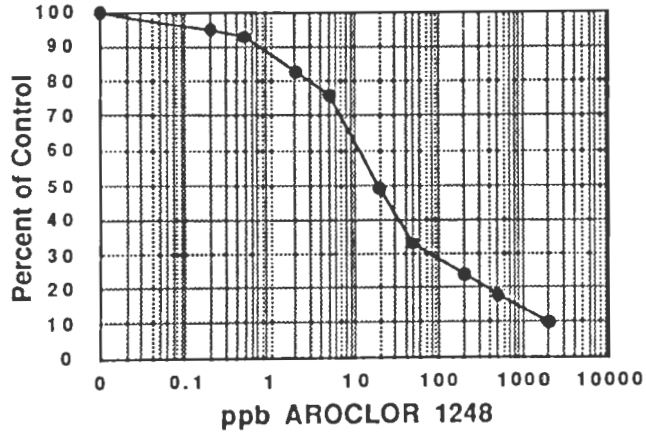


Figure 2. EIA of Aroclor 1248 in Water



Practical Limits in Field Determination of Fluorescence Using Fiber Optic Sensors

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Purpose

The long-term aim of our research program is to develop an instrument useful for the field determination of aromatic organic contaminants. Concentration ranges of interest are in or below the ppb range. This approach may be applied to ground water analysis, in both the saturated zone and in the vadose zone, and for water or wastewater treatment process monitoring.

Our earlier work reported on the usefulness of fiber optic sensors in detection of aromatic organic ground water contaminants such as the benzene, toluene, ethylbenzene, and xylenes (BTEX) fraction of petroleum fuels. We use a laser fluorimeter with fiber optic sensors for in-situ measurements. The lower limits of detection observed for compounds excited in the ultraviolet (266 nm) appear to be restricted by the optical qualities of the field instrument, including the sensor. For example, the dynamic response range of fluorescence signal versus concentration is narrow when excitation occurs in the ultraviolet as opposed to visible (532 nm) with dye tracer studies (1, 2, 3).

Optical noise limiting the dynamic range of the instrument could have sources inside or outside the instrument. Optical evaluation of the system has involved fluorescence lifetime analysis, which has produced results in two areas. The first area is in determination of the source of instrumental spectral noise (1). The second area is in application of fluorescence lifetimes as an identification and measurement tool (4, 5).

Scope

This report outlines the suspected sources of spectral noise that limit the dynamic range of the instrument, and presents some application of the use of fluorescence lifetimes analysis as a measurement tool.

Methods

In-situ measurement of ground-water contaminants using unmodified fiber sensors has been the focus of our work. Our research group has built and field tested a second generation prototype instrument. The prototype instrument's theory, construction, and testing results have been presented elsewhere (1, 2, 3, 6). In summary, it uses a Nd:YAG pulsed laser (Laser Photonics MYLA laser operating at 0.5 Hz), with an internal frequency doubling crystal, as a 532 nm light source. The 532 nm light is again frequency doubled to 266 nm with an appropriate crystal (BBO, Quantum Technology) and coupled to an optical fiber (Superguide UV 600N, Fiberguide Industries) that is placed in a protective tefzel sleeve along with an identical emission detection fiber. Both fibers terminate in a stainless steel sensor, which holds the fibers in the water to be analyzed.

Fluorescence and scattered excitation light collected by the emission detection fiber is carried back to the surface for analysis. Either a monochromator (H-20, Instruments SA, Inc.) or a set of glass cut-off filters can be used for the requisite fluorescence light isolation and detection. Light intensity is measured either using a photomultiplier (PMT) (Hamamatsu). A measurement of scattered

excitation light is also made to use for power normalization. When measuring fluorescence intensity, the PMT current outputs are converted to voltages using an electronic boxcar integrator (EG&G/Princeton Applied Research), and the voltages are stored in a portable personal computer (Compaq) used as a data logger. For fluorescence lifetime measurements, signals from the PMT's are fed to a digitizing oscilloscope (LeCroy Model 9450, dual channel, 350 Mhz, 400 megasamples/second per channel) with 50 ohm input impedance at a sampling interval of 2.5 nanoseconds. The oscilloscope is triggered by a photodiode (Hamamatsu 1722 PIN photodiode) which is illuminated by a fraction of the 266 nm excitation laser light just before focusing into the excitation fiber.

Sensor lengths, which correspond to useful well depths, of up to thirty meters have been used in the field, with most useful data obtained with 10 m sensors. Laboratory investigations have typically used shorter sensors, with vapor analysis experiments using fiber lengths of 1.85 m, while solution analysis experiments usually use sensor lenghts of 10 m.

Vapor phase analyses were performed by suspending a sensor in a sealed glass dessicator or flask over a solution of known concentration of the analyte. Henry's law could then be used to predict the vapor phase concentration above the liquid (7).

Results

Fluorescence lifetime measurements on gasoline samples show that such measurements may be a useful means of determining solution concentration. A log-log plot of fluorescence lifetime values versus concentration for unleaded gasoline shows a straight line for data from less than 0.01 to more than 500 ppm. A best-fit line through the data is described by the equation log (lifetime) = 1.66 + 0.181 log (ppm).

Vapor phase analysis of phenol shows linear response of fluorescence for phenol vapor concentrations of 0.1 up to 1000 micrograms per liter of air.

Interferences from turbidity are indicated by the decreasing fluorescence seen from a 1 mg/l phenol solution in water when increasing amounts of silt were added to the solution.

Conclusions

1. Spectral noise in the instrument, originating in the flashlamp of the laser in addition to some fiber fluorescence, limits the dynamic range of the instrument.

2. Fluorescence lifetime analysis may be an additional parameter useful in determining concentration.

3. Vapor analysis suggests that vadose zone analysis may be possible by performing analyses on air instead of water.

4. Turbidity interferes with fluorescence of aqueous solutions, and its scattering effects may contribute to observed dynamic range limitations.

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The Colloidal Borescope
A means of assessing local colloidal flux and groundwater velocity in porous media

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The colloidal borescope is a waterproof video camera capable of viewing indigenous colloids in a monitoring well. Through optical magnification, the movement and density of these colloids is easily assessed. The instrument shows promise of providing an improved methodology for determining both local groundwater flow velocity and colloidal transport potential.

Because observations are taken at the microscale, data obtained are indicative of the local transport parameters of the subsurface flow system. By taking numerous measurements at different spatial locations, heterogeneities of the flow system in both the vertical and horizontal sense may be defined. Preferential flow zones and fractures may thus be located. The ability to determine the spatial variability of relevant transport parameters is also necessary for the effective use of stochastic transport models.

Field use of the colloidal borescope indicates that colloidal parameters are very sensitive to external perturbations. The slightest disturbance induces pressure waves and turbulent flow which greatly affect colloidal density and migration rates. An interesting field experiment confirming this sensitivity involved dropping a slug into a well some 5 meters away from a well in which the instrument was recording steady-state movement. The results were dramatic as the colloidal migration pattern literally exploded into a turbulent flow pattern. One can imagine the affects even the most gentle pumping techniques must have on turbidity and colloid density during sampling. These observations indicate the instrument provides a much more accurate method of assessing natural colloidal densities and migration rates.

Observations to date indicate a steady, laminar flow field in the borehole which has an excellent directional correlation with specific discharge in the surrounding aquifer. Knowledge of groundwater flow direction allows direct assessment of the affects pumping and injection systems have on the natural flow field. The effectiveness of groundwater extraction/injection systems may thus be investigated by observing the flow direction near the radius of influence of the system to see if the designed flow field is being achieved.

Groundwater flow velocities in the surrounding aquifer are inferred from potential flow theory relationships between flow through a wellbore and specific discharge in the surrounding aquifer. While both field and laboratory observations confirm a direct relationship between these two parameters, these same observations indicate wellbore

velocities are consistently higher than those predicted from potential theory. The observed relationships suggest potential theory may not be adequate to characterize the flow patterns at the scale of observation. The development of a consistent theoretical explanation for these observed relationships is sure to provide new knowledge about the underlying physical processes involved. The colloidal borescope thus provides an exciting new means of investigating the physical phenomena affecting flow in porous media at the pore scale. These observations offer a means of enhancing conceptual understanding and of developing improved transport models.

FIELDABLE ENZYME IMMUNOASSAY KITS FOR DRUGS AND ENVIRONMENTAL CHEMICALS

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Abstract

Immunoassays (e.g., RIA, EIA) have been demonstrated to be useful for rapid, convenient detection and semiquantitative analysis of drugs and various environmental pollutants. Bio-Metric Systems, Inc. (BSI) has developed a rapid, sensitive, self-contained, disposable, EIA device designed to allow untrained personnel to perform in field situations. This format has been developed for drugs in urine or on surfaces and for environmental contamination in soil or water. The analyte in the test sample competes with an enzyme-analyte conjugate for a limited number of immobilized antibody sites. This AccuPress™ Test format can detect analytes at 10 ppb in biological fluids, water, and soil, with positive results indicated by clearly visible color development within 10 minutes. This format is designed to have all dry components and to have an ambient shelf life of greater than one year. The format is readily adaptable for use with numerous low molecular weight analytes.

Introduction

Chemical pollution and the use of illicit drugs in the U.S. are two of our most important social problems. Monitoring environmental samples for various man-made hazardous chemicals has become necessary in order to protect the populace from the carcinogenic and toxic effects of such materials. Of particular concern are certain polychlorinated organics such as pentachlorophenol (PCP), chlorinated dibenzo-p-dioxins (CDD's), and chlorinated dibenzofurans (CDF's) which are known to be extremely carcinogenic. Because of the known association of CDD's and CDF's with PCP and the possibility that food-producing animals are exposed to these compounds through treated wood, one must be aware of the possibility that food and water supplies can become contaminated by the chemicals. Likewise, despite all the recent publicity regarding drug abuse, evidence seems to indicate that the importation and use of illicit drugs in the United States continues unabated [1-5]. Contributing factors to this problem are the large financial rewards generated by the illicit drug trade and the seemingly insatiable demand by the American drug user. Because of these factors, law enforcement agencies need to know which drugs of abuse are most prevalent in trafficking; and they must possess the analytical capabilities for the detection of these illicit materials.

Most of the present day methods for analysis of environmental hazards and illicit drug samples have been based mainly on conventional chromatography techniques such as gas chromatography (GC) [6,7], high performance liquid chromatography (HPLC) [8,9], and gas chromatography - mass spectrometry (GC-MS) [10,11]. Although these methods give excellent resolution and are highly sensitive, they exhibit certain disadvantages such as: 1) the need for extensive cleanup treatment before analysis; 2) expense of solvents and instrument maintenance; 3) need for trained personnel in a laboratory setting; and 4) length of time for analyses.

The development of immunochemical techniques has added a new dimension to the detection and identification of low concentrations of pollutants and drugs. These methods are based upon the displacement of, or competition with, labeled analyte from an antibody-hapten complex by sample analyte and the subsequent detection of the labeled analyte by instrumental methods. These techniques provide high sensitivity, good reliability, relatively fast results (usually within a few hours), and require less expensive equipment. At present, two different types of immunoassays have been

developed: radioimmunoassay (RIA) [12-15] and enzyme immunoassay (EIA) [16-19] for the detection of cocaine, heroin, and environmental toxins. Both assays are quite sensitive, require minimal sample pretreatment, and allow several assays to be run daily. However, the major disadvantage of most EIA's is the requirement for expensive laboratory equipment in a laboratory setting. Furthermore, with the radioactive technique there are the additional problems of radioactive waste disposal and specialized handling.

Experimental Approach

Bio-Metric Systems, Inc. (BSI) has developed prototype AccuPress EIA test kits for both the analysis of PCP in water and soil, and cocaine and heroin on surfaces. The tasks required to produce the kits were: 1) obtain and evaluate antibody specific to PCP, cocaine, and heroin; 2) prepare enzyme-hapten conjugates; 3) investigate various extraction and sampling methods; 4) optimize reagents; 5) perform component and system stability testing; and 6) conduct simulated field trials using fortified samples.

Antisera Procurement

Antibodies specific for PCP were purified from antiserum that had been prepared by immunizing rabbits with either keyhole limpet hemocyanin (KLH)-PCP or bovine serum albumin (BSA)-PCP immunogen. The PCP-KLH immunogen was produced by direct coupling of 2,3,5,6-tetrachloro-4-aminophenol to KLH by diazotization. An alternate immunogen was prepared by coupling PCP through the phenol portion of the moiety to the BSA. This was accomplished by coupling PCP-valeric acid with BSA either by: 1) direct attachment of the free carboxylic acid moiety to the amines on the protein by use of 1-ethyl-3(3-dimethylaminopropyl) carbodiimide (EDC) or 2) coupling the N-oxysuccinimide ester (i.e., NOS) of the acid by established methods [20]. Polyclonal antibodies which were specific to cocaine and heroin were induced utilizing immunogens prepared by similar procedures to those used for PCP.

Enzyme-Hapten Conjugate Preparation

One of the most critical steps in the development of our assay is the formation of the enzyme-hapten conjugate. The appropriate enzyme-hapten conjugate must be able to: 1) be bound by the immobilized specific antibody; 2) compete with the analyte for antibody bonding; and 3) maintain sufficient enzyme activity to generate a signal when low concentrations of analyte are present in test samples. We have developed assays which utilize the enzyme pair-glucose oxidase (GO)/horseradish peroxidase (HRP). In previous work we have used GO-hapten conjugates and immobilized enzymes; however, recently we have prepared GO-biopolymer conjugates to which were added various haptens. We have found that this step allows better binding of the enzyme-hapten conjugate to the immobilized antibody. The GO-biopolymer conjugate can be prepared by first oxidizing the biopolymer with periodate, then adding the GO followed by reduction of the resulting Schiff bases with $NaBH_4$ to yield a stable GO-biopolymer conjugate. The carboxylic acid derivatives of the hapten analogs prepared for the production of immunogens were coupled to the enzyme (GO) or modified GO (i.e., GO-biopolymer) by one of the following methods: direct attachment of the analogs (i.e., free carboxylic acid moiety) to the amines on the protein by use of EDC, or by coupling of the N-oxysuccinimide ester (i.e., NOS) of the hapten by established methods [20].

Sampling and Extraction Procedures

One of the biggest challenges to the development of EIA's for the analysis of PCP in soil and drug residues on hands and surfaces is to develop suitable sampling procedures for extraction of the desired analytes. Although hexane or toluene are used for extraction of PCP residues from soil, these solvents are not compatible with an immune test system, such as our AccuPress test format (Figure 1). However, since PCP is highly soluble in MeOH [21], and MeOH is compatible with our AccuPress reagents in less than a 40% concentration [22], MeOH was chosen as the extraction solvent for use in our assay. The basic protocol as developed for PCP was the following: Ten gram soil samples were spiked with 0, 20 ppb, 100 ppb, and 500 ppb PCP in methanol. The PCP was thoroughly mixed into the samples which were then dried at 37°C for two hours in order to mimic naturally occurring contaminated samples. The soil samples were extracted by vigorous shaking for one minute with 40% MeOH/PBS. The extracts were filtered through a 1.2 µm filter and the filtrate (1.0 ml) applied directly to the sample well of the AccuPress test module. The antibody disk was washed with five drops of PBS/3% PEG, after which one drop of conjugate was added and incubated for two minutes. The two segments were then pinched together and released. The color development was read after five minutes. Based upon an arbitrary color scale designation of 0-5, 20 ppb of PCP in soil gave a color rating of 3. A positive response was easily distinguishable from the 0 ppb sample which resulted in a colorless readout (rating of 0).

During the prototype development of the AccuPress test for drugs on surfaces, BSI developed a sampling vial which served both as a sampling device and also as an application device. As depicted in Figure 2, the sampling vial consisted of a sample swab attached to the dropper top. Also attached to the dropper top was a filter that would

remove any extraneous materials from the sample solution during application of the test (A). The user would simply remove the dropper top with the attached swab from the sample vial and swab the area to be tested (B). Next, the dropper top was replaced and sampler vial shaken. If testing a solid, a small amount of the solid was transferred to the sampler vial, followed by replacing the top, and shaking the sampler vial. The dropper cap was then removed and 5-10 drops of the sample to the AccuPress test (C). The development of this sampler made the prototype AccuPress tests very convenient to use.

AccuPress Test Format

The AccuPress test format (Figure 1) consists of four parts: 1) antibody disks (A); 2) read-out disks (B); 3) absorbent blotting reservoir (C); and 4) a crush vial containing lyophilized antibody, while the read-out disks (B) contain an immobilized enzyme (HRP), the chromogen (ABTS), and a substrate (glucose) for the enzyme-hapten conjugate. Also, a reservoir (C) containing an absorbent pad is located beneath the antibody disks, and the enzyme-hapten conjugate corresponding to the desired analyte is lyophilized in a small crush vial (D). The user simply reconstitutes the lyophilized conjugate (D) by squeezing the tube, crushing the ampule, allowing the conjugate enough time for complete dissolution (ten seconds). Next, five to ten drops of sample are applied to the antibody disks and the disks are rinsed with wash solution to remove any extraneous material. One drop of the reconstituted conjugate is added to the antibody disks (A) and incubated for one to two minutes. The user then folds the top plate containing the read-out disks (B) over the bottom plate containing antibody disks (A), pinches for approximately three seconds, and the results are read in five to ten minutes with a positive result being indicated by color formation.

This assay format exhibits distinct advantages over other enzyme immunoassay formats (e.g., ELISA). First, the sample size is less limited since by exposing the antibody disk to a large volume of sample (i.e., up to 800 µl), the analyte can be concentrated on the disk, thus increasing the sensitivity of the assay (Figure 1). Second, a wash step with PBS allows any possible interfering substances still present in the environmental sample to be washed off the antibody disk. Third, the enzyme-hapten conjugate can be added after the sample, which should also increase sensitivity. Finally, this format allows one to use controls more easily and could also be easily adapted as a multi-analyte assay.

Reagent Optimization

Since the reagents for both the AccuPress test for PCP and the test for drugs on surfaces were prepared by similar methods, only generalized procedures will be described using the PCP test as an example.

In order to carefully control the amount of immunoglobulin (IgG) coupled to the antibody disks, the antiserum was purified to >95% IgG by standard methods. The antiserum was fractionated with saturated ammonium sulfate (SAS), pH 7.8, by addition of an equivalent volume of SAS to neat antiserum (50% saturation). After stirring for two hours at room temperature, the antiserum was centrifuged. The pelleted material was redissolved to one-half the original volume with 20 mM phosphate buffer, pH 7.2, and dialyzed exhaustively against 20 mM phosphate, pH 7.2. The dialysate was then purified over Whatman DE-52 anion exchanger. The IgG peak was pooled and characterized for total protein (Pierce BCA Protein Reagents) [23] and for total IgG (ICN Rabbit IgG radial immuno diffusion kits) [24]. The IgG was then prepared for coupling to paper disks or stored in PBS, pH 7.2, at -70°C, in 100 mg aliquots.

Antibody disks were prepared and evaluated to determine the amount of specific antibody needed to be coupled to the disk in order to obtain the desired sensitivity. Antibody disks were prepared using ratios of DE-52 purified antibody per 50 disks. The levels investigated were 20 mg/50 disks, 10 mg/50 disks, 5 mg/50 disks, and 2.5 mg/50 disks. A study was done to determine which load of antibody could be used in our test format to optimally achieve the desired sensitivity. The coupling efficiency or the optimal amount of specific antibody/disk was determined by measuring the protein concentration [25] before and after coupling and by radiolabeled uptake experiments using radiolabeled analyte. This radiochemical procedure involved the incubation of the antibody disk with [^{14}C]-analyte for 45 minutes. The amount of radioactive analyte bound to the antibody allowed one to calculate the pmoles of analyte bound per antibody disk.

As previously noted, one step in the development of our assay is the production of the enzyme-hapten conjugate. The amount of hapten on the enzyme-hapten conjugate is critical for achieving the required characteristics. If insufficient or excessive hapten groups are coupled to the enzyme, the conjugate either will not bind adequately to the antibody, or it will bind so well that native analyte cannot compete effectively. Thus, hapten coupling experiments had to be performed to determine the range of hapten groups needed on the enzyme to achieve the desired binding characteristic. Several conjugates were prepared by coupling hapten-NOS to GO using various molar ratios of hapten to enzyme (e.g., 20, 50, 100X) in the reaction mixture. Analysis of the number of remaining amines by a standard 2,4,6-trinitrobenzene sulfonic acid (TNBS) assay [26] after coupling of the hapten-NOS to the enzyme, as

compared to unmodified enzyme, indicated the approximate load of the hapten on the enzyme (i.e., 50% amine reduction). The enzyme-hapten conjugates prepared using 100 mg of hapten derivative to 50 mg GO consistently produced the best conjugates for our EIA development with regard to enzymatic and immunological activity.

Read-out disks were prepared using HRP covalently coupled to chromatography paper disks through a diamine spacer. The modified HRP was prepared by first oxidizing the carbohydrate portion of the HRP with periodate, then adding the diamine, followed by reduction of the Schiff base with $NaBH_4$ to yield a stable HRP-diamine derivative. Enzymatic activity was measured before and after amine modification (Table 1). After immobilization of the enzyme, the disks were incubated with a solution of glucose, chromogen (2,2'-azinobis[3-ethylbenzothiazoline-6-sulfonic acid], ABTS) and proprietary stabilizer in PBS/1% polyethylene glycol (PEG) 4000 for 60 minutes. The liquid was decanted and the excess moisture was wicked away. The disks were placed in trays, frozen at -70°C for 20 minutes, and lyophilized overnight. The disks were stored at room temperature in a humidity controlled room (19% R.H.) until used. Accelerated stability studies at elevated temperatures (i.e., 37°C, 55°C) indicated that the read-out disks are quite stable with only a 20 to 30% loss of enzyme activity after 34 days at 55°C (Figure 3). The disks performed well in the assay, showing little or no background in the absence of free analyte, while giving an easily observable response when analyte was present.

Component and System Stability

Our AccuPress EIA test format (Figure 1) consists of three components: antibody disks, read-out disks, and lyophilized enzyme-hapten conjugate, all containing biological reagents whose activities can be affected by environmental factors (e.g., temperature and humidity). Because of this, it is difficult to prepare a rapid enzyme immunoassay suitable for field use which would exhibit a minimum shelf life of one year when stored at room temperature. Therefore, stability testing was carried out on the individual components and whole test kits at various time points during storage at four different temperatures. Although both AccuPress test kits and components for both drugs and PCP were evaluated, only the PCP test kit data is presented, which is quite representative of both test kits.

Antibody disks were prepared as previously reported, lyophilized, and stored for two weeks before the stability study was initiated. The disks used for the radiolabeled uptake study were packaged in bilaminar foil pouches with a desiccant pack and a N_2 infusion immediately before heat sealing. The packages were stored in the appropriate temperature controlled environments for the duration of the study. The testing protocol was as follows: A standard stock solution of 10 dpm/µl of [^{14}C]-pentachlorophenol was prepared and stored at -20°C. On test days, an aliquot of stock solution was diluted in 0.01 M phosphate, 150 mM NaCl, pH 7.2. The antibody disks stored at various temperatures were allowed to equilibrate to room temperature. One ml of diluted radiolabeled PCP per antibody disk was incubated in 1.5 ml microcentrifuge tubes (five PCP disks and five control-normal rabbit serum antibody disks) for two hours with shaking on an orbital shaker. After incubation, 500 µl of the supernatant was removed from each tube for liquid scintillation counting. The quantity of bound PCP was expressed in pmoles/disk.

The stability of the enzymatic activity of the GO-hapten conjugates was also investigated. A stock conjugate reagent was packaged in crush vials for use in the stability testing. The appropriate dilution of the conjugate was determined using the appropriate antibody disks. A concentrated form of the stock conjugate was added to the stabilization media and aliquoted into polyethylene tubes for lyophilization. After lyophilization, a reconstitution buffer, encapsulated in an onion skin glass vial, was added to the tube. The dropper top with filter was applied to the top of the tube. The vials were packaged in foil pouches with a desiccant packet and the test module, and stored at the selected temperatures until tested by direct enzymatic analysis. Four separate crush vials per storage temperature were reconstituted and tested by the Worthington Kinetic Glucose-Oxidase assay. The same vials were used for performance testing in the whole kit stability evaluation. The mean of the determined rates for four vials (per temperature per time point) were converted to specific activity. At each time point, an aliquot of native GO was assayed in quadruplicate as a control. The stock of native GO was prepared at 1 mg/ml, aliquoted and stored at -70°C.

The stability of the enzymatic activity on the read-out disks at various elevated temperatures was also investigated. Read-out disks were incubated with stabilizers and lyophilized. The dry read-out disks were stored in foil pouches with a desiccant packet and flushed with N_2 before sealing. The pouches were stored at the selected temperatures until tested by either direct application of a standard amount of enzyme or were assembled into kits for performance testing. For the actual evaluation, the disks were allowed to equilibrate to room temperature and were stored in a desiccator until tested. A standard aliquot of GO (the same as the control used for the Worthington kinetic assay) was diluted to 1 µg/ml. The disks to be tested were laid out on a white sheet of paper and 15 µl of 1 µg/ml GO was added to each disk. Color development was monitored and recorded at 1 minute and 5 minutes compared to an arbitrary color chart having five spots of progressing color intensity.

Assembled AccuPress test kits were prepared and evaluated in an accelerated temperature study. The preparation of the kits and testing protocol are presented as follows:

Preparation of Kits: Antibody disks were prepared using ammonium sulfate preparation of antisera at an IgG level corresponding to 50 disks per 5 ml of whole antisera with four different stabilization formulations. These disks were then evaluated for performance. Read-out disks used for the whole kit testing were prepared as previously described. Conjugate was titered to match antibody disks and lyophilized in polyethylene tubes. Glass onion skin vials with premeasured aliquots of PBS were placed in the tubes and they were sealed with a Porex filter and dropper top. Kits were assembled in the dry room (14% relative humidity) and sealed in bilaminar foil pouches after N_2 flush.

Testing Protocol: Stock standard PCP was diluted into 40% MeOH/PBS to a concentration of 100 ppb (= to 100 ng/ml). Negative control was 40% MeOH/PBS. The testing protocol was as follows:

- 10 drops (0.25 ml) of positive control were added to the positive well.
- 10 drops (0.25 ml) of negative control were added to the negative well.
- 8-10 drops of neutral pH wash solution were added to all wells. (Allergan Lens Plus®).
- Conjugate was reconstituted by squeezing crush vial and shaking vigorously.
- One drop of conjugate was added to each well.
- It was incubated for 2 minutes.
- The module was pinched together for 2-3 seconds.
- Color development was monitored for 10 minutes, and recorded at 5 and 10 minute intervals.

The results of our component and whole test module stability studies using the PCP format as a model demonstrated that we had excellent stability for both the components and the whole test module. For example, we were able to demonstrate a 95% retention of PCP antibody activity after storage at 55°C for one month (Figure 4). Similarly, the enzyme-hapten conjugate and read-out disk also were stable when stored at 55°C for one month (Figures 5 & 6). Examination of the performance of the whole test modules (Figure 7) indicated that the modules were quite stable at 55°C for 35 days. It is apparent that the components and the whole test modules are stable and exhibit a shelf life of at least one year when stored at room temperature.

Reliability Testing

During the in-house testing, we investigated the reproducibility of the test device in detecting PCP residues in soil. The four types of soil (sand, clay, black dirt, Minnesota river sediment) were collected and dried. Clay was heat dried in a vacuum oven. Black dirt, sand and river sediment were air dried. All soil samples were sieved through a #14 mesh screen. The soil samples were weighed out at 10 gms per vial and spiked with PCP at varied concentrations in 100 µl of methanol to equal 0, 10 ppb, 50 ppb, 100 ppb, 1000 ppb. Ten samples were prepared for each PCP level per soil type. Each soil extract was tested in duplicate in a blind study.

Extraction & Assay Procedure:

- To each 10 gram sample, add 10 ml of 40% MeOH/PBS.
- Shake the vials vigorously for 1 minute.
- Allow the sediment to settle for a minimum of 5 minutes.
- Filter the supernatant using a syringe, through an ED-141 prefilter placed in the syringe barrel and a 1.2 µ S&S Uni-Flo filter.
- Add 0.5 ml of filtered extract to the module sample well.
- Wash with 8-10 drops of neutral pH buffer.(Allergan Lens Plus).
- Crush conjugate ampule and shake to reconstitute.
- Discard the first drop of conjugate in a waste container.
- Add **1 drop** of conjugate to each well.
- Incubate the conjugate for 2 minutes.
- Pinch the module together for 2-3 seconds.
- Monitor the color development for 10 minutes, recording the 5 and 10 minute color. A chart with 5 spots of increasing green color intensity is used as a reference.

Since the AccuPress test is intended as a qualitative screen, we have used the following definition of positive and negative results. If a color less than or equal to 1.0 on our 5 step color chart develops in 5 minutes, then the results are classified as negative. Any test which develops a color greater than a 1.0 in 5 minutes is classified as positive.

When applying this rule to the above samples, the following conclusions were drawn:

1. For sand: No zero analyte samples generated color greater than 0.25; there were no false positives; 90% of the 10 ppb samples were positive (by definition); and all samples >10 ppb were positive.

2. For Mississippi river sediment: No zero analyte sample generated color greater than 0.25; 90% of the 10 ppb samples were positive (by definition); and all samples >10 ppb are positive.

3. For black dirt: No zero analyte sample generated

color greater than 0.25; 100% of the 50 ppb samples generated color of 1.0 or greater.

4. For clay: No zero analyte sample generated color greater than 0.25; 60% of the 10 ppb samples generated color of 1.0 or greater and 100% of the 50 ppb samples generated a color of 1.0 or greater.

Our results (Figure 8) suggest the greater extraction efficiency for sand and river sediment compared to black dirt and clay type soils at low levels of PCP contamination (between 10 and 500 ppb). When testing soils suspected to have high levels of contamination (>1 ppm) the results for all soil types converge and the color generated with this test is maximized.

Summary

Data presented demonstrates that BSI has developed an easy-to-use enzyme immunoassay that can be used to measure PCP in soil at concentrations of 10 ppb or greater. The test kit has many distinct advantages over other screening tests which are currently commercially available for other small molecular weight analytes: 1) the assay has a positive read-out system; 2) the use of wash steps eliminates interfering substances; 3) no laboratory equipment is needed, eliminating the purchase, calibration, or maintenance of any equipment; 4) the assay is fast (less than a total of ten minutes is needed for the results); 5) all of the necessary reagents for the assay are present in the assay kit, consequently the assay is very easy to use by unskilled personnel; and 6) the enzyme immunoassay has been miniaturized to maximize speed, portability, and ease of use. Also, we were able to obtain evidence, through accelerated time studies, that the test components and whole kits were stable for one year when stored at room temperature.

Acknowledgments

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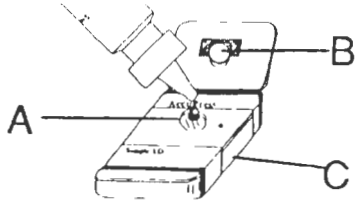
Table 1. Modified HRP Activity after Purification

	Activity Units/ng protein
HRP-DADPA (Pre-purification)	700 ± 63
HRP-DADPA (Post-purification)	365 ± 49

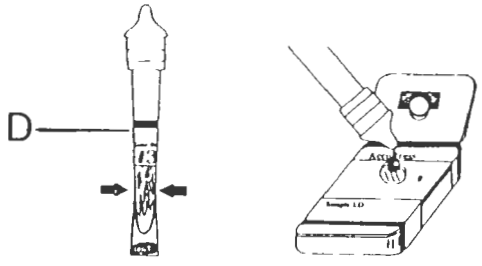
n = 6

NOTE: All components should be at room temperature.



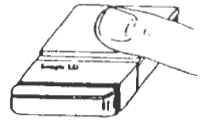
1. Open foil package and remove test module, color development tube, and wash tube. (Just before use.)

2. Sample application: Remove red cap from sample bottle and apply 10 drops (±5 drops) to the sample well of the module.



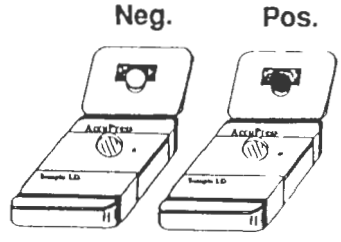
3. Wash application: Twist tab off wash tube and squeeze entire contents into sample well.

4. Color development tube application: Hold tube upright and squeeze tube where indicated to crush ampule inside. Shake vigorously for 10 seconds.



- Carefully apply ONE DROP of color development solution to sample well.
- Incubate for 1-2 minutes.

5. After incubation, press module closed for 2-3 seconds. Release and open. (Press only once.)



6. Open the module and monitor color development. Record the result at 5 minutes.

A POSITIVE RESULT WILL SHOW A GREEN COLOR AS DARK OR DARKER THAN THE REFERENCE COLOR.
A NEGATIVE RESULT WILL REMAIN WHITE OR BE LIGHTER THAN THE REFERENCE COLOR.

FIGURE 1. AccuPress™ Test

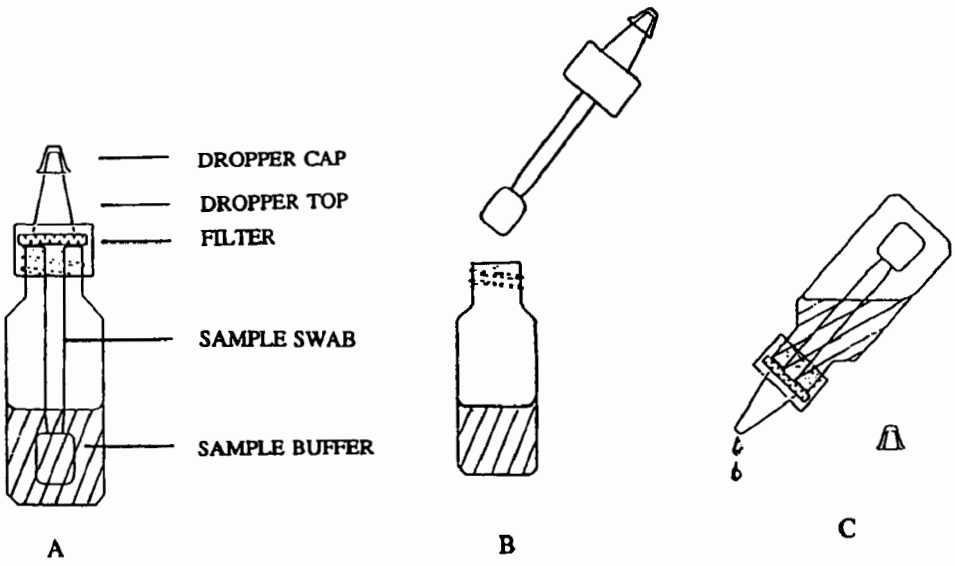


FIGURE 2. SAMPLER/EXTRACTION DEVICE

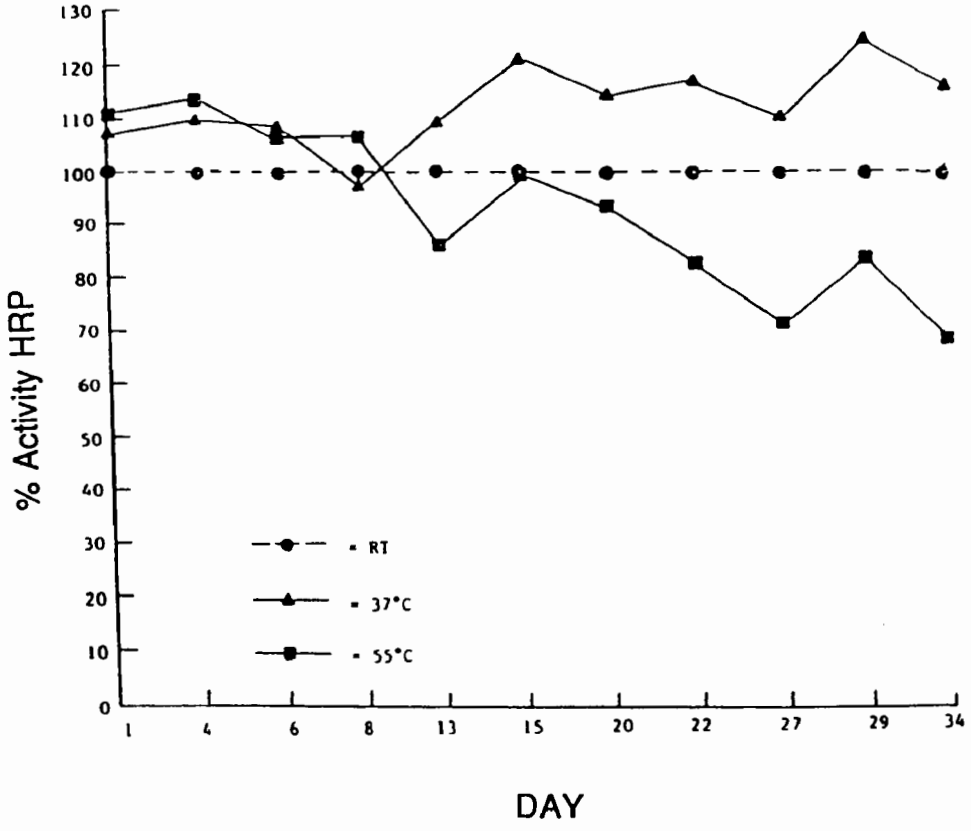


FIGURE 3. READ-OUT DISK STABILITY

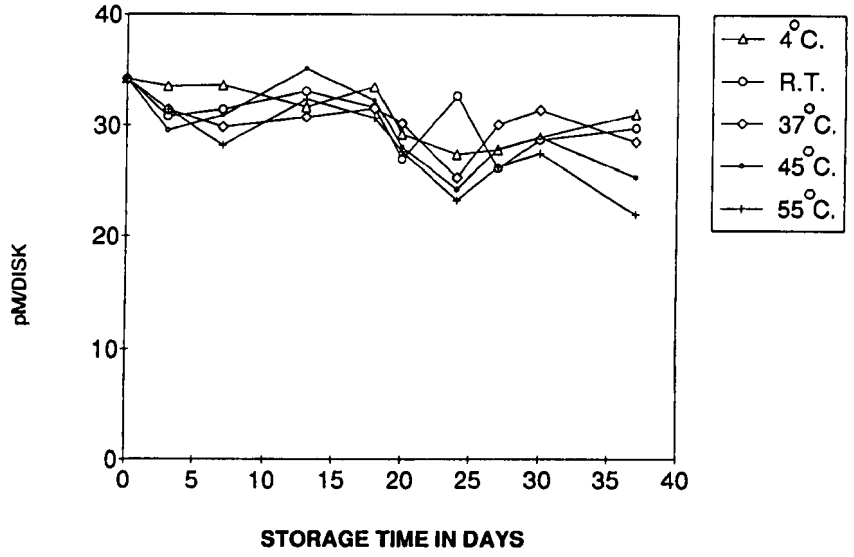


FIGURE 4. PCP ANTIBODY DISK STABILITY RADIOLABEL UPTAKE

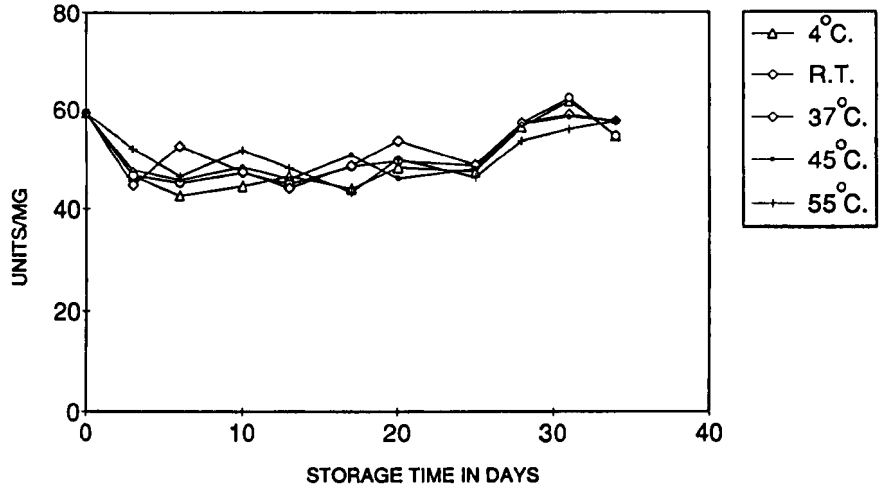


FIGURE 5. PCP CONJUGATE STABILITY

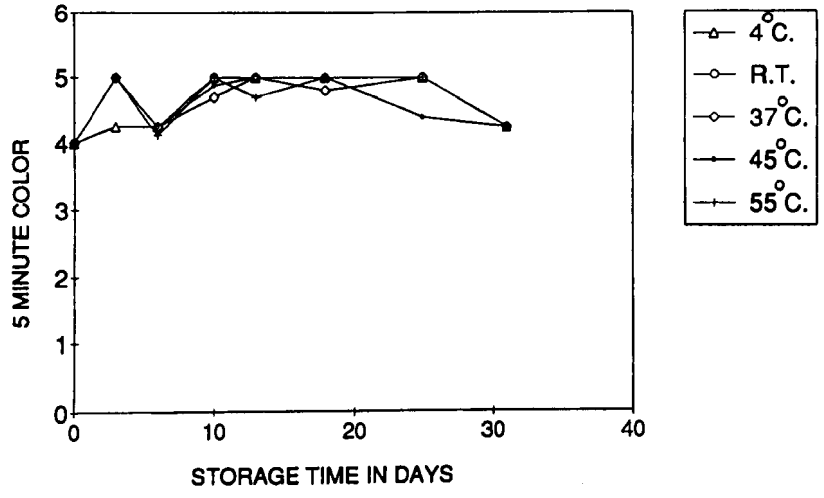


FIGURE 6. READ-OUT DISK STABILITY

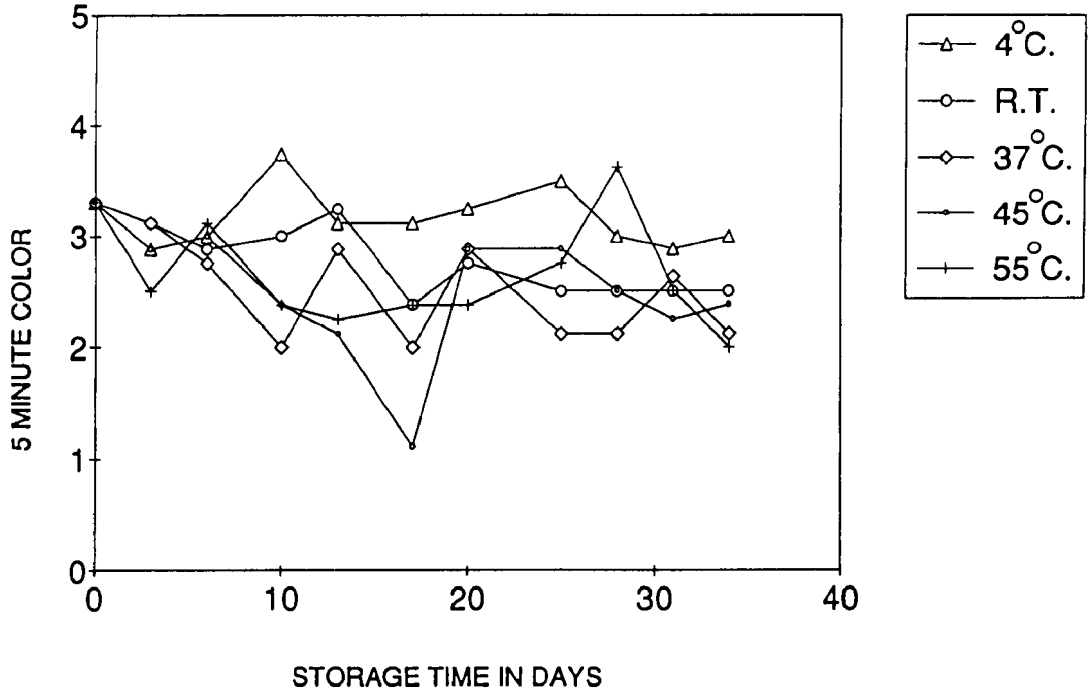


FIGURE 7. STABILITY TESTING
PCP ACCUPRESS TEST KIT

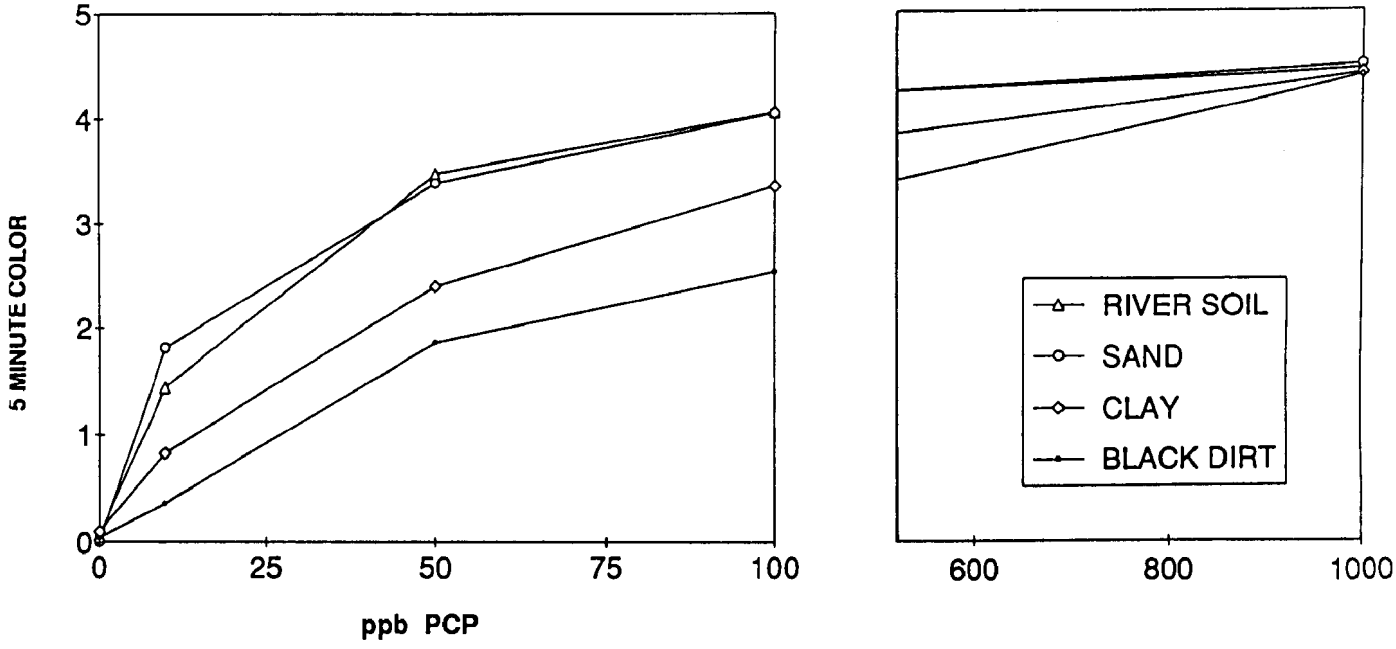


FIGURE 8. PCP ACCUPRESS TEST
VARIOUS SOIL TYPES
(N=10 EACH DATA POINT)

XUMA EXPERT SYSTEM FOR SUPPORT OF INVESTIGATION AND EVALUATION OF CONTAMINATED SITES

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1. INTRODUCTION

In Baden-Württemberg, programmes are carried out to investigate and to register the contaminated sites and to evaluate their environmental hazard. The expert system will help in this work. The XUMA (German acronym for expert system on environmental hazards of contaminated sites) expert system is being developed within the framework of a joint research project of the Institut für Datenverarbeitung in der Technik of the Kernforschungszentrum Karlsruhe and the Abteilung Boden, Abfall, Altlasten of the Landesanstalt für Umweltschutz Baden-Württemberg [1]. It is being implemented on a Texas Instruments Explorer II with the Inference ART development environment and the RTMS database system. The programs are written in LISP and ART.

2. SURVEY

The following functions are covered by the system:

1. Evaluation
2. Preparation of an analysis plan
3. Acquisition of analysis results
4. Assessment
5. Explanation facility
6. Knowledge acquisition

The evaluation function primarily deals with the determination of a numerical value for a first comparative estimation of the environmental hazard of contaminated sites. This value is then used for setting priorities during the investigation and sanitation of waste sites. The second function supports the user when a case-specific analysis plan for the contaminates site is prepared. The third function is used for the input of the results of the chemico-physical analyses into the system. The fourth function supports the assessment of a case, i.e.a comment in form of an expert opinion. The fifth function helps the user reconstruct the derivation of the statements inferred and the last function enables the authorized experts to modify and complete the domain knowledge acquired within the knowledge base.

In the following, the central application function of the system, the assessment function, as well as the explanation facility and first experiences gained with these functions are described in further detail.

3. ASSESSMENT

The basis of the assessment of a contaminated site are the results of investigations. The chemical and physical investigations are very important. The expert has the problem to valuate a lot of analysis data.

XUMA will help the expert in doing this with the function "Assessment". On the basis of the analysis results statements are devired for the assessment of the hazard level. Indications of further investigations are given as well as other assessment statements like indications of inconsistencies in the analysis data, control of plausibility. In an other function, that is not yet realized, the local situation including hydogeology will be considered

[2]. The function "preparation of an analysis plan", helps to find an individual analysis plan with the investigation parameters, that are of concern for example on a contaminated soil within an industrial plant. Contaminated soil, wastes, eluates of the wastes, leakage water, groundwater, surface water, air, soil will be analysed. For the assessment the analysis data, information taken from the sampling records and informations from the record of the chemical analysis are of concern.

XUMA contains rules for the assessment of

- parameters
- one chemical analysis of a sample
- all chemical analysis of one sample, for example a contaminated soil and the eluate
- all analysis results of sample of discrete areas
- all analysis results and informations of the case.

More than 25 tables of limit values or threshold values for water, soil and air with more than 100 different parameters are taken into the knowledge base of the system as well as rules explaining the special scope of a table. Values of this limit values tables and threshold values tables were associated with 6 quality classes. Quality class I is corresponding to the background values, quality class II is "tolerable", class III means "further investigation necessary", IV, V and VI medium, high and very high hazard level. Example: If the analysis result of a parameter of groundwater is smaller or equal 0.2 times the limit value of the german drinking water quality table, then it is quality class I. The rules of associating the concentration values to quality classes are the result of experiences with the risk assessment of a great number of contaminated sites.

Assessment of the Analysis: 201.83
25.07.1983 Eluate
Analysis Results

Colour, qualitative	= yellow	
Electric conductivity	= 430	uS/cm
Ammonium	= 0.200	mg/l
Chloride	< 10	mg/l
Cyanide, total	= 0.750	mg/l
Phenol, total	= 0.900	mg/l
Dry matter	= 1146	mg/l
Residue on ignition (550 C)	= 1112	mg/l
Hydrocarbons (IR)	3.400	mg/l
Mineral oil	= 3.400	mg/l
Loss on ignition at 550 C	= 34	mg/l

Assessment Results
Assessments on the Basis of Limit Valu Tables:

'Dry matter'	is put into quality class II - permissible (TVO).
'Ammonium'	is put into quality class II - permissible (TVO).
'Chloride'	is put into quality class I - within the range of background values (EG-TW).
'Cyanide, total'	is put into quality class interval IV to VI (TVO).
'Mineral oil'	is put into quality class IV - medium hazard potential (NDL-GW).
'Phenol, total'	is put into quality class V - high hazard potential (NDL-GW).
'Electric conductivity'	is put into quality class II - permissible (TVO).

Definite Statements:
The portion of organic matter in the dry matter is about 2 % (calculated). A considerable portion of the substances contained is not analyzed.
The value of 'dry matter' is normal.
The value of 'residue on ignition' is normal.
The parameter 'colour, extinction at 436 nm' should be analyzed.
There are indirect indications of 'crude tar' to contained. Reason: colour.
Potential Statements:
There is some indication that the organic portion in the dry matter might be high. Reason: dry matter >> electric conductivity.
Total Result:
The analysis is put into quality class interval V to VI.

FIGURE 1: Example of the assessment of an analysis

The tables were classified in groups for groundwater, surface water, soil etc. Within one group, rules are defined, for which purpose and with what priority the tables are to be used. If there is no possibility to find a value for a parameter in one group of tables, e.g. groundwater tables, rules are given to use other groups of tables, e.g. drinking water tables. If there is no value in any of the tables for one parameter, XUMA proposes different parameters with similar chemical character (e.g. o-Xylol for p-Xylol). Examples of rules for the summarization of the assessment statements are shown in figure 2.

Rules with regard to limit value tables:

If leakage water is to be assessed,
and the value of at least one parameter is quality class IV - VI,
then the sewage tables are to be used.

If a measured value x is compared with the Dutch soil table
and B Value $< x \leq$ C value is valid for the B and C values of the parameter,
then the measured value belongs to quality class III.

Rule of assessing an individual analysis parameter:

If pH value < 5,
then the solubility of heavy metals is increased.

Rule of summarizing the results on the sample level:

If the turbidness of a water sample is clear in the sampling record and not clear in the laboratory analysis,
then the sample has changed chemically after sampling.

Rule for summarizing the results on the case level:

If 'cyanide, total' or 'hydrocarbons (IR)' is high or very high in leakage water samples,
then the ground water should be analyzed.

FIGURE 2: Examples of assessment rules

The assessment of a case gives statements on the hazard level (quality class), the need of further investigations, statistic and definite and potential statements.

XUMA can give some help for present technical investigations or remedial actions. The field screening analytical data will be transmitted to the expert system which gives an assessment for an actual case. So the following actions e.g. further sampling or remediation of the waste will have a better basis.

4. EXPLANATION

It is of particular importance for the acceptance of the system that its conclusions are clear and may be reconstructed by the user. For this purpose, an explanation facility has been implemented [3]. The derivation of the statements is explained to the user by means of texts written in the natural language. Each statement displayed is mouse-sensitive. The explanation facility is called by clicking on a statement with the mouse. Now, the user can choose between the local or global justification of the statement. In local justification (Fig. 2), the statement itself is listed together with the last rule that has led to this statement and with the conditions fulfilled (premises). In global justification, the complete tree of derivation is shown, i.e., the derivation of the statement from the analysis results and the facts and rules included in the static knowledge base is represented. The derivation structure is represented by indentations.

Local Justification

The fact to be explained is:

The portion of organic matter in the dry matter, calculated from residue on ... ignition, is about 38 %.

It was deduced by the rule G2-RESIDUE-ON-IGNITION-2:

If loss on ignition and dry matter are known,
... then the portion of organic matter can be calculated to be approximately:
... loss on ignition/dry matter.

The following premises are fulfilled:

The analysis '207.83 25.07.83 Eluate' resulted in: dry matter = 210 mg/l.
The analysis '207.83 25.07.83 Eluate' resulted in: loss on ignition = 80 mg/l.

FIGURE 3: Example of the local justification of a statement.

5. EXPERIENCES

XUMA was tested in the LfU. It was surprising how easy the system is to be used even for a user without experience in computers. The system is a good assistant to help the expert in risk assessment. Maybe that some of the rules seem to be simple or trivial if they are seen isolated. If rules are combined and used without any exception, the statements are very helpfull for the expert.

Even inconsistent assessments can help to find errors in the analysis data or in the rules. The expert is then able to create better rules or modified quality classes. A risk assessment is not only given on the basis of one discrete value as a yes-no decision it is furthermore the result of comparing various standard value tables with defined scope.

So the expert will have the necessary tolerance for the special assessement of individual cases. Risk assessments are transparent, standardized as far as possible and reproducible. The system can be used only by risk assessment experts.

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A RAPID RESPONSE SAW-GC CHEMICAL MONITOR FOR LOW-LEVEL VAPOR DETECTION

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INTRODUCTION

Chemical vapor monitors (CVMs) are generally not sufficiently sensitive, selective, or reliable enough to detect a multiplicity of vapors in less than 2 min. There is, therefore, a need for a CVM which can simultaneously detect a variety of vapors in the presence of interferents. In addition, the detection of a specific vapor must be conclusive so that false alarms are minimized. Detection in less than 2 min requires either highly selective multiple detection methods if several vapors are present or separation so that each vapor can be detected and identified. The sensitivity for each vapor must also be sufficient to allow detection at desired or required levels.

SAW sensors have been used to detect vapors at low concentrations [1]. However, the SAW detection limits reported to date for agents such as GD and HD are much higher than the limits other devices are capable of reaching. Detection limits of approximately 100 ppb (0.6 mg/m^3) for GD and 5 ppm (32 mg/m^3) for HD have been reported. It will be shown in this paper that much lower levels may be obtained for GD and HD when the system described herein is used. In addition, results on the detection of methyl benzoate and phenyl acetone using the same system as used for CW detection will be provided.

BACKGROUND

The CVM unit contains major modifications which allow significantly improved response times. Ambient vapors are collected on a thermally desorbed type concentrator by pumping air through a glass tube packed with concentrator material (Figure 1; concentration). At the end of a fixed 20 sec interval, the concentrator is heated and the collected vapors desorbed onto the GC column. Desorption occurs in about 6 sec and provides chromatographic peaks that are compatible with the SAW detector (Figure 1; injection). An additional 4 to 8 sec is typically needed, however, in order to obtain complete injection of the vapor plug onto the GC column.

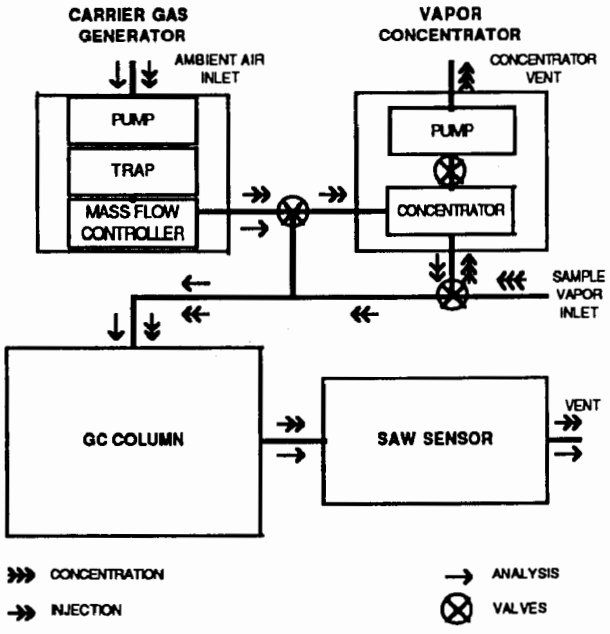

Fig. 1. Kodak's Chemical Vapor Monitor Showing Concentration, Injection, and Analysis Stages of Operation.

The GC column greatly enhances the selectivity of the system by separating the vapors (Figure 1; analysis). Each vapor plug which elutes from the GC column at a different time is immediately injected onto a SAW sensor. A second, uncoated SAW sensor located nearby is used as a reference. When combined with a frequency mixer, this configuration provides a frequency

difference (Δf) that is easily measured and relates to concentration.

The CVM has several other subsystems. The sequencing of valves, concentrator, pumps, and the acquisition of SAW sensor data is controlled by a Macintosh™ computer. A second subsystem provides clean air/carrier gas to the GC column with a small pump that draws ambient air through molecular sieve and charcoal scrubbers. A solid-state mass flow controller is used to guarantee a stable carrier gas flow under varying conditions of pump and scrubber aging. A typical output of the CVM is given in Fig. 2 and shows the concentration, injection, and analysis characteristics of the device.

EXPERIMENTAL

Each SAW sensor was first tested as an individual sensor with each vapor of interest at one or more concentrations. The sensor was then incorporated into the CVM and system testing performed.

Vapor Generation and Verification

Vapors were generated using a Microsensor Systems, Inc. VG-7000 Automatic Vapor Generation System. All vapors supplied to the CVM were monitored using a Hewlett Packard 5890 Gas Chromatograph containing an FID detector. For the SAW sensor testing, periodic checks of the vapor concentration were made every 11 minutes. For the CVM tests, vapor concentration was determined by sampling the final portion of vapor which impinged upon the CVM concentrator. This procedure was performed in order to ensure verifiable vapor concentrations.

SAW Sensor Preparation

Selective coatings of ethyl cellulose (ECL) and fluoropolyol (FPOL) on SAW sensors were prepared using proprietary thin film coating techniques. All coatings were observed under a microscope to

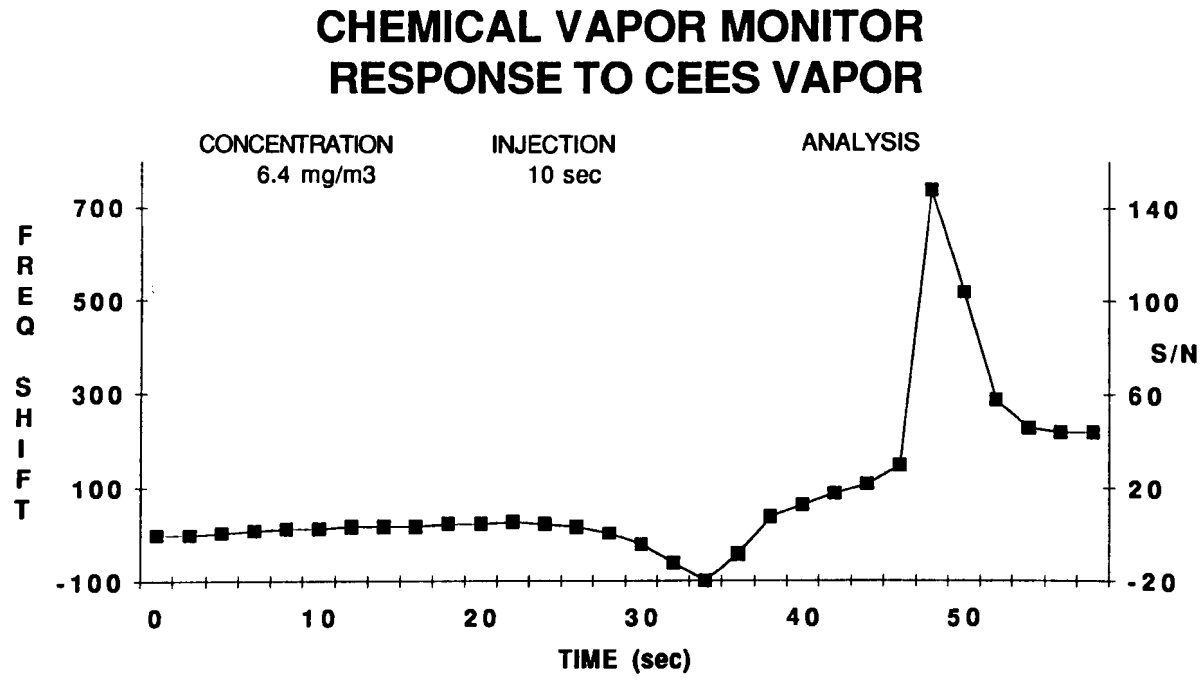

Fig. 2. Typical CVM Output

determine uniformity of the coating. Only uniform and well adhered coatings were used in this study. The thickness of a coating was determined by recording the frequency shifts of the device both before and after coating.

SAW Sensor Testing

Individual SAW sensors were tested using various concentrations of the vapors of interest. The SAW sensors were exposed to the vapors for a minimum of 20 minutes. A signal to noise ratio of at least 3:1 was chosen as a criterion for acceptable data.

CVM Testing

The general operation of the CVM was described above. Standard operation is a 20 second concentration period, a 12 second injection period, and an 88 second analysis time. Deviations from this standard will be indicated in the results section when appropriate.

RESULTS

Results were obtained using two types of SAW sensors. The first tests used a modified version of an established type of sensor (Type I). This was followed by extensive testing of a new type of SAW sensor (Type II). Both SAW sensor test results and CVM test results are reported below.

SAW Sensor Testing

Table 1 provides the frequency shifts observed from selected experiments when the ECL-I, FPOL-I, ECL-II, and FPOL-II sensors were tested with various concentrations of CEES, DMMP, methyl benzoate, and phenyl acetone.

Chemical Vapor Monitor Testing

During CVM testing the vapor flow was connected to the concentrator input of the system; flow rates through the concentrator were monitored. The results of selected tests using the first type of SAW sensor are shown in Table 2.

TABLE 1
SAW Sensor Results

Sensor	Vapor Concentration (mg/m^3)		SAW Response* (Hz)
ECL-I	CEES**	2100	2400
FPOL-I	DMMP**	91	4,710
ECL-II	CEES	17.8	58
	DMMP	20.6	362
	MB**	2.4	75
	PA**	1.7	88
FPOL-II	CEES	516	248
	DMMP	2.3 ± 1.1	773
	MB	19.2	222
	PA	6.48	265 ± 60

*80 Hz noise level (Type I); 5 Hz (Type II)
**CEES - chloroethyl ethylsulfide; DMMP - dimethyl methylphosphonate; MB - methyl benzoate; PA - phenyl acetone

TABLE 2
Chemical Vapor Monitor Results

Sensor	Vapor Concentration (mg/m^3)		CVM Response* (Hz)
ECL-I**	CEES	6.1	570
FPOL-I***	DMMP	17.6	1600
ECL-II	CEES	5.27	82
FPOL-II	DMMP	23.2	495
	MB	27.2	213
	PA	11.0	150

*Response obtained in less than two minutes; 2 Hz noise level unless otherwise specified
**5 Hz noise level; 10 second injection period
***10 Hz noise level; 14 second injection period

DISCUSSION

These results indicate that detection limits for GD and HD using the new type of SAW sensor should be considerably less than previously reported [1-2]. Table 3 gives extrapolated detection limits and response times for both the SAW sensor experiments and the CVM experiments. The extrapolated detection limits are determined from

the values reported herein using a 3:1 signal to noise ratio.

TABLE 3
Extrapolated Detection Limits

Type	Vapor	Extrapolated Detection Limit (mg/m^3)	Response Time (min)
SAW Sensor			
Type I	CEES	210	20
	DMMP	4.6	40
Type II	CEES	4.6	20
	DMMP	0.05	40
	MB	0.48	20
	PA	0.29	20
CVM			
Type I	CEES	0.16	1
	DMMP	0.33	1
Type II	CEES	0.38	2
	DMMP	0.28	2
	MB	0.77	2
	PA	0.44	2

It should be noted that optimization of coating thickness was performed much more extensively with the Type I sensor. Significant improvements in the Type II sensor are expected in the future as further optimization of coating thickness and subsystem parameters are performed. The much lower noise level of the Type II sensor is the principal advantage of using this technology since both sensors should provide approximately the same response when the same thicknesses and types of coatings are utilized.

The results also reveal that the greatly increased sensitivity of the Type II SAW sensor is not carried over to the detection of DMMP using the complete CVM unit. FPOL coated sensors do not equilibrate as quickly with DMMP as with the other vapors. The peaks observed during all DMMP testing were much broader than for all other cases. Significant tailing of peaks was observed. Different GC columns and higher temperature operation of the SAW sensors may help to narrow the peak width and improve the detection limit for DMMP.

The results also show the response of the two sensors to methyl benzoate and phenyl acetone. It is believed that this is the first time that detection of such vapors with SAW detectors has been reported. The extrapolated detection limits indicate that relatively low levels of these vapors can be detected with SAW sensors. No effort has yet been made to develop special selective coatings for these two vapors.

CONCLUSION

Our studies have shown that SAW technology can be used to detect DMMP and CEES at concentrations below 1 mg/m^3 in less than two minutes. We have also reported for the first time the behavior of methyl benzoate and phenyl acetone to SAW sensors typically used for chemical agent detection. Concentrations below 1 mg/m^3 are also indicated for these two vapors. Because of the preliminary nature of some of the data presented herein, we anticipate even lower detection levels in the future as operational parameters and selective coatings are optimized.

ACKNOWLEDGEMENTS

The authors would like to thank Arthur Snow of the Naval Research Laboratory for providing us the fluoropolyol used in these experiments.

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PASSIVE CRYOGENIC WHOLE AIR FIELD SAMPLER

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The portable, passive cryogenic sampler has been designed by the Idaho National Engineering Laboratory (INEL) for the collection of whole air samples without the loss or concentration of any atmospheric constituents. The principle of operation is the collection by bulk gas flow and condensation of a whole air sample into a previously evacuated cylinder held at liquid nitrogen temperature using a reservoir. The ability of the sampler to collect a highly compressed gas sample without concentration of condensable gases permits a large number of gas constituents to be analyzed from a single sample, even when analytes vary widely in their boiling points.

Design criteria for the portable, passive whole air sampler are listed in Table 1. The sampler, constructed in-house of readily commercially available components, is shown in Figure 1.

The sampler evaluation was performed in three phases. The first phase determined sample flowrate, sample size, resultant sample pressure, and sample collection lifetime as a function of the liquid nitrogen additions. The second phase analyzed simulated whole air samples for bulk composition, noble gases, selected chlorofluorocarbons, and tritium before and after collection in the cryogenic air sampler. In the third phase actual field samples were collected and analyzed for bulk composition and chlorofluorocarbon content. These samples were then concentrated, separated, and analyzed for noble gases. Also included in the third phase was the analysis of altered whole air samples, blindly and randomly introduced into the sample analysis scheme as a means of detecting sample tampering.

Results of the evaluation of the design criteria for the sampler are listed in Table 2. A partial listing of past customers and their application of the sampler is found in Table 3. The need of a low cost passive cryogenic sampler that can collect many whole air samples at remote locations with minimal logistical support will become widespread in the future.

We have found the sampler to meet or exceed all of the characteristics intended for it. The sampler is capable of the collection of samples without concentration or loss of any sample constituents regardless of boiling point.

The required sample volume of 100 L at STP has been successfully achieved, and samples as large as 131.2 L have been collected. Most samples are between 70 and 90 L. The volume of sample collected is dependent upon the sample duration and flowrate. By selection of the proper combination of sample duration and flowrate, samples of accurately known size from a few to 100 liters may be collected unattended within 30 minutes or over a period of time of 2 hours.

Laboratory tests on known standards demonstrate that no concentration or loss of atmospheric constituents occurs.

No electrical power is required for operation of the sampler, which would enable it to operate in hazardous environments such as where potentially explosive mixtures of hydrogen and oxygen are found.

The sampling lifetime can extend to 4 hours with refilling of the liquid nitrogen reservoir.

TABLE 1
Design Criteria for Whole Air Sampler

1) Sample Volume of 100 Liters
2) No Concentration or Loss of Constituents
3) Sampling Lifetime Greater Than 2 Hours
4) Small (50cm x 15cm) & Lightweight (20kg)
5) No Electrical Power
6) Operator Safety
7) Ease of Operation

TABLE 2
Development of Cryogenic Whole Air Sampler

Parameter	Results
Sample Flowrate	Controllable, 1 cc to 3 L/Min
Sample Volume	Nominally 100 Liters, 130 L Maximum
Sample Pressure	Nominal 2000 psi, 3650 psi Maximum
Sampling Lifetime	30 Min to 10 Hours
Sample Concentration	Noble Gas Ratios, Unaltered
Sample Loss Tests	Chlorofluorocarbons, 100% Recovery Tritium, 100% Recovery

TABLE 3
Past Applications of the Passive Cryogenic Whole Air Sampler

Customer	Facility	Application	Analytes
DOE- Office of Materials	ICPP	Hydrogen-Rich Off-Gas Study	Permanent Gases
US Air Force	Proposed for White Sands, KA-III Series	Fuel/Air Explosives	Combustion Products, Oxygen
DOE- Office Waste Mgt	ICPP	Environmental Sampling	$^{85}Kr, N_2, O_2$ Ar, CO_2
US Air Force	TREAT Pulse Reactor INEL	Environmental Sampling	Kr, Xe, Freon-11 Methyl-chloroform
DOE- Defense Programs	Advanced Test Reactor INEL	Off-Gas Studies	$^{41}Ar, Kr, Xe$ $CFCl_3, CH_3CCl_3$ Freon-113
DOE-Office Arms Control	INEL Research	Evaluation of Arms Control Verification	$^{3}H, Kr, Xe, He,$ $N_2, O_2, Ar, H_2,$ Freon-12, CO_2, Freon-113
US Air Force	ICPP	Fission Products in Ar Carrier Gas	Fission Product Gases

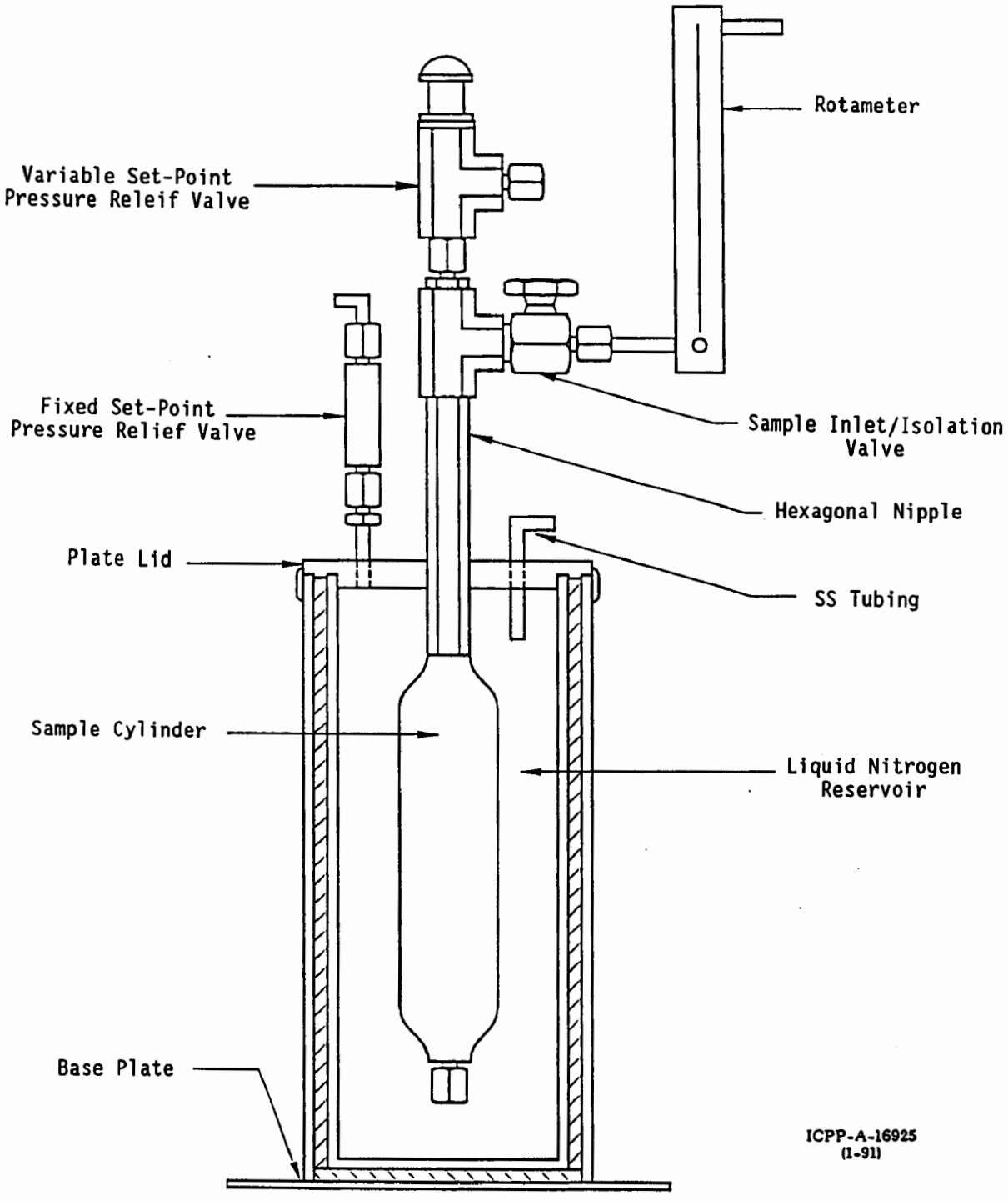

FIGURE 1

PASSIVE CRYOGENIC WHOLE AIR FIELD SAMPLER

Effectiveness of Porous Glass Elements for Suction Lysimeters to Monitor Soil Water for Organic Contaminants

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ABSTRACT

The objective of this effort is the development of a porous glass suction lysimeter which can be used to sample organic contaminants associated with unsaturated soil matrices. Current ceramic suction lysimeters are ineffective in sampling hydrophobic compounds since their surface chemistry is hydrophilic, effectively repelling organic species.

Methods for preparing porous glass elements with controlled porosity have been developed. Elements with air entry values (as measured by the bubbling pressure method) corresponding to effective pore sizes as small as 2 microns with high saturated hydraulic conductivities have been achieved.

The performance of porous glass elements in sampling organic contaminants in aqueous media is being evaluated. Aliphatic (1-octanol) and aromatic (ethylbenzene) compounds dissolved in water were used as the tests solutions. Tests are also being performed with inorganic constituents in the test water to determine the ability of the test elements to sample inorganics. Initial results indicate that the porous glass elements are able to effectively sample organic and inorganic constituents in the test solutions. These data indicate that analyte concentrations in the water sampled through the porous glass elements are within about 10% of the test solution concentrations.

BACKGROUND

The U. S. Environmental Protection Agency (EPA) requires vadose zone monitoring at active land treatment and disposal facilities for hazardous wastes. The state of California has extended this requirement to practically all active and closed storage, treatment, and disposal facilities for hazardous waste, solid waste, and underground storage tanks. Routine analysis of samples collected with suction lysimeters is considered an important element in the vadose zone monitoring requirement. Most of the suction lysimeters in use now were developed for the agricultural industry to monitor leachate from crops. These data are used to program the application of fertilizers and soil amendments. Another device, the tensiometer, is used in conjunction with the suction lysimeter to monitor soil moisture; this information is used to program irrigation. This same equipment is now being used to monitor the land treatment of certain hazardous wastes, e.g. refinery separator sludge and wood preservative waste. Many of the components of interest in these wastes are organics and heavy metals.

The suction lysimeter's porous element, through which soil water is drawn under vacuum, has been purposely designed to be hydrophilic to facilitate the transport of the aqueous phase. Porous elements currently in use are most frequently ceramic. However, TFE-fluorocarbon, nylon mesh and alundum have also been used. The porous element is typically treated with acid and water to remove contamination and enhance hydro-

philicity. Unfortunately, the resulting hydrophilic nature of the porous element presents an effective barrier to sampling of non-polar components. Organics, whether dissolved in the aqueous phase or existing as a separate phase are significantly under-sampled by existing suction lysimeters. One recent field study of soil-pore water sampling systems showed no correlation between organics found by sampling compared with analysis of soil cores (1). Additional studies have shown that xylene (2), DDT (3), and fecal coliform (4) are not effectively sampled by ceramic suction lysimeters. In addition, a number of inorganic parameters, heavy metals in particular, are also attenuated by ceramic suction lysimeters. Simultaneously, a number of inorganic constituents are leached from ceramic suction lysimeters into soil water samples. While TFE-fluorocarbon porous elements are less prone to significant adsorption or desorption of inorganics, they also under-sample organic components. Additionally, the large pore sizes of TFE media restrict their range of operation to wetter soils than can be sampled by ceramic suction lysimeters.

Ideally, a suction lysimeter should provide a sample which accurately represents the soil liquid phases at the sampling location. This would include all components, organic as well as inorganic, dissolved in the soil water and any non-aqueous, i.e. organic, phases. While sampling all components representatively, the lysimeter should also be inert so it does not leach any chemical species into the sample. To achieve this ideal goal, the porous element must be very stable over a wide range of aqueous and organic conditions and be neither hydrophilic nor hydrophobic. Such a perfect porous element is probably unachievable. However, elements made of porous glass could form the basis for approaching this goal. Porous glass elements can be formulated which are inert to organic and aqueous media over wide ranges of pH and dissolved components. Also, the surface structure can be controlled to moderate its hydrophilicity/hydrophobicity. This control can be achieved by modifying the composition of the glass, modifying the thermal processing of the glass, and, if necessary, by chemically treating the glass to incorporate desired chemical species on the surface. This paper describes the results of laboratory studies aimed at the development of porous glass elements for use in suction lysimeters to provide more accurate sampling of organic as well as inorganic species.

EXPERIMENTS WITH HIGH SILICA POROUS GLASS ELEMENTS

Preparation of the Elements

A series of porous glass discs were prepared from powdered high silica borosilicate glass by sintering. The solid state sintering mechanism for different glass systems is well-known and, to a large degree, applies to porous glasses. Densification and the resultant reduction in porous volume occurs in two separate regimes when high silica porous glasses, as used in this research, are sintered. The onset of the first stage starts above 750°C, at which point the micro-pores start to disappear. The driving force for this process is a reduction in the surface energy. Above 950°C, the second stage of sintering begins. In this stage, neck formation occurs between the individual grains of glass, affecting the macro-pores. It is important to control the overlap of the two stages, with more emphasis on the second stage since this stage controls the macro-porosity of the system.

A systematic study was conducted to evaluate the degree of densification when sintering powdered porous glass. The objective was to gain control over the pore structure of the elements for the porous glass suction lysimeter.

The porous elements were prepared by firing at different peak temperatures. The glass was held at the peak temperature for various times ranging from 30 to 90 minutes. Heating and cooling rates were maintained constant for all the samples. Densities of the resulting glass discs were measured and normalized against the density of the solid glass having the same composition (the density of solid high silica glass with 4-5% boron oxide is approximately 2.25 g/mL). The densification and fractional porosity as a function of firing temperature (60 minute firing time) are shown in Figure 1. As can be seen in this graph, porous glass powder sintered at 1200°C for 60 minutes achieves an 85% densification. A series of scanning electron micrographs, showing the structure of porous glass elements prepared at temperatures of 1100 and 1150°C for 60 minutes and 1200°C for 90 minutes are shown in Figures 2a-c. These micrographs visually show that the pore size and fractional volume decrease with increasing firing temperature and firing time.

Pore Size and Hydraulic Conductivity Measurements

Bubbling pressure, or air entry value, measurements were performed on the porous glass elements prepared. At first, a lucite disc holder was used. This worked well at low pressures but leaked at higher pressures. A second holder, made of stainless steel was prepared which worked well over the full range of pressures studied. Figure 3 shows both the lucite and stainless steel holders.

The pore size corresponding to the air entry value was calculated by the following equation:

$$d = 30\ Y/P \qquad (1)$$

where d is the pore size in microns, P is the bubbling pressure (the pressure at which air first comes through the porous disc) in mm Hg, and Y is the surface tension of water in dynes/cm at the temperature of the experiment. At room temperature, Y is 73.05 dynes/cm. It should be noted that the pore size measured by this procedure is an effective pore size; the actual pore sizes vary as can be seen in the scanning electron micrographs (Figure 2).

Air entry value measurements were performed on a number of porous discs prepared over a range of sintering temperatures and times. The results are plotted in Figures 4 and 5. In Figure 4, the effective pore size is plotted as a function of firing time at three different firing temperatures (1050, 1150, and 1200°C). Figure 5 shows the effect of firing temperature on effective pore size when the firing time is held constant at 60 minutes. These graphs clearly show that the pore size can be varied down to 2 microns (firing at 1200°C for 60 minutes).

The flow rate through a series of the porous glass elements was also studied. These data were used to calculate the hydraulic conductivity and determine the relationship between effective pore size and hydraulic conductivity. The same holder used to measure the air entry value was used to measure the flow rate. For these experiments, the flow was induced by maintaining a vacuum on the porous glass disc. The experiments were performed using a vacuum of 63.5 cm (25 in.) of Hg. The fluid used for these experiments was deionized water, which was drawn from a burette able to measure volume to 0.1 mL. The flow through each disc was measured for at least two runs and the results averaged.

Figure 6 shows the measured flow rate as a function of sintering temperature (60 minute firing time). It also plots the pore size against the same abscissa. This graph shows that as the sintering temperature increases, the flow rate decreases along with the pore size, as would be expected.

The hydraulic conductivity was calculated using the following equation:

$$K = (Q/t) * (L/A) * h \qquad (2)$$

where Q is the volume of water flowing through the element in time, t, L and A are the thickness and cross-sectional area of the element, respectively, and h is the pressure differential across the element. Figure 7 plots the hydraulic conductivity against pore size. The data indicate a linear relationship between hydraulic conductivity and effective pore size.

The hydraulic conductivity of the porous glass elements appear larger than that of ceramic suction lysimeter elements of the same pore size. For example, the saturated hydraulic conductivity of a Soilmoisture Corporation ceramic suction lysimeter with an air entry value of 1 bar (pore size 2.1 microns) is 3.36E-7 cm/s. Figure 7 shows the saturated hydraulic conductivity of a 2 micron porous glass element to be about 1E-5 cm/s, almost two orders of magnitude greater than the ceramic element.

A series of nominal 2 micron pore size elements were prepared. The measured pore size and hydraulic conductivities of the elements are reported in Table 1. The average pore size was 2.1 microns with a standard deviation of 0.8 micron. The average hydraulic conductivity was 1.8E-6 cm/s with a standard deviation of 0.6E-6 cm/s. The pore size and hydraulic conductivity of the elements range by a factor of about 2. The hydraulic conductivities of these elements are almost an order of magnitude higher than that of a comparable Soilmoisture Corporation ceramic suction lysimeter, although not as high as the porous glass element reported in Figure 7.

Sampling Efficiency

Experiments were performed to determine the permeability of the porous glass discs to inorganics dissolved in water. Inorganic test solutions contained sodium chloride, barium chloride, lead chloride, and potassium chromate. The results of these tests are shown in Table 2. For all tests, a 61.0 cm (24 in.) Hg vacuum was maintained across

the elements. The concentration of the inorganics was measured by Direct Coupled Plasma (DCP) Spectroscopy. The table shows good correlation between the concentrations in the sample solution as compared to the test solution. The average ratio of sample to test concentrations was 0.88 with a standard deviation of 0.16.

Problems Observed

Several problems were observed with the borosilicate porous glasses used in the first set of experiments. One problem was that when the porous glass powder used to make the elements was exposed to air for extended periods (hours), the resulting elements were very fragile (they tended to crack easily). It was hypothesized that this could be due to the formation of internal cracks caused by drying or by formation of silica gel within the pores. This problem was resolved by keeping the porous glass powder in water until it was used to form the elements.

A second, more serious, problem was clogging of the elements over time. It was hypothesized that components of the glass were leaching into and precipitating in the interstices of the elements. To alleviate this problem, the porous glass was modified by the addition of zirconia to produce a more durable glass matrix. The results with this zirconia glass are reported in the following sections.

EXPERIMENTS WITH ZIRCONIA GLASS POROUS ELEMENTS

Preparation of the Zirconia Glass Elements

The composition of the porous glass powder used to make the test elements was modified by the addition of 4-5% zirconia. This modification was made to produce a more durable glass which would be more consistent and less likely to clog. The glass was prepared by sintering the powder at 1150°C for 60 minutes.

Pore Size and Hydraulic Conductivity

Table 3 provides the pore size and hydraulic conductivity measured on several elements of the zirconia glass. The consistency, in terms of pore size and hydraulic conductivity, among elements was much better than the earlier test elements. However, the pore size was approximately 3 microns. Revised heat treatments should be able to lower the effective pore size to the 2 micron range.

Sampling Efficiency

Experiments were conducted to determine the permeability of the porous glass discs to organics dissolved in water. Organics used in the test solutions were ethylbenzene and 1-octanol. For all tests, a 61.0 cm (24 in.) Hg vacuum was maintained across the elements. The concentration of the organics was measured with a Total Organic Carbon (TOC) analyzer.

The test organic solutions were prepared by carefully placing a layer of the organic chemical on top of a large beaker of water. The liquids were allowed to equilibrate over several days. The water in the bottom of the beaker was periodically sampled (without disturbing the interface between the two phases) and its TOC content measured. When the TOC content of the water became constant, it was carefully removed from the beaker so that no droplets of organics were entrained.

The evaporation of the organic component from the test solutions under vacuum was studied. Figure 8 shows the significant decrease in the TOC of the test 1-octanol solution as a function of time when the solution was kept under a 61.0 cm Hg vacuum. The data is linear when plotted against the square root of time, indicating that the rate of evaporation is controlled by the diffusion of organic to the surface of the liquid. A similar experiment conducted with ethylbenzene showed no decrease in TOC as a function of time. The difference in the rate of evaporation of the two compounds is due to the (a) their volatilities, and (b) their polarity. Since ethylbenzene is less volatile than 1-octanol, it evaporates at a slower rate. Also, since ethylbenzene is more polar than 1-octanol, it forms stronger hydrogen bonds with water molecules, also retarding its rate of evaporation.

This observation is very important in the development of a suction lysimeter for sampling organics in soil water. Organic components which tend to volatilize easily from aqueous solution could be lost due to evaporation. This problem can be corrected either through capture of the evaporated organics on an adsorbent, such as carbon. Alternatively, the TOC could be corrected mathematically using calibration data such as Figure 8. Capture and subsequent analysis of volatilized organics would obviously be a more desirable approach.

The performance of the zirconia porous glass elements in sampling organic solutions is summarized in Tables 4 and 5. The ability of the zirconia porous glass elements to sample the ethylbenzene solution was excellent. The difference between the TOC in test and sample solutions was always less than 3 ppm, a error of about 4%.

The tests conducted with the 1-octanol solution, Table 5, showed the effects of octanol evaporation. However, when the TOC measurements are corrected for the octanol evaporation using Figure 8, the results are quite good. For the 1 hour suction period used in these experiments, the correction factor is 1.36. This correction factor was used to generate the column of corrected TOC's in Table 5. The average value of the corrected TOC's is 305.0 ppm compared to 298.9 ppm TOC in the test solution. This represents only a 2% error.

Thus, these data, while limited, demonstrate an excellent ability to sample organic compounds in soil water.

CONCLUSIONS

This paper documents the significant progress being made toward the development of a porous glass suction lysimeter capable of sampling organic and inorganic constituents in soil water. The ability to make porous glass elements with pore sizes as small as 2 microns with high hydraulic conductivity has been demonstrated. Also, initial experiments indicate that the elements can accurately sample organics and inorganics in water. Work is continuing to optimize the preparation, including the composition and thermal treatment, of the porous glass elements and to develop a comprehensive set of data on the ability of the optimized porous glass elements to accurately sample soil water.

Future work will evaluate optimized porous glass elements with simulated and real soils, leading to the development of a suction lysimeter using porous glass elements.

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Table 1
Pore Size and Hydraulic
Conductivity of Porous Glass Elements

Element	Pore Size, microns	Hydraulic Conductivity cm/s
1	2.3	1.9×10^{-6}
2	2.1	1.6
3	3.5	2.8
4	3.5	2.6
5	2.3	1.2
6	1.6	1.2
7	1.1	1.2
8	2.3	1.2
9	1.9	1.6
10	1.3	2.5
11	3.5	2.6
12	1.2	2.6
13	1.6	1.2
14	1.6	1.4
Mean	2.1	1.8×10^{-6}
Std. Dev.	0.8	0.6×10^{-6}

TABLE 2

TESTS WITH INORGANICS IN AQUEOUS MEDIA

Inorganic	pH	Test Concentration (ppm)	Sampled Conc. (ppm)	Ratio
NaCl	7.0	196	206	1.05
	7.0	196	198	1.01
$BaCl_2$	1.8	69.4	67.5	0.97
	1.8	69.4	66.1	0.95
$PbCl_2$	4.4	102	66.4	0.65
	4.4	102	63.6	0.62
$K_2Cr_2O_7$	6.2	94.7	81.9	0.86
	6.2	94.7	91.1	0.96
			MEAN	0.88
			STD. DEV.	0.16

TABLE 3

PORE SIZE AND HYDRAULIC CONDUCTIVITY OF ZIRCONIA POROUS GLASS ELEMENTS

Pore Size, microns	Hydraulic Conductivity, (cm/s)
3.0	7.4 E-06
3.0	7.6 E-06
2.8	7.4 E-06
3.0	5.4 E-06
3.0	5.3 E-06

TABLE 4

SAMPLING OF AQUEOUS ETHYLBENZENE SOLUTIONS

Porous Glass Element	Total Organic Carbon, ppm	
	Test Solution	Solution Sampled
1	72.95	74.83
2	72.95	72.02
3	72.95	75.92
4	72.95	78.48
5	79.07	76.83
6	79.07	76.11
7	79.07	78.68
8	79.07	78.94

Table 5

Sampling of 1-Octanol Solutions

Porous Glass Element	Total Organic Carbon, ppm		
	Test Solution	Solution Sampled	Sample Corrected for Evaporation
1	298.85	214.2	291.3
2	298.85	211.6	282.8
3	298.85	209.6	285.1
4	298.85	247.0	335.9
5	298.85	220.8	300.3
6	298.85	230.4	313.3
7	298.85	236.2	321.2

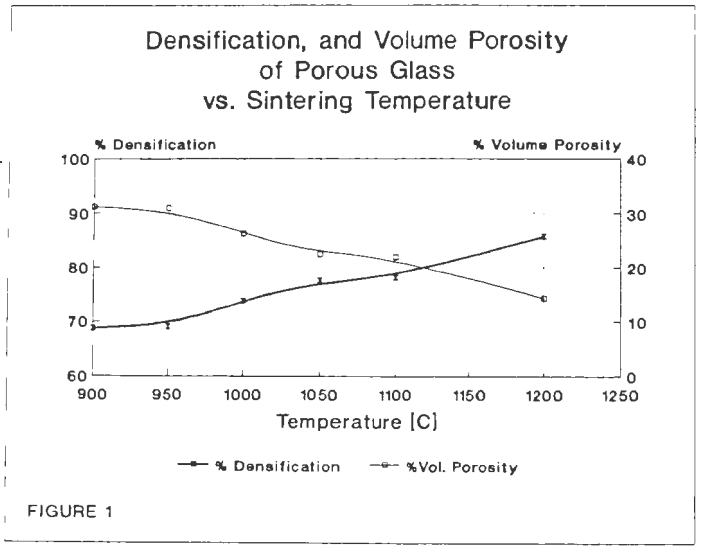
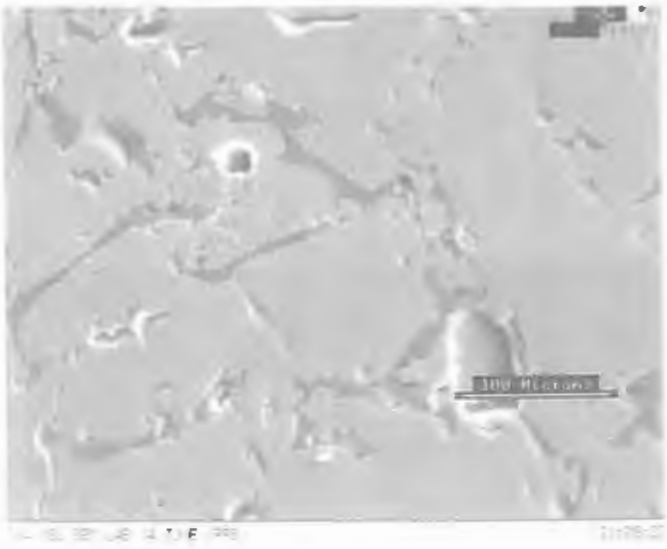
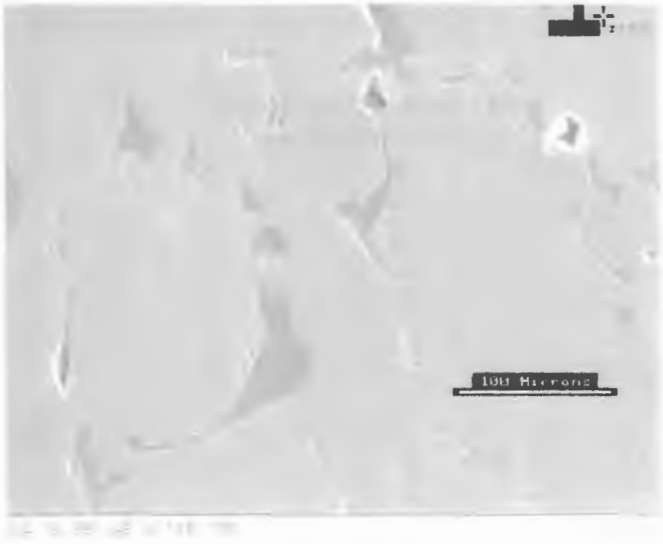

Densification, and Volume Porosity
of Porous Glass
vs. Sintering Temperature
% Densification
% Volume Porosity
100
90
80
70
60
40
30
20
10
0
900
950
1000
1050
1100
1150
1200
1250
Temperature [C]
% Densification
%Vol. Porosity

FIGURE 1

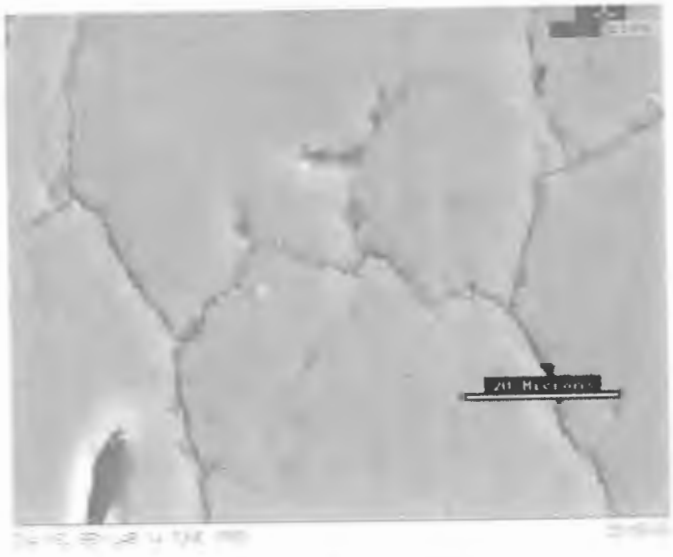
FIGURE 2A
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



Firing Temperature: 1100° C
Firing Time: 60 minutes

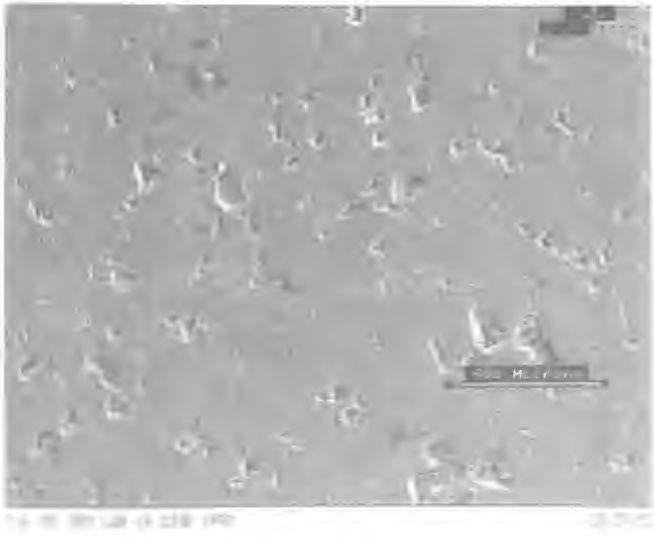


Firing Temperature: 1150° C
Firing Time: 60 minutes



Firing Temperature: 1200° C
Firing Time: 60 minutes

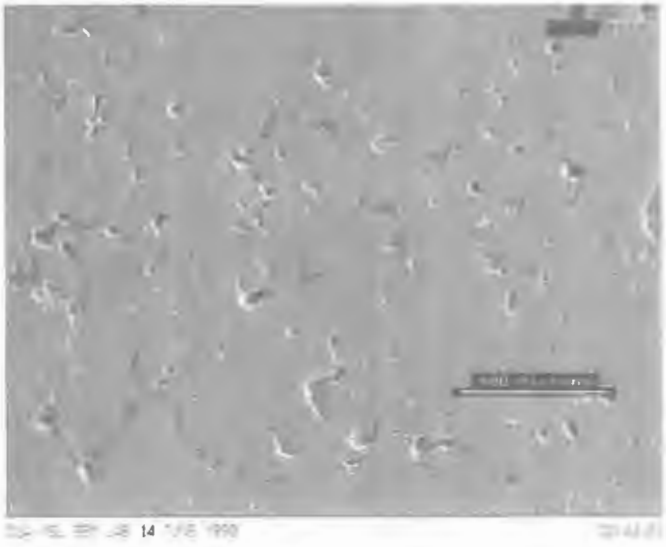
FIGURE 2B
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



Firing Temperature: 1150° C
Firing Time: 60 minutes

Firing Temperature: 1100° C
Firing Time: 60 minutes

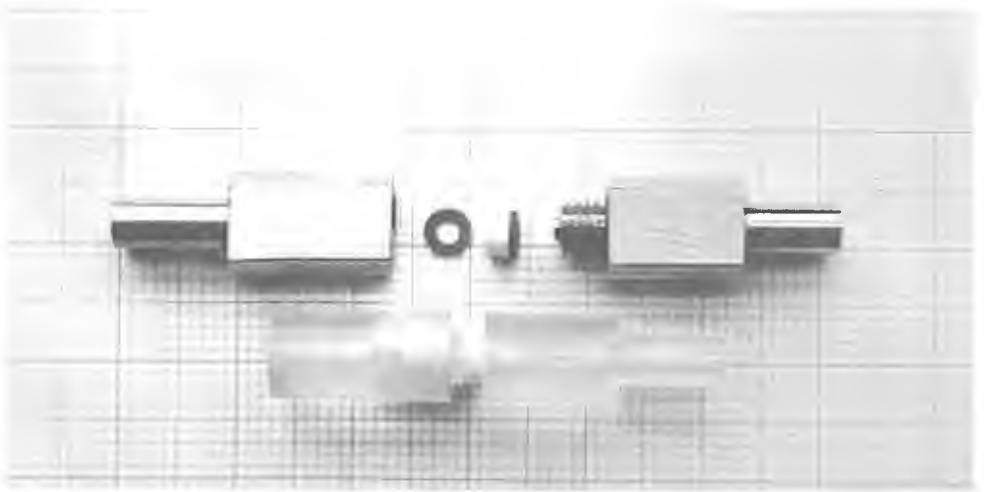
FIGURE 2C
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



Firing Temperature: 1200° C
Firing Time: 60 minutes

FIGURE 3

Lucite and Stainless Steel Holders for Porous Glass Elements



(Scale: heavy grid lines are one inch apart)

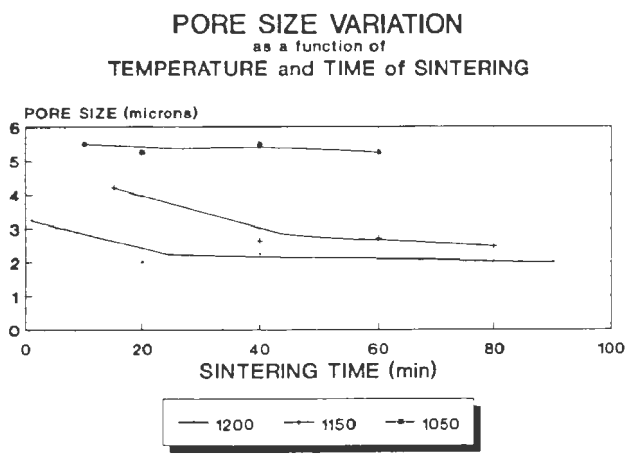


FIGURE 4. Pore size was measured by the technique.

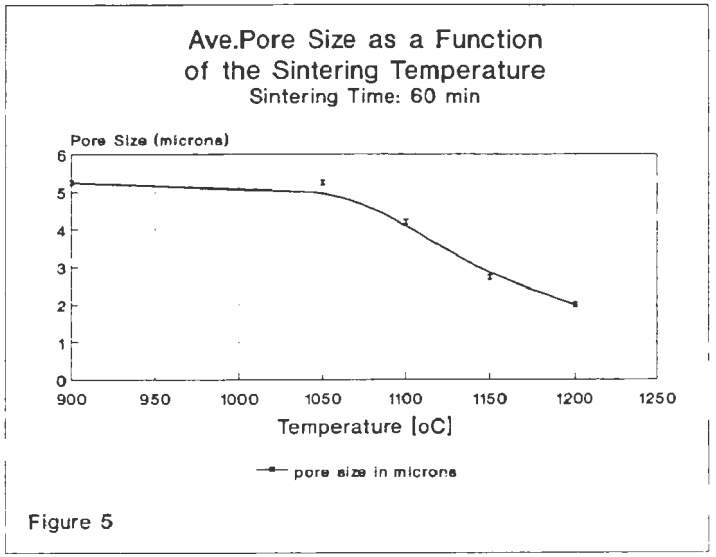


Figure 5

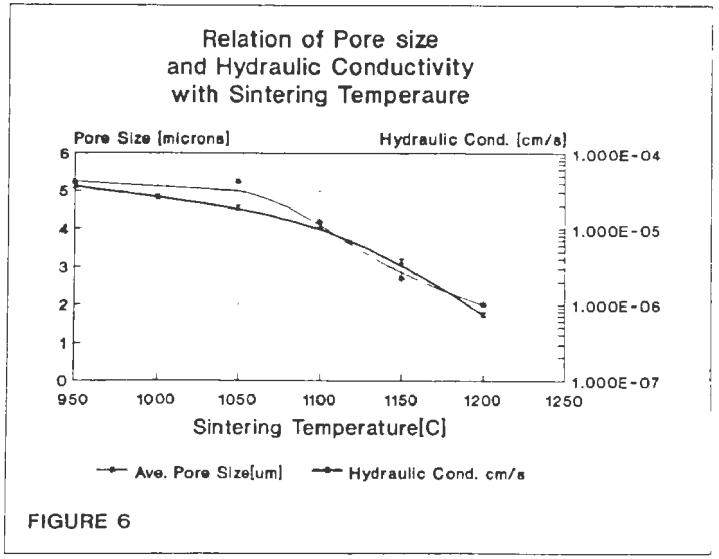


FIGURE 6

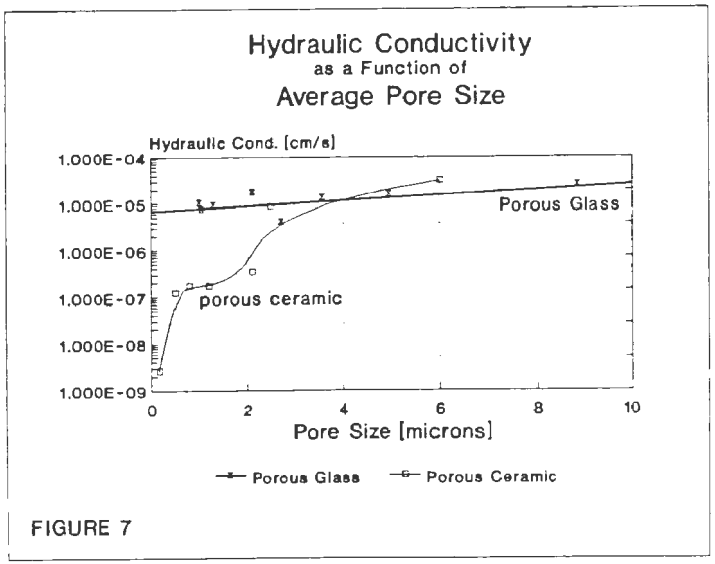


FIGURE 7

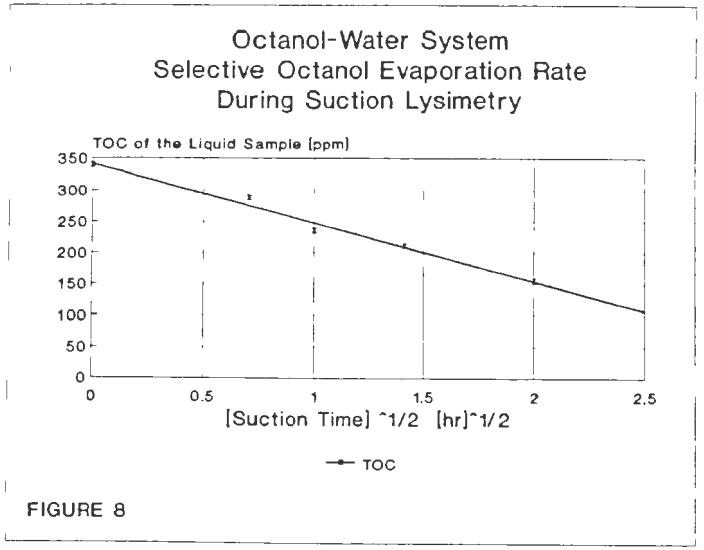

Octanol-Water System
Selective Octanol Evaporation Rate
During Suction Lysimetry
TOC of the Liquid Sample (ppm)
350
300
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
[Suction Time] ^1/2 [hr]^1/2
TOC

FIGURE 8

COMPARISON OF MOBILE LABORATORY XRF AND CLP SPLIT SAMPLE LEAD RESULTS FROM A SUPERFUND SITE REMEDIATION IN NEW JERSEY

Jon C. Gabry, Ph.D.

ABSTRACT

A mobile laboratory X-ray fluorescent spectrophotometer (XRF) was utilized to determine soil lead concentrations in 2,725 samples obtained during a Superfund Site remediation in New Jersey. These sample results assisted in guiding remedial excavation activities at the site. One hundred twenty-five site soil samples were split and analyzed for lead by the on-site mobile laboratory utilizing a XRF and by a USEPA Contract Laboratory Program (CLP) laboratory utilizing atomic absorption (AA) and/or inductively coupled argon plasma (ICAP) methodologies. In general, XRF results were usually higher than the CLP split sample results. Although unknown, XRF spectral emission interference and/or incomplete homogenization of the sample prior to splitting are the most probable causes of these differences. The XRF generated duplicate and split sample mean RPDs that were comparable or better than those obtained from the CLP laboratory and another EPA funded study.

INTRODUCTION

The use of XRF spectrophotometers for elemental analysis of soil samples in analytical field screening programs at hazardous waste sites is increasing. The purpose of this paper is to present a comparison of on-site mobile laboratory XRF and CLP split sample results obtained from a Superfund site remediation in New Jersey. At this site, a XRF was utilized to determine soil lead concentrations in 2,725 samples obtained to guide remedial excavation activities. The site, a former used oil reprocessing facility, is situated on the coastal plain with a uniform sandy soil type across the entire site.

METHODS

A portable X-MET 840 XRF spectrophotometer was used in an on-site mobile laboratory to determine soil lead concentrations. Prior to the analysis of any site soil samples, the XRF was configured to the on-site soil matrix and calibrated. This was accomplished by obtaining a composite of clean native site soil that was sent to a CLP laboratory which subsequently generated 10 spiked native soil calibration standards verified by AA and/or ICAP CLP methods encompassing soil lead concentrations ranging from 20 ppm to 1000 ppm. The on-site XRF was subsequently calibrated with these standards using the L-beta spectral line of lead to avoid any possible inter-element interferences by arsenic present within the site soil. All soil samples were dried and ground with a mortar and pestle prior to XRF analysis which followed the instrument manufacturer's instructions and utilized a counting time of 300 seconds. Quality assurance protocols performed during sample analysis included the analysis of native soil blanks and continuing calibration verification standards, and duplicate sample analysis at a frequency of 1 per 20 samples. Based upon the analytical data obtained, a detection limit of approximately 20 ppm lead in soil was estimated for the XRF.

One hundred twenty-five site soil samples were split and analyzed for lead with the on-site XRF and by a CLP laboratory utilizing AA and/or ICAP methodologies. All split samples

were homogenized in the field prior to splitting. Additionally, multiple split samples were submitted blindly to both laboratories as part of the quality assurance program.

RESULTS

Split sample relative percent difference (RPD) values for mobile lab XRF versus CLP results ranged from 5.2 to 173.2 with a mean RPD of 77.4 ± 48.7 (n=76). These results were comparable to an EPA funded study (1) which exhibited XRF versus CLP RPD results ranging from 16.6 to 131.5 with a mean RPD of 76.5 ± 45.7 (n=6).

For intralaboratory duplicate analyses performed on the split samples, the CLP laboratory exhibited a mean RPD of 20.0 ± 26.7 (n=9) whereas the on-site XRF had a mean RPD of 6.6 ± 5.2 (n=4). Multiple split samples submitted blindly to the laboratories had mean RPD's of 163.7 ± 15.7 (n=3) for the CLP laboratory and 65.7 ± 48.7 (n=7) for the on-site mobile laboratory utilizing the XRF. Duplicate analysis performed by an independent laboratory contracted by the state had a RPD of 171.8 with the two analytical results differing by a factor of 13.2.

In general, XRF results were usually higher than the CLP split sample results by factors ranging from 1.09 to 13.91 with a mean factor of 3.01 ± 3.05 (n=76). A similar trend was noted in an EPA funded study (1) which exhibited higher XRF versus CLP results by factors ranging from 1.18 to 4.84 with a mean factor of 2.68 ± 1.6 (n=6).

Although unknown, XRF spectral emission interference and/or incomplete homogenization of the sample prior to splitting are the most probable causes of the observed differences between XRF and CLP results presented. Additionally, the mass of soil analyzed for each method (e.g., 10-20 gms for XRF versus 1.0-1.5 gms for AA and/or ICAP) and/or analyte losses during extraction for AA and/or ICAP methodologies may be contributing factors to the observed differences noted.

CONCLUSIONS

As the data indicate, the XRF is capable of generating soil lead results that are comparable or better than those obtained from a CLP laboratory and/or an EPA funded study (1). Although these results were obtained for sandy coastal plain soils, similar results can be inferred for other soil types and elements provided that the XRF is configured to the native soil type and spectral counting lines are carefully chosen to avoid inter-element interferences. Since XRF analysis is highly matrix dependent, the accuracy and reliability of XRF results are greatest on those sites that exhibit a uniform soil type that the XRF can be configured and calibrated to. Sites with many different soil types of varying compositions are not amenable to XRF usage since the XRF must be configured and calibrated with each soil type in order to provide results that are comparable to AA and/or ICAP methodologies.

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Screening of Groundwater for Aromatics by Synchronous Fluorescence

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BACKGROUND, PURPOSE AND SCOPE

Pollution by petroleum, oil, and lubricants is a ubiquitous national problem. The aromatic constituents contained in these pollutants can generally be induced to fluoresce. The problem of identifying individual compounds, in what is often a complex mixture of fluorescing constituents, can be enhanced by resorting to a technique known as synchronous fluorescence (SF) (1).

The first application of the SF technique for screening polynuclear aromatic (PNA) contaminants in groundwater was described in the proceedings of the First International Symposium on Field Screening Methods (2). In the interim, we continued to develop the technique and continued long-term examination of groundwater taken from specific wells on the Department of Energy (DOE) reservation. Our eventual purpose is to show that SF screening is an acceptable field screening method at Levels I and II (3). Our efforts in achieving this end have been slowed by limited funding. Nevertheless we are able to report worthwhile progress; reference spectra and minimum detection levels (MDLs) were determined for 17 PNAs, a rapid solid-phase extraction and concentration method was developed and multi-year screening of groundwater from a specific well was continued.

EXPERIMENTAL

A detailed description of the method for making SF measurements is contained in reference 1. In making the currently reported SF measurements, we used a Perkin Elmer LS-50 spectrometer. In order to optimize resolving power, compound selectivity and sensitivity, slit widths of 2.5 nm were used for both excitation and emission light beams. The wavelength difference between the excitation and emission monochromators was set at the minimum possible value for this spectrometer, which was 5 nm. The scanning speed used to obtain the reported data was 300 nm/min.

A solid-phase extraction and concentration procedure was devised for lowering the MLD to 10 ppb or less of each of the 17 PNAs investigated. A home-made cartridge packed with C18 bonded-phase material was employed as the solid extractant. The PNA-containing water sample (250 mL) was first forced from a syringe through the cartridge. The exiting PNL-free water was discarded. N-propanol (2 mL) was next passed through the cartridge to elute the adsorbed PNAs which were now concentrated 125-fold. The selection of n-propanol as organic solvent was based largely one our having at hand, n-propanol with a low fluorescence background between 250 nm and 500 nm.

RESULTS AND DISCUSSION

After extraction from water and concentration by 125-fold into n-propanol, calibration curves of concentration versus SF response were determined. The data for the 17 PNAs are summarized in Table 1. The noted SF is the wavelength at which a single peak or the major one of multiple peaks occurs; 9 of the 17 PNAs produced a single peak at a $\Delta\lambda$ of 5 nm. The MDL for each PNA is based on a signal strength three times that of the standard

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deviation in the background. The MDLs range from about 1 ppt for benzo(k)fluorathene to about 5 ppb for pyrene.

A complete screening measurement can be made in about 5 minutes; the extraction and concentration step takes about 3 minutes and the spectroscopic measurement takes about 2 minutes. An example of this concentration and SF measurement is shown in Fig. 1 for a sample of groundwater spiked with 5 ppb of naphthalene.

The EPA Contract Laboratories Program requires participants to be able to quantitatively analyze PNAs on the EPA priority list at 10 ppb (4). We have shown that the SF method with a concentration stage (125 x) is capable, in principle, of matching this strict requirement.

The capability of the SF method for qualitative screening of groundwater over a period of 4 years can be visualized by referring to Fig. 2. Between 1988 and 1990, a constituent fluorescing at about 500 nm has appeared in the groundwater taken from well GW15; the fluorescence in the region of 280 nm stayed essentially unchanged. It remains to identify the composition of the entities fluorescing at 280 nm and 500 nm and determine whether they are of natural or anthropogenic origin.

A field screening method based on UV fluorescence has been described by Popp et al. (5) and is listed as Method FM-25 in reference 3. A measure of the total PNA concentration is made using two wavelength pairs. The method was practiced at two wood treating sites; some samples were analyzed by both the UV-fluorescence screening method and the conventional Contract Laboratory Program (CLP) GC/MS method. There was an order of magnitude relationship between the results of the UV-fluorescing screening and the conventional CLP GC/MS analysis for PNAs.

It remains to apply and compare the SF screening with the UV-fluorescence screening and CLP GC/MS techniques. One could then evaluate the advantages that would accrue from making more compound specific screening measurements using SF. The SF technique should have the greater compatibility with the CLP GC/MS method because the SF screening can be tailored to measuring the sum of the 18 PNA compounds on the hazardous substances list.

CONCLUSIONS

Progress continues in developing SF as a field laboratory, quick-screening technique for Level I and Level II analysis of PNA in groundwater. An easy concentration step permits analysis of individual PNA at concentrations of 10 ppb or less. Direct SF measurements of groundwater taken from a specific well over a period of several years show that qualitative changes in fluorescing constituents can readily be followed. The next phase of development should include comparative testing against the conventional UV-fluorescence screening and CLP GC/MS methods.

ACKNOWLEDGEMENTS

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Fig. 1. Synchronous fluorescence spectrum of naphthalene at 5 ppb after 125-fold concentration

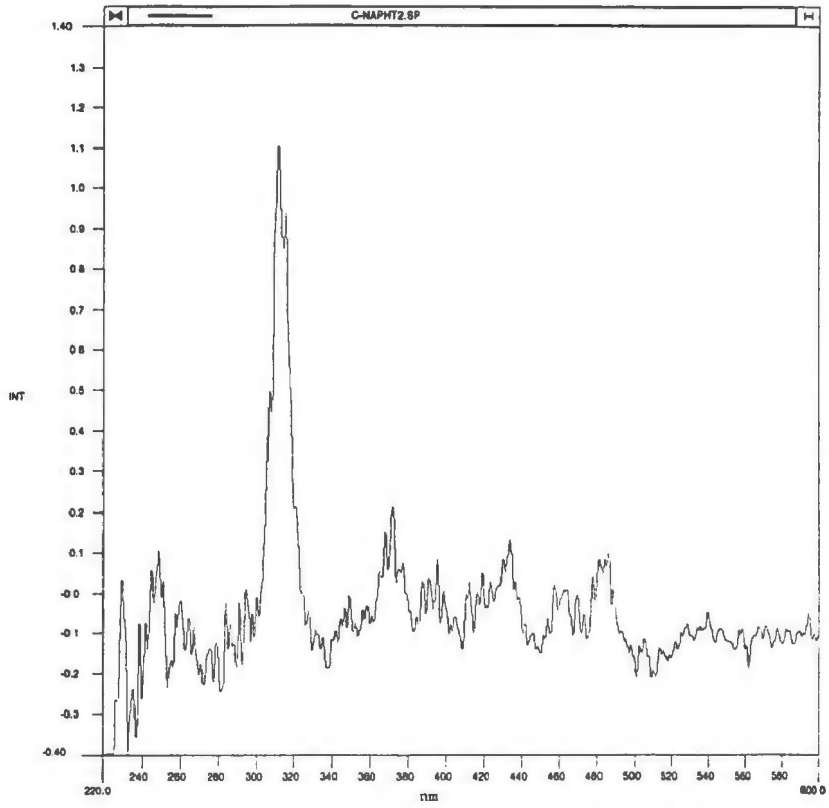

Fig. 2. Qualitative SF screening of fluorescing constituents in groundwater from a well (GW15) on the DOE Oak Ridge Reservation

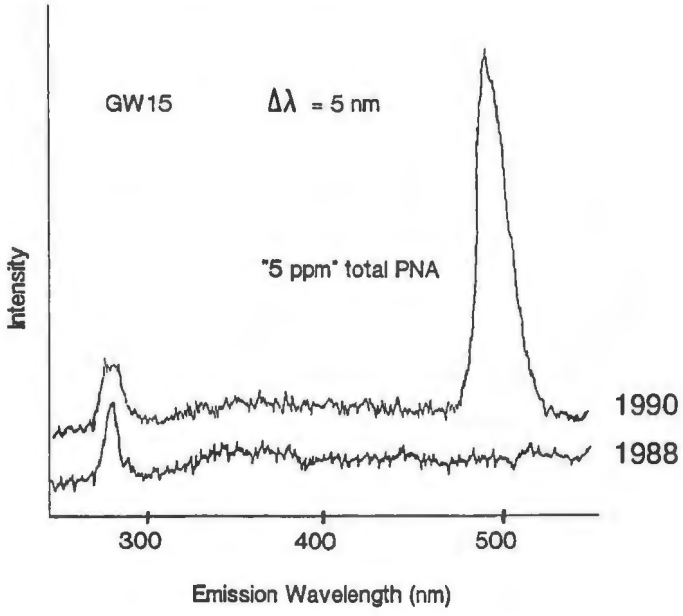

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Table 1. Synchronous fluorescence maximum and minimum level of detection after 125-fold concentration of 17 PNAs on the hazardous substance list

Compound	SF Maximum (nm)	MLD*
Fluorene	299.5	3 ppt
Naphthalene	311.5	1.8 ppb
Acenaphthylene	316.0	1.6 ppb
Acenaphthene	316.2	22 ppt
2-Methylnaphthalene	319.5	0.4 ppb
Phenanthrene	339.5	0.4 ppb
Chrysene	355.0	0.8 ppb
Pyrene	366.1	5.2 ppb
Anthracene	374.0	13 ppt
Benzo(a)anthracene	383.0	0.6 ppb
Dibenzo(a,h)anthracene	392.7	23 ppt
Benzo(b)fluoranthene	392.7	4.2 ppb
Fluoranthene	396.6	5.5 ppb
Benzo(h)fluoranthene	400.5	1 ppt
Benzo(a)pyrene	402.5	10 ppt
Benzo(g,h,i)perylene	433.1	3.8 ppb
Indeno(1,2,3-c,d)pyrene	459.1	30 ppb

*PNA in propanol
Perkin Elmer LS 50 Spectrometer
2-1/2 minute scan
2.5 nm slitwidths
= 5 nm

IN SITU DETECTION OF TOXIC AROMATIC COMPOUNDS IN GROUNDWATER USING FIBEROPTIC UV SPECTROSCOPY

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INTRODUCTION

Contamination of groundwater with organic compounds is a common problem at Department of Energy (DOE) facilities and other sites. Among the more prevalent contaminants are benzene, toluene, ethyl benzene, and xylenes (BTEX) which are used individually as solvents and are also major components of gasoline and other fuels. Leaking underground fuel storage tanks are significant contributers to groundwater pollution. Polycyclic aromatic hydrocarbons (PAH) are also possible groundwater contaminants, originating from fuel leaks or other sources.

Because aromatic contaminants are so ubiquitous, two needs related to their detection have arisen:

1. Rapid, cost-effective screening methods are needed as an alternative to slow, expensive conventional analyses.
2. The fate of aromatic contaminants in groundwater needs to be determined. An understanding of paths and rates of migration or biodegradation is crucial to the design of effective remediation strategies.

One approach that can meet both of these needs is a sensor that can detect aromatic compounds directly in groundwater. Our previous experience with derivative ultraviolet absorption spectroscopy, DUVAS (1-3), suggested that this might be a useful tool for this application. At the first meeting of this Symposium, we presented results demonstrating the feasibility of performing groundwater analysis in situ using a fiberoptic probe (4). Here we report on the development of a field-portable spectrometer and a fiberoptic probe based on that earlier work.

EXPERIMENTAL

Spectrometer construction. An 8in x 14in x 6in aluminum box was used for the spectrometer (see Figure 1). Although a more powerful xenon lamp was used for the light source in previous benchtop experiments, a deuterium lamp (Hamamatsu, Bridgewater, NJ) was employed in this work. Higher UV output was obtained from the monochromator as a result of the superior focal characteristics of the deuterium lamp. A homemade power supply was used with the lamp. An additional supply was included in the spectrometer to power the CVI (Albuquerque, NM) Model DK120 (Albuquerque, NM) monochromator (110mm focal length) and the photodiode detector housed in the probe (see description below). The monochromator was stepped via an external DK-1200 controller, also manufactured by CVI. Both power supplies were powered from a small car battery linked through an inverter. Light from the deuterium lamp was coupled into the monochromator through an f/1 fused silica lens. Light emerging from the monochromator was coupled into the optical fiber through another f/1 lens. The signal voltage returning from the probe to the spectrometer was sent to an IBM-compatible personal computer containing a Data Translation (Marlboro, MA) Model DT-2811 A/D board. Data collection and processing was handled with modified SpectraCalc (Galactic Industries, Salem, NH) software.

Fiberoptic probe. Previous experiments (4) showed that a one-fiber, detector-in-probe design could increase significantly the maximum sensing distance of a probe using UV light over a more traditional two-fiber design. The design was used to produce the in situ probe diagrammed in Figure 2. The probe will be described in detail elsewhere, however a brief description follows. A 25m, 600μm core, high-OH, all-silica optical fiber (Polymicro Technologies, Phoenix, AZ) was used to bring UV light to the probe. The light emerging from the fiber was focused through a 1cm optical sample path onto a photodiode detector (United Detector Technology, Hawthorne, CA) protected by an optical flat. Water entered the optical path through slits in the side of the probe. Photodiode power and the detected signal were transmitted through 5-conductor cable. Both the optical fiber and electrical cable were protected by a

thick-walled air hose connected between the probe and the spectrometer. The probe body was constructed of stainless steel and was about 6in length and 1¼in diameter, fitting easily into 2in or 4in diameter groundwater monitoring wells.

Samples. Benzene standards were prepared by diluting concentrated methanol solutions with distilled water. The contaminated groundwater samples were collected from well GW-15 at the Bear Creek Burial Grounds on the Oak Ridge Reservation.

RESULTS AND DISCUSSION

Analytical capabilities. The probe was first tested under laboratory conditions to determine its capability for long-distance measurements. Improved signal processing and reduced electronic noise allowed detection of benzene at concentrations down to less than 1µg/mL when a 50m fiber was used. PAH can be determined even more sensitively, with lower detection limits ranging to below 1ng/mL for compounds such as anthracene. For benzene, a linear calibration of absorbance vs. concentration was obtained regardless of fiber length.

Figure 3 is a spectrum of 1µg/mL benzene spiked into uncontaminated groundwater. A combination of Fourier filtering, smoothing, and second derivative signal processing was used to produce the characteristic benzene "fingerprint" (Figure 3B) from the almost featureless transmission trace (Figure 3A). One advantage of the second derivative approach is that it tolerates reasonable levels of sample turbidity without need for a double-beam design, which would be difficult to incorporate into our probe. However, if a sample is so turbid that little or no light reaches the detector, then a measurement can not be made.

Groundwater samples. The Bear Creek Burial Grounds on the Oak Ridge Reservation has a significant groundwater contamination problem. Pollutants include chlorinated solvents and light aromatic solvents. Over a period of 5 years we have been monitoring benzene and toluene concentrations in groundwater wells at the site. Figure 4 tracks benzene concentrations in one well (GW15); the trend is similar in other wells. Although benzene levels dropped by a factor of 5 in the first 30 months, they have changed little since 1989, levelling off at a disconcerting 20µg/mL.

In order to evaluate the performance of the fiberoptic DUVAS system, we compared analytical results for GW15 water with results obtained using a laboratory DUVAS instrument and independent gas chromatographic analysis (Purge Method 5030 and GC Method 8000). The comparison is summarized in Table I.

Table I
Benzene in GW15 - Comparison of Methods

Method	Sample	Conc. (µg/mL)
In situ DUVAS	---	18.8
Ex situ DUVAS	1	17.9
	2	17.2
GC	1	24.2
	2	17.4

Because the GC method involved several sample preparation steps and relied on a one-point calibration for quantitation, it is not surprising that the greatest variation was observed in the GC data. Total GC analysis time was about 3 hours for the two samples (including the standards). In contrast, it took approximately 30 minutes to run a five-point calibration curve and the two samples using the DUVAS instruments (no sample preparation was required). Clearly, either DUVAS approach offers considerable cost savings over the GC method. Again, the laboratory DUVAS method also demonstrated better precision than the GC method. The fiberoptic DUVAS results were close to those of the laboratory instrument, clearly demonstrating that analytical performance is not compromised in the field instrument. The results also suggest, at least for this well-mixed shallow well, that samples collected with a bailer and properly contained are representative of actual groundwater concentrations. It is also notable that an exceptionally short holding time (about 20 hours) was used prior to laboratory analysis of the samples. This, of course, is not typical.

CONCLUSIONS

A fiberoptic DUVAS probe and field portable spectrometer have been fabricated and tested. The instrument provides reliable measurement of aromatic contaminants in groundwater, as demonstrated at a local groundwater well. In future work, we plan to use the device at a jet fuel spill site where current analytical results are ambiguous. Depth profiling within undisturbed wells will be conducted to help locate the fuel, believed to be in a narrow subsurface zone.

ACKNOWLEDGEMENT

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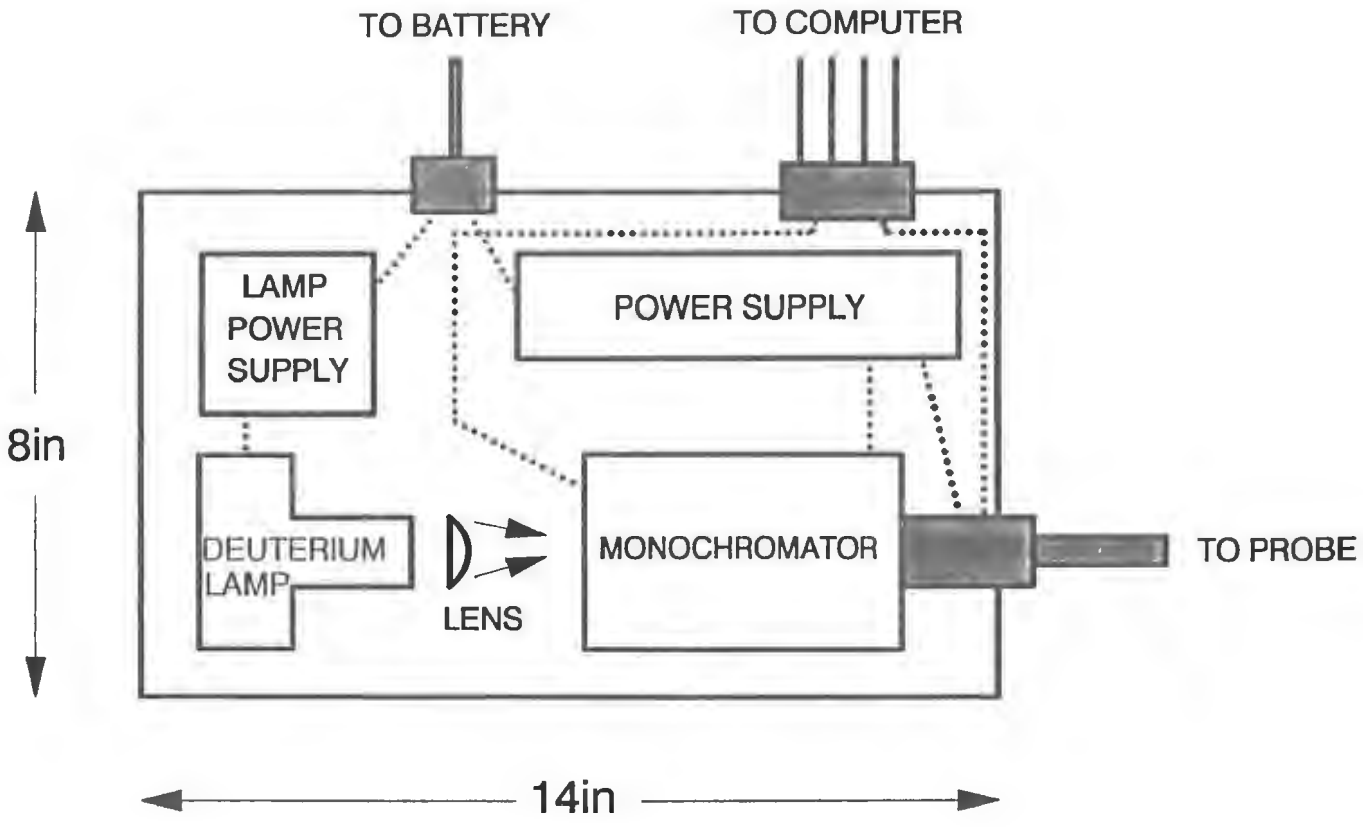

Figure 1. Portable spectrometer for use with fiberoptic DUVAS probe.

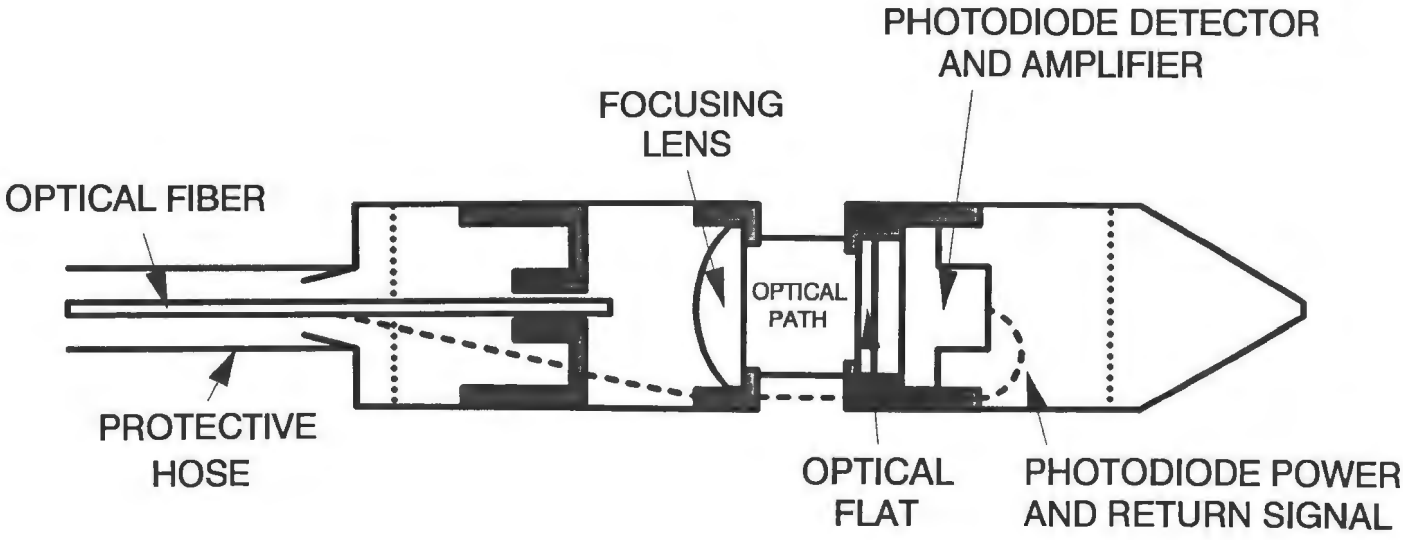

Figure 2. Cut-away view of fiberoptic DUVAS probe.

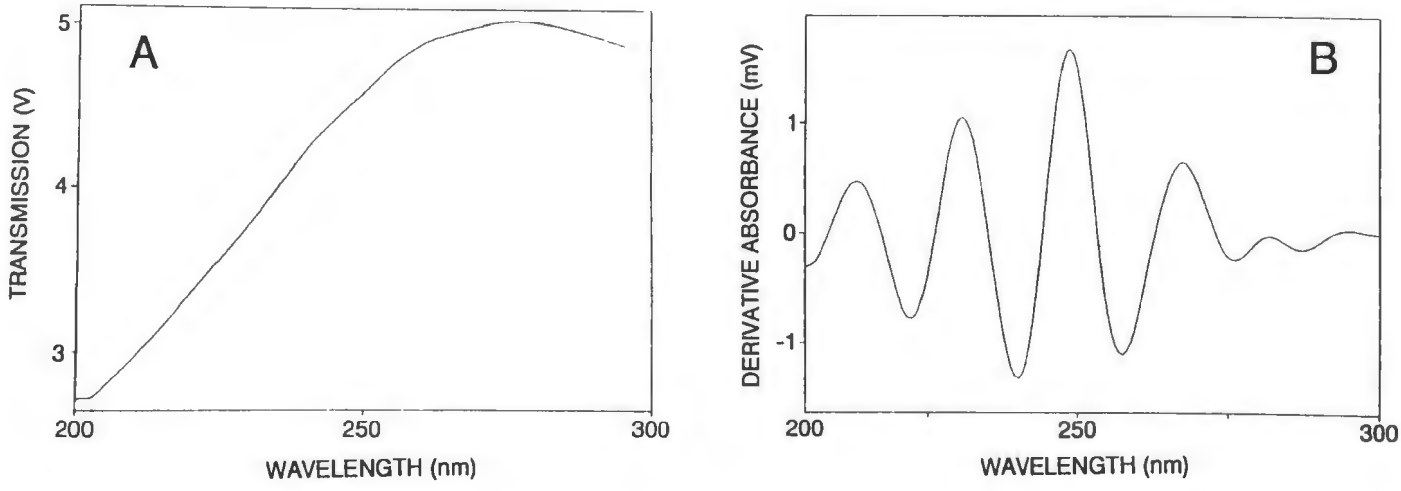

Figure 3. (A) Transmission and (B) second derivative spectra of benzene in groundwater using the fiberoptic DUVAS.

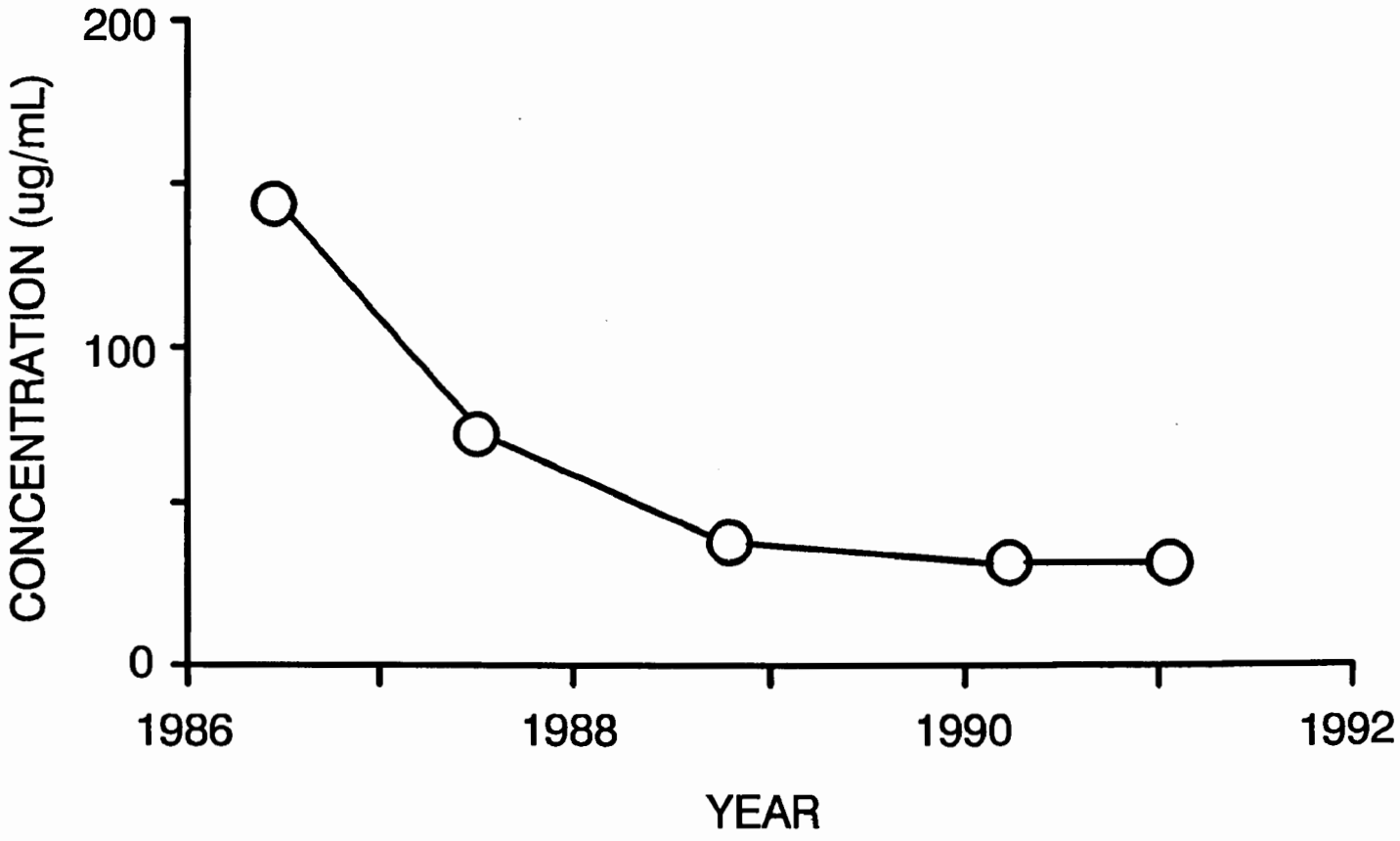

Figure 4. DUVAS monitoring of benzene in groundwater well GW15.

DEVELOPMENT OF FIELD SCREENING METHODS FOR TNT AND RDX IN SOIL AND GROUND WATER

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INTRODUCTION

One of the most serious environmental problems facing the Army is the presence of soil contaminated with residues of high explosives at sites where the munitions were formerly manufactured, stored, used or demilitarized. TNT and RDX are the two residues most commonly encountered because these explosives were extensively produced and do not rapidly decompose. Since TNT and RDX leach through the unsaturated zone with downward percolating water, they pose an immediate problem to ground water; thus contaminated soil must be treated or isolated. Though laboratory methods for analyzing munitions residues in soil and water are now available (1,2), reliable field methods are also desirable so that zones of high contamination can be located during initial surveys and the interface between clean soil and contaminated soil identified during cleanup.

DESCRIPTION OF METHODS

The procedures for the soil (3,4) and water methods are similar (Fig. 1). For the soil method about 20 g of soil is shaken with 100 mL of acetone to extract the munitions residues and the extract is filtered using a disposable syringe filter. The methods then depend on the production of colored reaction products when separate aliquots of these extracts are subjected to two simple reaction sequences (Fig. 2). For TNT, a portion of the extract is reacted with a strong base, and if TNT is present, the reddish colored Jackson-Meisenheimer anion is produced. Several other trinitroaromatics also produce reddish anions and hence are potential interferences (3,5). For RDX another portion of the extract is passed through a disposable anion exchange cartridge to remove any nitrate or nitrite. Then the extract is acidified and reacted with powdered zinc (4). This converts RDX to nitrous acid, which is detected by adding a Hach NitriVer 3 powder pillow (Fig. 2). The development of a red or orange color is indicative of the present of RDX or one of several other military explosives that are potential interferences (HMX, nitroglycerine, PETN or nitrocellulose). The intensity of the color produced can be measured with a battery-operated spectrophotometer. The absorbances at 540 nm for TNT and 507 nm for RDX are linearly related to concentration (3,4). Detection limits are about 1 µg/g for both TNT and RDX.

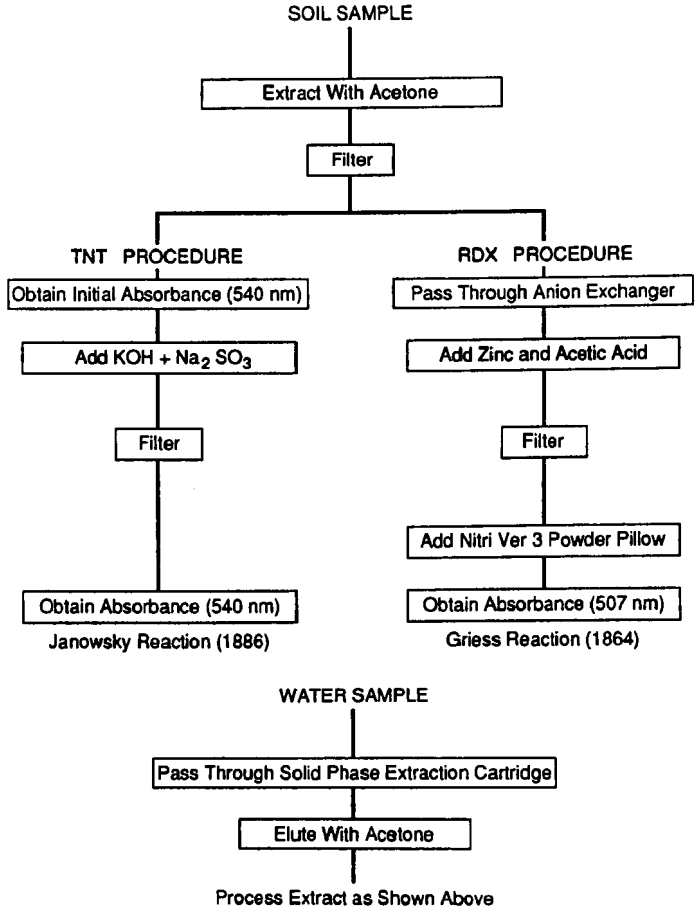

Figure 1. Flow diagram for field methods.

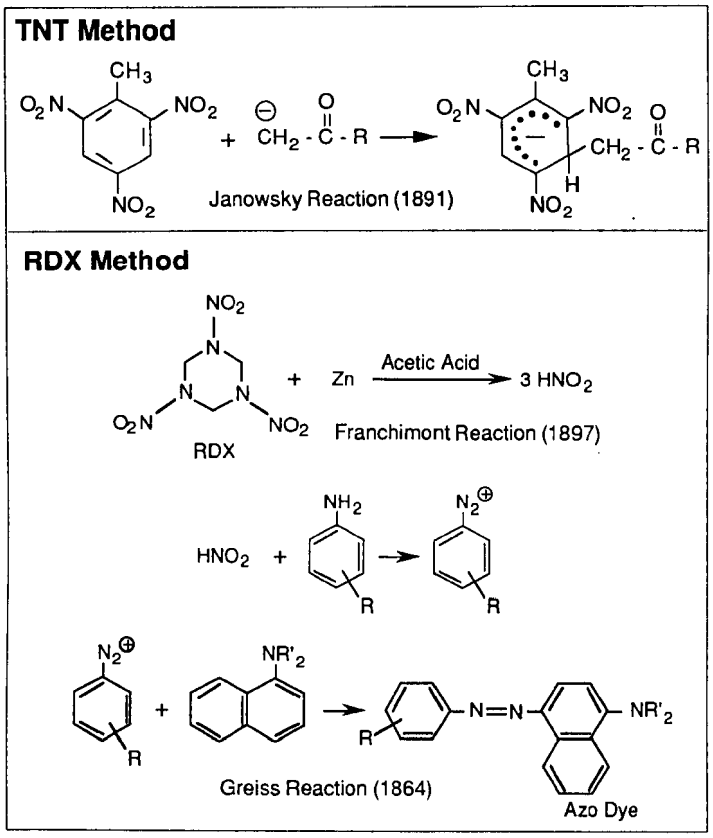

Figure 2. Reactions for TNT and RDX methods.

The method for ground water first involves preconcentration by passage of 500 mL of water through a HaySep R solid phase extraction cartridge (Fig. 1). The analytes are then desorbed with 10 mL of acetone and the acetone extract processed as described above. Detection limits in water are about 5 µg/L.

RESEARCH RESULTS

Soil Extraction

In order to determine how rapidly acetone extracts TNT and RDX from soil, a number of field-contaminated soil samples from nine different sites were extracted with acetone as described above. Soils were also extracted using the standard laboratory method and the TNT and RDX concentrations in both extracts determined by RP-HPLC (1). The results indicate that extraction with acetone is rapid and recoveries after only 3 minutes of manual shaking are not significantly different from the more rigorous laboratory method (3,4).

TNT Method

1. Absorbance spectrum. The visual absorbance spectrum of the reddish colored Jackson-Meisenheimer anion from TNT in acetone revealed absorbance maxima at 462 and 540 nm (3,5). Acetone extracts of soils with high organic matter content are yellow with absorbance maxima near 400 nm. Use of a background measurement before addition of reagents and measurement at 540 nm minimize this interference (3).

2. Effects of various concentrations of water in acetone extracts. Extraction of field soils with acetone will result in extracts containing variable concentrations of water. A test was conducted to assess the effect of variable water concentrations on the absorbance of TNT anions in acetone. Absorbance was found to be dependent on the amount of water present in the acetone. When no water is present, absorbance is low, probably as a result of poor solubility of the solid reactants (KOH and Na_2SO_3) in acetone. When relatively large amounts (>20%) of water are present, the absorbance is also low. At intermediate concentrations of water in acetone (1–17%), however, similar absorbances (±15%) are obtained. If a 20-g sample of wet soil is extracted with 100 mL of acetone, the 1–17% range of water in acetone would correspond to soil moisture contents ranging from 4–83% (on a wet weight of soil basis). This range of moisture content is typical of the large majority of surface soils.

3. Reagent contact time. Several experiments were conducted to determine if reagent contact time (1–20 min) had an effect on the absorbance obtained. TNT solutions were prepared in acetone containing 3.8% water. The results indicate that the absorbance first increases and then declines with contact time, the times being somewhat concentration dependent. One interpretation is that the rate-limiting step is dissolution of the solid reactants. If this is true, the concentration of water in the acetone is also likely to have an effect, and the optimum reagent contact time will be sample specific. The rate of decline of absorbance for excess contact time, however, is relatively slow. The reason for the reduction in absorbance for longer contact times is discussed elsewhere (3,6).

Based on these tests, a reagent contact time of three minutes was selected. For high TNT concentrations, three minutes may be insufficient to attain the maximum absorbance, but the absorbance will exceed 1.0 A.U. for this case and extracts will have to be diluted anyway. For very low TNT concentrations or solutions with less dissolved water, the measured absorbance will be reduced but the reduction will be very small. For field measurements, the ambient temperature can have an influence on the proper reagent contact time. Observation of the rate of color development for the standard will assist in selecting the most appropriate time for a given temperature.

4. Stability of filtered solutions. A test was conducted to determine if the colored anions formed from TNT were stable with time after filtration. Filtration removes the colored anions from further contact with the solid reactants and results indicate that absorbance measurements are reliable for at least two hours (3).

5. Comparison of TNT concentration estimates for soil extracts. A series of field-contaminated soils were extracted with acetone and the extracts were analyzed using the field method

Table 1. Comparison of colorimetric and RP-HPLC analysis of soil extracts.

Sample origin	TNT concentration Colorimetric Field Method (μg/g)	TNT concentration RP-HPLC method (μg/g)	TNB concentration RP-HPLC Method (μg/g)	RDX Concentration Colorimetric field method (μg/g)	RDX Concentration RP-HPLC method (μg/g)	HMX Concentration RP-HPLC method (μg/g)
Vigo Chemical Plant (Ind.)	13.5	11.7	<d*	—	—	—
Hawthorne AAP (Nev.)	5.49	4.53	<d	5.52	2.6	<d
Nebraska Ordnance Works (Neb.)	2.39	0.065	2.72	15.6	13.6	2.3
Nebraska Ordnance Works (Neb.)	592	340	157	1058	1247	115
Hastings East Indus. Park (Neb.)	85.3	67.6	2.7	—	—	—
Weldon Springs Training Area (Mo.)	4.02	0.96	0.3	—	—	—
Sangamon Ordnance Plant (Il.)	32.7	21.5	0.68	—	—	—
Weldon Springs Training Area (Mo.)	145	163	19.3	—	—	—
Hawthorne AAP (Nev.)	8.67	5.79	3.2	—	—	—
Nebraska Ordnance Works (Neb.)	146	63.5	74.1	—	—	—
Raritan Arsenal (N.J.)	85.3	71.7	<d	—	—	—
Nebraska Ordnance Works (Neb.)	0.38	0.39	<d	—	—	—
Lexington-Bluegrass Depot (Ky.)	15.0	5.90	<d	—	-	—
Chickasaw Ordnance Works (Tn.)	<d	0.21	<d	—	—	—
Hawthorne AAP (Nev.)	1.20	0.79	<d	—	—	—
Weldon Springs Training Area (Mo.)	0.33	0.075	<d	—	—	—
Hawthorne AAP (Nev.)	—	—	—	223	127	56.0
Raritan Arsenal (N.J.)	—	—	—	10.5	4.38	*t*
Nebraska Ordnance works (Neb.)	—	—	—	2.66	3.65	*t*
Nebraska Ordnance works (Neb.)	—	—	—	1104	1143	105
Nebraska Ordnance works (Neb.)	—	—	—	10.0	19.0	3.45
Nebraska Ordnance works (Neb.)	—	—	—	129	104	12.0
Nebraska Ordnance works (Neb.)	—	—	—	20.5	59.9	13.0
Nebraska Ordnance works (Neb.)	—	—	—	1.74	<d	<d

* <d = concentration less than detection limit.

and the standard laboratory procedure (1,3). Results are shown in Table 1.

The results using the field method were correlated against both the TNT estimate by HPLC and the sum of TNT and TNB. The concentration estimates for TNT from the field method and the sum of TNT and TNB by HPLC were not significantly different (3). Thus it appears that the field results are best represented as the sum of TNT plus TNB.

RDX Method

1. Removal of nitrate and nitrite using ion exchange. Soil samples containing nitrite or nitrate would give a false positive if the nitrite and nitrate are not removed prior to reaction of RDX with zinc. This is accomplished by passing the extract through a disposable 3-mL strong anion exchanger (Supelco Alumina A). Experiments indicate that over 98% of the nitrate in a 9.8-mg/L test solution was removed using this procedure (4).

2. Optimization of amounts of zinc, acetic acid and contact time on the conversion of RDX to nitrous acid. A series of experiments were conducted to determine the effects of these variables on the conversion of RDX to nitrous acid (Fig. 2). All three factors were found to be significant (4). Optimum results were obtained when 0.3 g of zinc dust, 0.5 mL of glacial acetic acid and a 15-s reaction time were used.

3. *Effects of variable concentrations of water in acetone extracts.* Acetone extracts of soil will contain variable concentrations of water and an experiment was conducted to determine how this affects the production of the azo dye (Fig. 2). The results indicate that the measured absorbance is a function of the water content with a maximum absorbance for a soil containing 25% water (wet weight basis). Only a small decline was found for higher water concentrations. If field soils appear very dry, we recommend addition of a small volume (~ 3 mL) of distilled water to the extract.

4. Background absorbance from blank soils. Acetone extracts of high humus soil are yellow in color. Once acidified, reacted with zinc and filtered, the yellow color is removed, resulting in a solution with no measurable background absorbance at 507 nm.

5. Comparison of RDX concentration estimates from field procedure with the standard laboratory method. Field-contaminated soils from a variety of Army sites were used to compare the RDX concentration estimated by the field method with those obtained by RP-HPLC analysis (4). The results using the field method were correlated against those obtained

by the lab method for both RDX alone and the sum of RDX and HMX (Table 1). The estimates of RDX concentration obtained by the field procedure were not significantly different from those obtained by the HPLC procedure for RDX alone or for the sum of RDX and HMX.

Field Testing

The soil methods have been field tested at Umatilla, Oregon, Newport, Indiana, Camp Shelby, Michigan, and Eagle River Flats, Alaska. The methods were found to be usable under field conditions and the estimates of analyte concentrations correlate well with estimates obtained by the standard laboratory procedures (3,4).

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QUANTIFICATION OF PESTICIDES ON SOILS BY THERMAL EXTRACTION-GC/MS

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Introduction

Site investigations and cleanup activities often require the rapid analyses of soil samples for semivolatile environmental toxicants. The widespread use of pesticides makes the development of rapid field-deployable quantification methods for this class of compounds particularly desirable. Recently, thermal extraction techniques have been investigated as a rapid alternative to classical soil analyses by solvent extraction-GC/MS. Samples are heated according to a preprogrammed temperature profile and evolvig volatiles analyzed by in-line GCMS methods. Thus, tedious wet extraction procedures are completely eliminated. However, the quantification of toxicants by this procedure poses problems. Thermal extraction efficiencies for toxicants do not necessarily reflect solvent extraction efficiencies. Indeed, they are typically lower and depend on the physical and chemical properties of matrices (soils) as well as those of analytes. Furthermore, toxicant extraction and analysis are combined into one procedural step and cannot be monitored seperately using internal standards and surrogate standards. Isotopic dilution mass spectroscopy, on the other hand, postulates the free exchange of labeled and non-labeled analyte molecules in a sample, an assumption that is generally correct for solutions, but questionable for solid samples. Thus, a comparison study of thermal and wet extraction procedures was undertaken using pesticide--containing soil standards with pesticide contents ranging from 1 ppm to 1000 ppm. Analytical results obtained with a thermal extraction system were compared to those obtained by Soxhlet extraction and subsequent analysis using a conventional gas chromatograph coupled to an ion trap mass spectrometer.

Instrumentation

Thermal extractions were performed on a Pyran Thermal Chromatograph coupled tob a Finnigan ion trap mass spectrometer. The system features an all-quartz analytical flow path to minimize catalytic sample decomposition and is fully automated to eliminate operator-induced variations. Soil samples were weighed into porous quartz crucibles and heated in the pyrocell compartment of the analyzer according to a preprogrammed temperature profile. All volatile components released during the heating phase were flushed through a splitter assembly by helium carrier gas and subsequently cryo-condensed onto a fused silica GC column. Analyte identification/quantification followed conventional GC/MS procedures. The analyte mixture was separated on a fused silica capillary column and analytes were identified and quantified by an in-line Finnigan ion trap mass spectrometer. For this study, the system was equipped with a 0.32 mm x 15 m x 2.5 µm DB-5 column.

Soil extracts were analyzed on a Varian 3500 Series gas chromatograph using the same type of column as before. The identical Finnigan ion trap mass spectrometer was used for analyte identification and quantification (by disconnecting-reconnecting the transfer line).

Experimental

A total of 18 soil samples was prepared and analyzed in triplicate by both methods: six samples each of Bastrop, Padena, and Weswood soils contaminated with 1000, 500, 100, 10, 5, and 1 ppm pesticides and spiked with two surrogate standards. Both methods were optimized independently; different column temperature

programming was used along with different tuning parameters for the mass spectrometer. Quantification for the thermal extraction system was achieved independently by using the two surrogate standards added to the soil samples during their preparation and by spiking isotopically labeled pesticide analogs onto the soil samples. Quantification for GC/MS was achieved with surrogate and internal standards in the usual manner. All quantifications were based on peak area ratios of analytes to standards for selected ion chomatograms. The following analytes were chosen: α-hexachlorocyclohexane, γ-hexachlorocyclohexane, aldrin, endosulfan, bis-(chlorophenyl)trichloroethane (DDT), and bis-(chlorophenyl)dichloroethane (DDE). For internal standards, 3,4,5,6-tetrachloro-2-xylene , 9-bromophenanthrene, 2-bromofluorene, and 4-bromobiphenyl. For isotopic dilution quantification, hexachlorocyclohexanes-13C6, adrin-13C5, endosulfan-D4, DDE-D8, and DDT-D8. Three soils were chosen for this series of experiments, Weswood soil, a sandy, organic-lean soil, Padena soil, organic-lean with high clay content, and Bastrop soil, a clay rich topsoil. The variation of pesticide contents in the samples over three orders of magnitude necessitated the use of variable split ratios between 1:10 and 1:40 and variable sample weights between 10 and 200 mg. Isotopic standards were spiked as solutions in dichloromethane directly onto the soil samples immediately before thermal extraction. The thermal extraction system was calibrated by determining the peak area ratios for equal concentrations of analytes and standards as average over four runs. Quantifications for the conventional GC system were based on the average of three six point calibration curves (50 - 550 ng pesticides injected). Mass spectra were acquired in full scan mode, 64-400 amu.

Conclusions

The Pyran system was shown to be capable of providing rapid (35 min) analyses of different soils for most of the pesticides included in this study. Virtually no background signal from organic materials contained in the soils was observed and clean total ion chromatograms were obtained. Problems with pesticide decomposition were encountered for dieldrin, endosulfan, DDT, and to a lesser extent for DDD. While DDT and DDD underwent dehydrochlorination to alkenes, endosulfan suffered loss of sulfur dioxide with subsequent ring closure to the corresponding isobenzofuran derivative, which was thermally extractable and quantifiable. Dieldrin was not thermally extractable; most likely due to its conversion to the corresponding diol by traces of water contained in the soils. DDE formed by dehydrochlorination of DDT is indistighuishable from DDE contained in the sample. As a result, recovery values found for DDE in the presence of DDT can be regarded as artificially high. Comparison of recoveries and percent standard deviations of recovery based on isotopic dilution quantification and internal standard quantification allowed us to distinguish between deviation of found from actual pesticide content due to variations of the thermal extraction process in the pyrocell (e.g. uneven packing of the soils in the sample crucibles, variable helium flow through the soils etc., which will effect pesticides and internal standards in the same manner, since both are uniformly distributed throughout the soils) and variations due to differences in the thermal desorption behavior for different chemicals (wich will not show for pesticides and their chemically identical isotopic analogs). The results showed that no free exchange exists of adsorbed pesticides and their isotopic analogs spiked onto the soils before analysis. Calculated recoveries based on internal standard quantification generally decreased as pesticide contamination decreased, as shown for Weswood soil samples. However, this did not hold for all pesticides: poor thermal extraction of standards in combination with high thermal extraction of analytes may result in calculated recoveries in excess of 100 percent. A pronounced dependence of extraction efficiencies on the type of soil analyzed was demonstrated. Soils with high clay content will generally allow lower recoveries than sandy soils for internal standard quantification.

Conventional solvent extraction was clearly less dependent on the chemical nature of the extracted analytes and their concentrations in the soils than thermal extraction. These results etablish thermal extraction as analytically useful tool for the rapid semiquantitative, in some cases quantitative, analysis of soil samples for semivolatile pesticides; however, with somewhat lower analyte recoveries and higher deviations than those obtained in conventional procedures.

A PORTABLE GAS CHROMATOGRAPH WITH AN ARGON IONIZATION DETECTOR FOR THE FIELD ANALYSIS OF VOLATILE ORGANICS

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ABSTRACT

The Environmental Response Team of the US EPA (ERT-EPA) has been deploying field portable gas chromatographs (CGs) for the characterization of Superfund sites and landfill throughout the country. Portable GCs allow rapid determination of volatile organic compounds (VOCs) and can both identify and quantify these compounds. Several researchers as well as the ERT have used data generated via portable GCs to estimate and model contamination plumes, fugitive emissions, and to direct remediation activities (1,2).

The Sentex portable GC, equipped with a high energy ionization detector, has been shown to be invaluable for determining the levels of VOCs at several EPA superfund sites.

The argon ionization detector (AID) has a high ionization energy and will yield a response form a wide variety of compounds whose ionization potential is at, or below, 11.7 electron volts (11.7 eV). These will include many aromatic, chlorinated alkanes, chlorinated alkenes, and nitrogen and sulfur containing compounds. Of particular interest are the halogenated alkanes which do not respond well using photoionization detector based portable GCs (3). The same AID can be easily converted to a Electron Capture Detector (ECD). The ECD is very responsive to halogenated compounds. The ECD works best using nitrogen instead of argon as the carrier gas. Carrier gases can be easily switched in the field to take advantage of the dual detector capabilities of the Sentex Scentograph GC. For general screening on a wide variety of compounds the ERT has used the Sentex GC in the AID mode for most of the Superfund sites investigated.

INTRODUCTION

The Sentex Sensing Technologies, Inc. (Ridgefield, N.J.) model Scentograph is a totally portable GC operating with a 11.7 Ev AID. Internal cylinders of argon carrier gas and calibration gas, as well as a 12 volt DC battery pack allows the Sentex GC to operate without external support from six to fourteen hours, depending on flow and oven temperature. All operations are controlled by the portable lap top computer (PC) interfaced with the GC. The PC permits the Scentograph to be automated and therefore can be set up to run unattended. An optional communications software package and modem can be used to control and operate the GC remotely via phone links. The PC will also archive all raw and processed data as well as initial operating parameters. The Sentex Scentograph GC software can identify a total of 16 compounds stored in the current operating calibration library. A one point, one for each of the 16 possible compounds, calibration is used to quantify the identified compounds. A post analysis software routine allows sample run to be compared to additional libraries, thereby allowing identification / quantification against hundreds of compounds.

THE SENTEX GAS CHROMATOGRAPH

The GC system itself consists of three major components: the programmable sampling pump and adsorption trap, the temperature programmable gc column and detector block, and the PC data system.

The programmable sampling system and trap consists of an internal sampling pump which can be programmed via the PC to draw a sample for various periods of time. Pump duration ranges from 1 to 999 seconds at a typical flow rate of 100 cubic centimeters per minute. The sample is drawn onto an adsorption trap of either Tenax or Carbosieve where the sample components are concentration on the surface of the trapping material. The trap is then heated from 1 to 4 seconds and backflushed to thermally desorb the concentrated sample components off the adsorption trap and onto the GC separations column. Various trapping materials besides Tenax and Carbosieve are available.

The temperature programmable block provides a stable heated zone, from 30 ^{0} C to 140 ^{0} C for both the GC analytical separations column and the GC detector. The

Sentex block heater yields very stable temperatures, reducing peak retention time drift present in other field portable GCs. Since the heater is of a high mass block design cool down times between run cycle can be prohibitively long. The temperature ramping routines available in the software have been found to be impractical for most of the rapid screening needs of the ERT. Consequently, all GC field operations, to date, have used isothermal oven temperatures, typically 30 to 80 ^{0} C. The GC oven is very small at 3" high, 3" wide, and 6" long. This constraint has made only packed GC columns usable. Recent modifications of the oven dimensions has allowed for the use of megabore capillary columns. At present capillary columns usable with the Sentex GC are only available through Sentex.

The dual AID / ECD detector system will respond to most compounds of environmental interest in either one mode or the other. The AID has been used predominately because it detects both aromatic and chlorinated hydrocarbons down to the low parts-per-billion, volume (ppbv) range. The AID has been found to be very stable and equilibrates within one half hour after initial setup. A grossly contaminated AID can be easily reconditioned by baking out the system at an elevated temperature for a short period of time. Field experience with the GC configured in the ECD mode has found the detector to take several hours to stabilize. The ECD is also more sensitive than the AID to the compound it responses to. It can be more easily contaminated and may take several hours at an elevated temperature to recondition a contaminated ECD. Both the AID and the ECD have a linear dynamic range of only 2 to 3 orders of magnitude and be easily saturated at the higher parts-per-million, volume (ppmv) concentration range. The dual detector system operates best at the 10 to 1000 ppbv range. For most of the field screening needs of the ERT this range is suitable. The AID / ECD detector uses a radioactive tritium foil (H_3) as a beta energy source. A modified NRC license available through Sentex is required. No wipe tests are required and air shipping is not a problem since the activity of the foil is below DOT restrictions.

CONCLUSION

The Sentex Scentograph gas chromatograph has been used for the analysis of volatile organic compounds at various EPA Superfunds by the US EPA Environmental Response Team. Detection limits have ranged from 5 to 50 ppbv for various aromatic and chlorinated compounds, when using the argon ionization detector. Screening applications include ambient air analysis, indoor air, stack emissions, and soil gas surveys. A wide variety of aromatic and halogenated hydrocarbons have been investigated (Table 1). The Sentex GC has yielded data that compared well to other conformational analysis, such as GC / MS (Table 2). In several cases the Sentex GC was the only field portable GC that could detect chlorinated alkanes, in the field, at the low ppbv range.

At present only vapor phase sample matrices have been sampled by the ERT. Optional equipment can be used to dynamically purge volatiles from soil and water matrices for subsequent GC analysis. Initial evaluation of this optional "purge and trap" apparatus has shown detection limits for benzene, toluene and total xylenes in soils to be in the low to mid ppbv range, depending on soil matrix and GC operating conditions.

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Table 1
COMPOUNDS DETECTED VIA SENTEX AID IN THE FIELD BY THE US EPA / ERT

Benzene
Toluene
o - Xylene
m,p - Xylene
Methyl chloride
Ethyl chloride
Vinyl chloride
Methylene chloride
1,1 Dichloroethane
1,2 Dichloroethane
1,1 Dichloroethene
trans 1,2 Dichloroethene
1,1,1 trichloroethane
Bis 2 chloroethyl ether
Trichloroethylene
Tetrachloroethylene.

Table 2
COMPARISION OF FIELD DATA FOR VINYL CHLORIDE SOIL GAS SAMPLES

SENTEX GC	GC / MS (tube)
1.15 ppmv	0.54 ppmv
1.01 ppmv	0.82 ppmv
2.45 ppmv	3.27 ppmv
ND(<0.005)	ND(<0.01)
0.20 ppmv	0.42 ppmv
0.18 ppmv	0.79 ppmv
ND(<0.005)	ND(<0.01)
0.82 ppmv	1.38 ppmv
7.43 ppmv	4.0 ppmv
0.006 ppmv	ND(<0.01)

SEAMIST -- A Technique for Rapid and Effective Screening of Contaminated Waste Sites

Carl Keller

Bill Lowry

The SEAMIST system was developed to allow the insertion and removal of absorbent collectors in long drillholes of marginal stability. However, the technique has such attractive attributes that its use is being extended to many other aspects of instrumentation and sampling from drillholes. The name SEAMIST is an acronym for Science and Engineering Associates Membrane Instrumentation and Sampling Technique. The technique is simple though not obvious.

The principle feature is a hole liner made of a tubular fabric or film called an "impermeable membrane" (Figure 1).

The membrane lines the drillhole and is pressed against the hole wall by a modest internal pressure (1-3 psi). The bottom of the membrane is gathered together (inside out) and tied with a cord, "the tether", which extends up the center of the hole to a reel, in a canister, at the surface. The top of the membrane is attached to a short pipe extending from the canister. The function is simply that turning the reel winds up the tether and inverts the membrane, peeling it outside in from the hole wall. The entire membrane can be wound onto the reel, inside out. Reversing the reel allows the membrane to reverse its motion, extending down the hole under pressure and everting as it descends to re-line the hole.

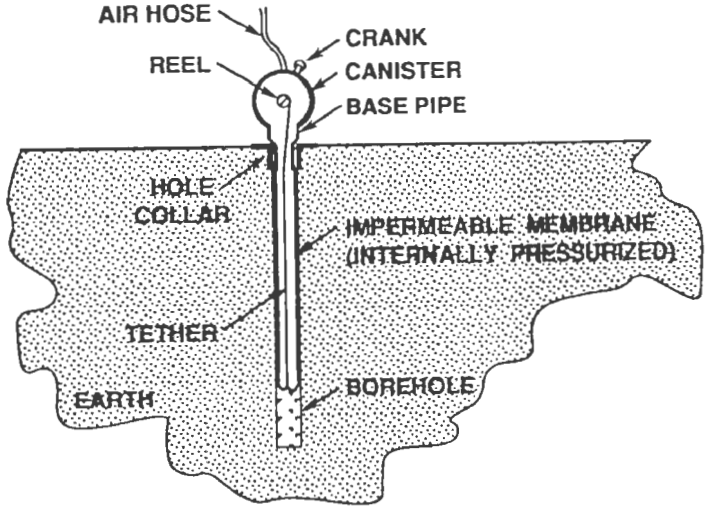

Figure 1. Components of the SEAMIST system.

As the everting membrane descends, it provides support of the hole wall. It also lines the hole like a continuous packer and prevents flow into the hole. The primary utility of that function is that the membrane can carry instruments into the hole by their being fastened to the membrane (e.g., thermo-couple, absorbent pads, fiber optics, tubing, electrodes, etc...) or, the larger instruments can be carried down on the tether (e.g., gamma logs, neutron logs, resistance logs or a video camera (using a clear membrane). The interior of the membrane is isolated from the exterior, except where ports and tubing allow access to the geologic medium.

Since the membrane supports the hole wall, a casing and backfill is not required in many holes. Therefore, one has access to the entire hole wall for collection of water or gas samples or for in situ measurements while the membrane is supporting the hole wall and sealing it against flow. The membrane insertion into a drillhole can proceed as quickly as 20 ft/min or faster. Since the insertion supports the hole and simultaneously carries instruments into place, one can actually case and instrument a 50 ft hole in under five minutes.

For long term installations, the interior of the membrane can be filled with water or sand (even "dirty sand", since it doesn't contact the medium to be measured). Later, the sand or water can be flushed or blown out of the hole, and the membrane and instrumentation can be removed or replaced.

The obvious utility for field screening purposes is that the SEAMIST is fast, relatively cheap, and removable. What is also an advantage is that the membrane nestles around each instrument or sampling port forming a membrane blister on the hole wall. The interior of that blister, and the associated instrument or port, is isolated from other such blisters at other elevations in the hole. In fact, one side of the hole is isolated from the other side. In principle, a reactive covering on the membrane can be emplaced and pressed against the entire hole wall to provide a two-dimensional map (azimuth and elevation) of contaminants in the wall material.

The instrument array shown in Figure 2 was designed for monitoring of a steam flood experiment yet in the planning stage. It is an example of instruments that can be emplaced by SEAMIST. The results are yet to come. The concept is young and in need of field testing.

Current research of this concept is funded by DOE (Argonne National Laboratory) for vadose measurements and by DOE (Sandia National Laboratory) for geothermal drilling applications. Since the SEAMIST system functions equally well horizontally and in constricted and crooked holes, that is probably its best application yet to be developed and tested.

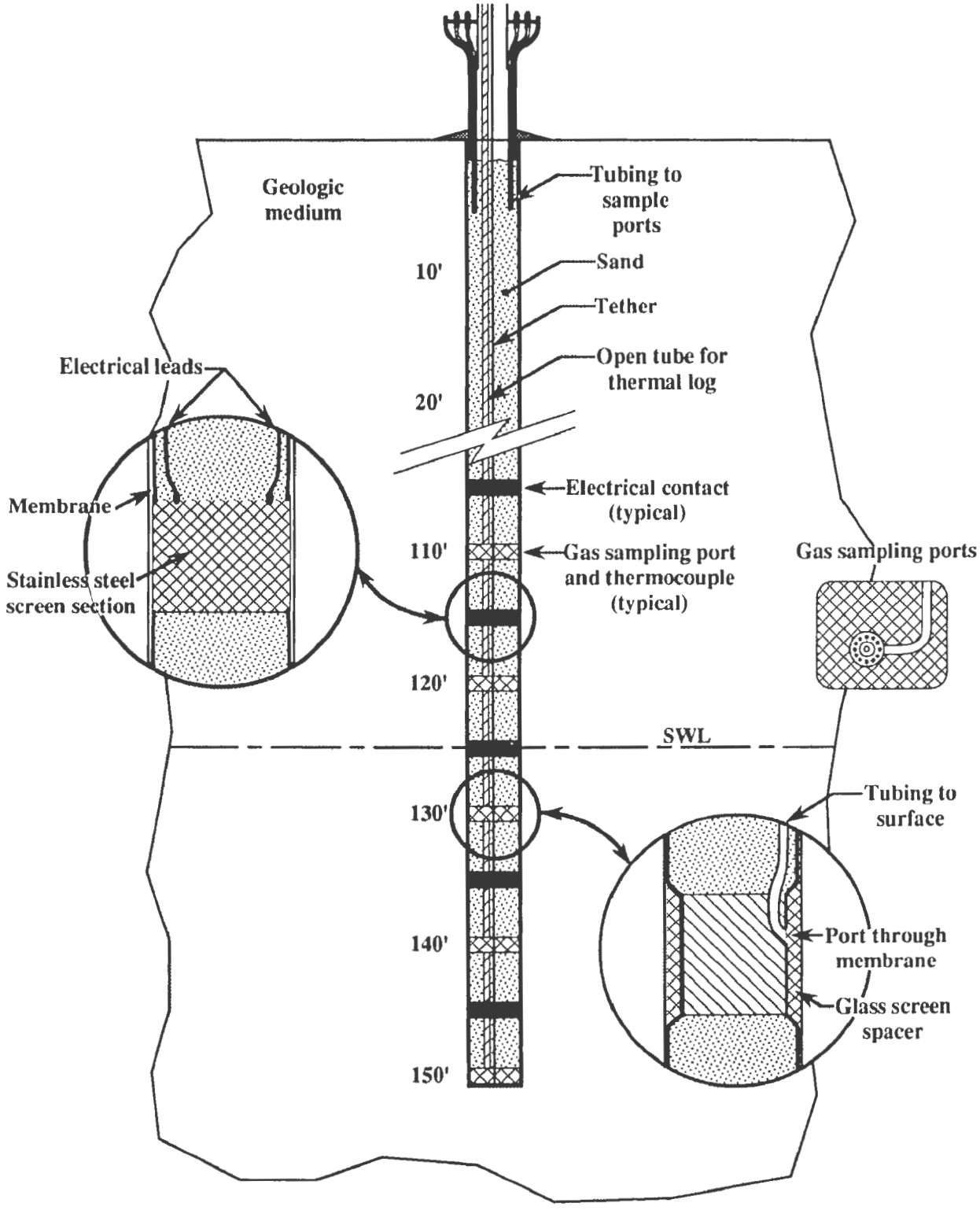

Figure 2. Membrane lined monitoring hole design for steam flow experiment.

PORTABLE GAS CHROMATOGRAPH FIELD MONITORING OF PCB LEVELS IN SOIL AT THE ELZA GATE PROPERTY

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ABSTRACT

Bechtel National, Inc. (BNI) conducted radiological and chemical surveys of the Elza Gate property in Oak Ridge, Tennessee, as part of the U.S. Department of Energy (DOE) Formerly Utilized Sites Remedial Action Program (FUSRAP).

Based on site history and preliminary characterizations at the site, it was determined that polychlorinated biphenyls (PCBs) were present across the site. Because PCB analysis with the use of a portable gas chromatograph (GC) is relatively fast and inexpensive, soil sample analysis results could be made available to help direct the field sampling program.

This paper provides a discussion of the manner in which PCBs were monitored in the field during ongoing sampling, the cost of these analyses, and a comparison of portable GC screening results with Contract Laboratory Program (CLP) laboratory results (1).

SITE DESCRIPTION AND HISTORY

The 8.1-ha (20-acre) Elza Gate property is located in the eastern portion of the city of Oak Ridge, Tennessee, now known as Melton Lake Industrial Park. Access to the site is off Melton Lake Drive, near its intersection with the Oak Ridge Turnpike (Figure 1).

In the early 1940s, the site was developed by the Manhattan Engineer District (MED) as a storage area for pitchblende (a high-grade uranium ore from Africa) and ore processing residues. Five warehouses were constructed on the site, three of which were used to store radioactive materials. The Atomic Energy Commission (AEC) used the site until the early 1970s, when it was vacated. After a radiological survey and appropriate decontamination activities were conducted in 1972, the site was deemed acceptable for use with no radiological restrictions (2). At that time, title to the property was transferred to the General Services Administration and then to the City of Oak Ridge. The property was subsequently sold to Jet Air, Inc., and used for the operation of a fabrication and metal plating facility.

In 1987, at the request of the Tennessee Department of Health and Environment, Oak Ridge Associated Universities (ORAU) conducted a survey at the site because of the possibility of contamination from the metal plating facility. This survey confirmed the presence of heavy metals and PCBs at the site.

In October 1988, a preliminary radiological survey of the site was conducted by Oak Ridge National Laboratory (ORNL) for DOE. The survey indicated that residual radioactivity exceeded the criteria for declaring a site eligible for remediation under FUSRAP. As a result, on November 30, 1988, the entire Melton Lake Industrial Park was designated a FUSRAP site (3).

In 1988, ownership of the property was transferred to MECO, a development company. The site is presently under further development for use as an industrial park. In addition to the five MED warehouses previously mentioned, smaller structures also may have been on site. None of the original structures remain, but the concrete pads on which the warehouses were built are still in place.

One building currently on the property was erected on an existent concrete pad. A second pad adjacent to this building is used as a vehicle parking lot and material storage

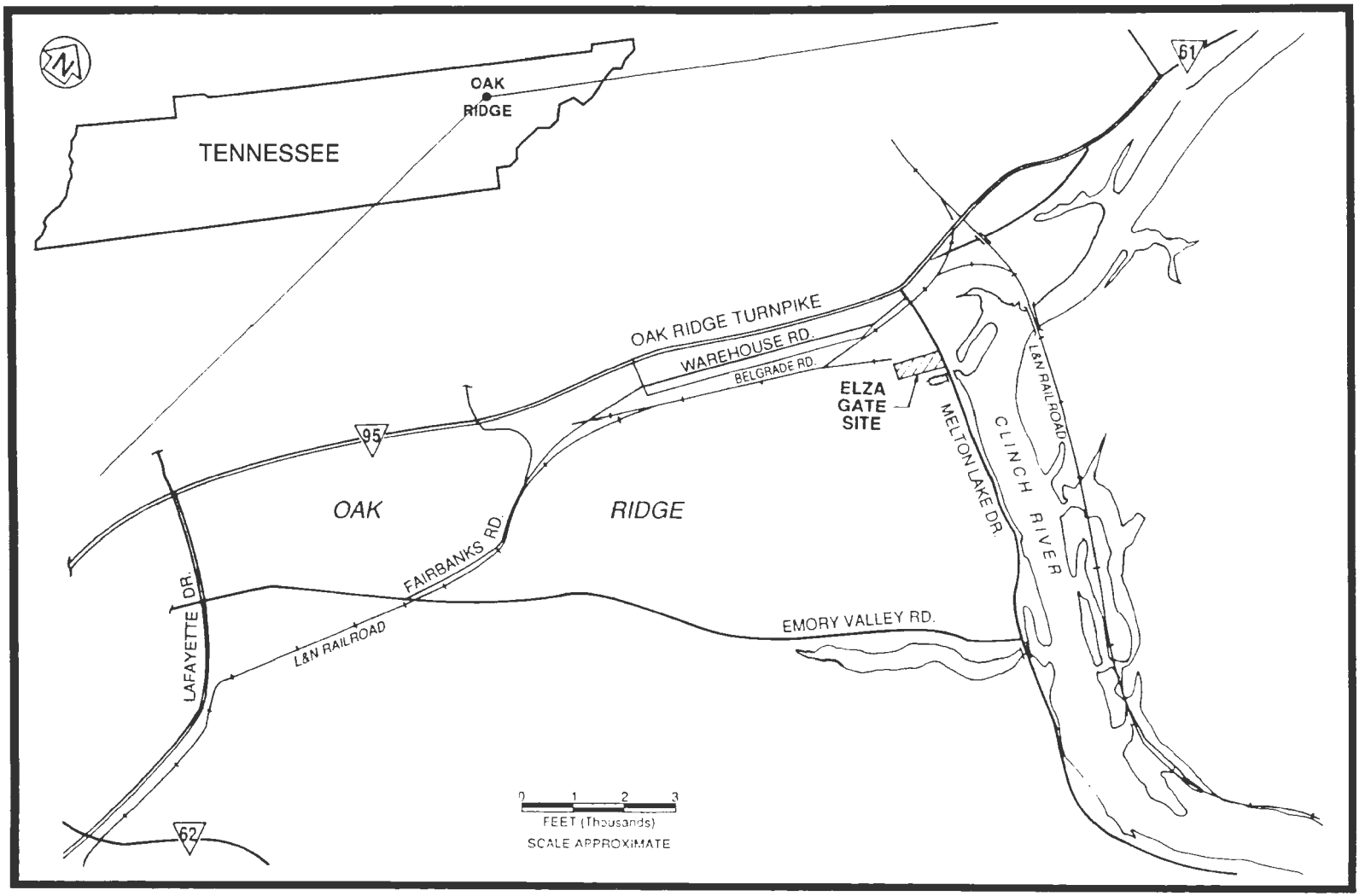

Figure 1 Location of the Elza Gate Site

pad. The site has undergone considerable modification since 1987, and the building is currently occupied by a manufacturer of storage containers. Modification of the property is expected to continue as the parcels are sold or leased.

SAMPLING LOCATIONS

Because PCBs were previously detected at low concentrations over the site area, all samples collected during the chemical characterization effort were analyzed for PCBs. Both systematic and biased locations were sampled. Systematic samples were collected from the corners and center of each 61-m (200-ft) grid block. Using the data from previous characterizations and information from the property history, biased sampling locations were selected. A hand held auger was used to collect three samples from each location for analysis. The samples were collected at 0.3-m (1-ft) intervals to a depth of 1 m (3 ft).

CHARACTERIZATION METHODOLOGY

Since conventional characterization using CLP laboratory protocols is costly and turnaround time required for CLP analyses is approximately 30 days, on-site screening of PCBs in soil samples using a portable GC was considered useful in making real-time decisions on the rationale for additional sampling locations during the ongoing chemical characterization.

A Hewlett-Packard 5890 portable GC equipped with a capillary column and an electron capture detector for monitoring PCB levels in soil was used on FUSRAP during the Elza Gate site characterization. The ability to detect PCBs on site while sampling is taking place is one of the key advantages of this field screening method (4) which was refined by Twomey, Turner, and Murray (5). The need for additional samples can be evaluated using this strategy while the sampling crew is still in the field. Another advantage is that this method permits comparison between the reproducibility of field data and that of CLP data because similar equipment and techniques are used.

The extraction procedure used for the Modified Spittler Method consists of placing 2 g of soil in a test tube and adding 0.5 ml water, 2.0 ml methanol, and 2.5 ml hexane (6). The sample is then vigorously shaken, and aqueous and organic phases are allowed to form layers. The hexane layer containing PCBs is withdrawn from the top of the mixture and injected into the GC.

While this extraction method is less efficient than the CLP prescribed procedure, it is very rapid and cost-effective. Using commonly available laboratory equipment, one analyst can easily extract 20 samples in less than 2 hr. The cost of analysis using this screening method (including sample preparation, analysis, and data evaluation) is between $50 and $100, compared to $300 for the equivalent CLP analysis. The savings in cost, coupled with the time savings (25 min for the field screen vs. 30 days for the CLP analysis), warrant the consideration of this screening method to complement CLP analyses.

The results BNI obtained using this method correlate well with CLP laboratory results from the same samples (Figure 2). The field screening results, while generally lower than values obtained by the CLP laboratory, give an excellent indication of locations where PCB concentrations are elevated and where additional samples should be collected for laboratory analyses. A comparison of Modified Spittler and CLP predictions of PCBs in soils is shown in Figure 3.

Major reasons for variability in results include the following:

- Since percent moisture was not determined for the screening samples, these results were not calculated on a dry weight basis.
- Even with the best efforts to homogenize the sample, concentrations of PCBs vary within the same sample.
- The extraction technique used with the screening method is less efficient than the CLP procedure in extracting PCBs from the soil matrix.

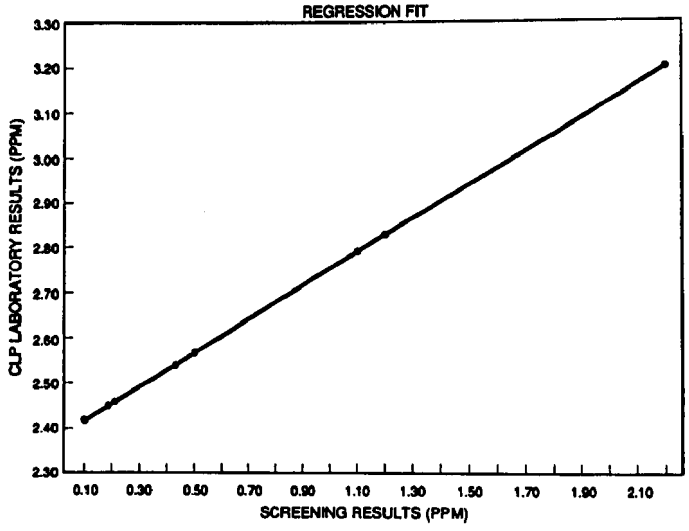

Figure 2 Correlation between Screening Results and CLP Laboratory Data for PCBs at the Elza Gate Property

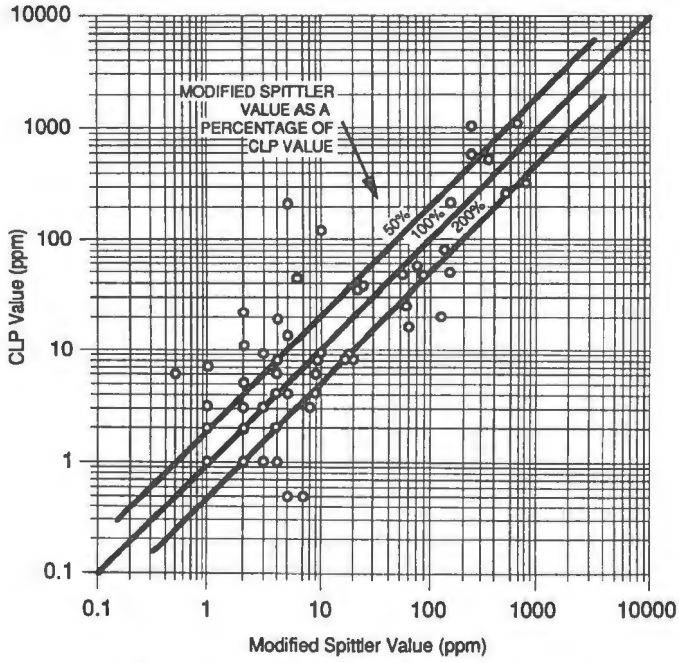

Figure 3 Comparison of Modified Spittler and CLP Predictions of PCBs in Soils and Sediments (Adapted From Fowler and Bennett 1987)

CONCLUSIONS

The Modified Spittler Method (5), originally developed by ABB Environmental Services chemists, has been refined to determine PCB concentrations in soil that represent excellent comparisons with results generated by CLP procedures.

The Modified Spittler Method has proved to be a fast, accurate, and cost-effective procedure for determining PCB concentrations in soil at the Elza Gate FUSRAP site. It permits collection and analysis of a larger number of samples during a field characterization and provides direction during the sampling effort, indicating to field personnel where additional soil samples should be collected for analysis. The result is a more thorough characterization requiring fewer field sampling efforts.

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Real Time Monitoring of the Flue of a Chemical Demilitarization Incinerator

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Introduction

Public Law 99-145 directs the Secretary of Defense to destroy the nations stockpile of lethal unitary chemical warfare agents and munitions stored throughout the continental United States by September 30, 1994 [1]. The U.S.Army has selected incineration as the best available technology for destroying chemical warfare agents [2]. The National Research Council has endorsed incineration as the method of choice for chemical agent destruction. Maximum protection of the environment, the general public and the personnel involved in this destruction is required. For this reason very stringent requirements are imposed for the maximum allowable concentration of the chemical warfare agents in the effluent of these incinerators. The allowable stack concentrations (ASC) for the two nerve agents, GB and VX, are 0.0003 mg/m^3, while the ASC for the blister agent HD is 0.003 mg/m^3. Moreover analytical instrumentation is needed that can detect these levels in real or quasi real time.

Normal analytical techniques employed to detect such low concentrations use preconcentration and separation techniques and are very time consuming [3]. The extreme sensitivity of atmospheric pressure ionization makes it a suitable technique to detect low concentrations of contaminants in air [4]. Moreover, the ability of atmospheric pressure ionizers to handle very large sample flow rates makes it possible to use this technique for real time detection. The specificity achieved by tandem mass spectrometry makes a system based on atmospheric pressure ionization tandem mass spectrometer (API-MS/MS) very attractive for monitoring low concentrations of pollutants in complex matrices like stack effluents. We report here the use of a commercially available API-MS/MS system to monitor for chemical warfare agents GB and VX, at concentrations near the ASC levels, in the flue of a demilitarization incinerators.

The API-MS/MS system was tested on the flue of a demilitarization incinerator at the Chemical Agent Munitions Disposal System (CAMDS) at Tooele Army Depot in Tooele, Utah. The incinerator was the liquid incinerator (LIC) which is used to burn the liquid chemical warfare agents themselves.

Experimental

The system used was a commercially available EXTREL Automatic Stack Sampling Mass Spectrometer (ASSMS). This system uses an atmospheric pressure ionization source coupled to a triple quadrupole mass spectrometer. This system is described elsewhere in detail [5], so only a brief overview will be presented here. A corona discharge operating at atmospheric pressure, with a discharge current of about 5 μA, is used as a source of primary ions. A low pressure region, operating at a pressure of about 1 torr is used to break up the weakly bound water clusters which are always present in a discharge operating at high pressures. The declustered ions are injected into the entrance of a triple quadrupole mass spectrometer. The mass spectrometer has three quadrupoles each with 3/4" round and 6" long cylindrical rods. The middle quadrupole is housed in a collision cell having end plates made from a leaky dielectric material to improve transmission [6]. A counting channel electron multiplier together with a scalar/counter and a threshold discriminator serves as the detection system. The triple quadrupole mass spectrometer was used in a multiple reaction monitoring (MRM) mode to monitor for the chemical agents.

A heat traced teflon transfer line was used to connect the inlet of the ASSMS system to the flue of the liquid incinerator. A felt pad impregnated with silver fluoride was placed inside the stack end of the transfer line to convert chemical agent VX to it's G-analog. This was necessary because vapors of VX can not be quantitatively transferred through a transfer line. The G-analog of VX is structurally similar to GB and can be quantitatively transferred through the transfer line. For detecting blister agent HD, benzene charge exchange was used in the atmospheric pressure ionization source to produce the molecular ion of HD[7]. A mechanical pump is used to move the stack effluent, at rates of up to 5 L/m, through the ionization source. A syringe pump is used to introduce solutions of the chemical agents in the transfer line, for calibration purposes.

This system was used to monitor the two nerve agents GB and VX and the blister agent HD. For the case of chemical agent GB the transitions $m/z=141 \rightarrow m/z=99$ and $m/z=141 \rightarrow m/z=81$ were monitored. For the case of VX (in reality G-analog) the transitions $m/z=127 \rightarrow m/z=99$ and $m/z=127 \rightarrow m/z=81$ were

daughter ion spectra. For added specificity the transition to the minor daughter ion has to be monitored. The minor daughter ion is at m/z = 99 for the nerve agents GB and VX while for blister agent HD it is at m/z = 63. For the case of the two nerve agents the minor daughter ion is less than 10% as intense as the primary daughter ion. Consequently this system has a higher detection limit when monitoring this minor daughter ion. For the two nerve agents the detection limit of the system for the minor daughter ion is about 20 ASC. For the case of the blister agent the minor transition is only slightly weaker than the primary transition and consequently the detection limit for this transition is 1.43 ASC.

This system was also tested on the exhaust of a filter stack. The filter stack provides a very clean matrix compared to the matrix provided by the flue of the liquid incinerator. The results of the tests performed on the exhaust of the filter stack are summarized in Table 2.

Table 2

Results of Statistical Analysis (Filter Stack)

Chemical Agent	Decision Limit	Limit of Detection
GB	0.08 ASC	0.15 ASC
VX	0.12 ASC	0.23 ASC
HD	0.05 ASC	0.13 ASC

Conclusions.

It has been demonstrated that a system based on atmospheric pressure ionization tandem quadrupole mass spectrometry can detect , in the flue of a chemical demilitarization incinerator, nerve agents GB and VX and blister agent HD near the allowable stack concentrations. In the absence of any matrix effects, this system can detect these agents at concentrations below 0.25 ASC. This has been demonstrated for the case of the filter stack exhaust.

Credits

This work was supported by The Program Manager for Chemical Demilitarization, Aberdeen Proving Grounds, Edgewood, MD. under contract no. DAAA15-86-C-0107. We thank Lanny Davis of Chemical Agent and Munitions Disposal System, Tooele Army Depot, Tooele, UT for his assistance during the course of this work.

monitored. For the case of HD the transitions m/z = 158 → 109 and m/z = 158 → 63 were monitored.

Results and Discussions

Calibration runs were performed on GB, VX and HD on four consecutive days, to obtain the detection limit of the system for detecting these agents in the flue of the liquid incinerator. On each day the system was challenged with six different concentrations of the chemical agents. We used six challenge concentrations in the range of .5 ASC to 20 ASC. The ASSMS system response at each challenge concentration was measured in triplicate. The above procedure was repeated on four days. The ASSMS system response thus obtained was converted to a found concentration. Regression analysis was performed on the resulting data to obtain statistical parameters pertinent to describing the performance of the system.

We followed the procedure used by U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) to determine certified reporting limits[8]. This procedure consists of performing a weighted linear regression of the fount v/s target concentration. Both upper and lower confidence limits, at any desired confidence level, can then be obtained. In this work we used a confidence level of 95%. Based on this analysis statistical parameters like the limit of detection (LOD) and decision limit (DL) can be calculated. LOD is the smallest true concentration that will be consistently detected. If the analyte is present in the sample stream at the LOD concentration level, the probability that it will be detected is at least 95%. True concentrations above the LOD are deemed detectable. DL is the maximum found concentration that will result, with a probability of 95%, from a stream containing no analyte. However, since the DL is usually less than the LOD this will not constitute a false positive. These two statistical parameters contain all the information needed to assess a systems detection performance. The results of this statistical analysis is given in Table 1.

Table 1

Results of Statistical Analysis (Liquid Incinerator Flue)

Chemical Agent	Decision Limit	Limit of Detection
GB	0.15 ASC	0.6 ASC
VX	0.84 ASC	1.79 ASC
HD	0.6 ASC	1.15 ASC

The results in Table 1 refer to the primary transition in the

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FIELD EVALUATION OF THE BRUKER MOBILE MASS SPECTROMETER UNDER THE U.S. EPA SITE PROGRAM

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INTRODUCTION

The Mobile Environmental Monitor (MEM), a field-deployable gas chromatograph/mass spectrometer (GC/MS) manufactured by Bruker Instruments, Inc., was demonstrated to assess the ability of this technology to perform in-field analyses of organic contaminants in soil and in water. The demonstration, conducted under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program, took place at two Superfund sites in Massachusetts during August and September 1990. Detailed studies and quality assurance designs provided the structure for each field demonstration. Real-world and performance-evaluation samples were analyzed by the MEM and by equivalent, standard EPA methodologies. Data generated by the MEM were compared to that obtained from the EPA methods and were used to assess specific performance characteristics.

BACKGROUND

The Superfund Program was established by Congress in 1980 to identify, prioritize, and remediate the nation's uncontrolled hazardous waste sites. Because the problems associated with hazardous waste sites have proved to be far more complex and diffuse than anticipated, Congress enacted the Superfund Amendments and Reauthorization Act of 1986 (SARA). Under SARA, EPA was charged with effecting more timely and cost-effective remedies for Superfund site remediations. The SITE Program satisfied the requirement (SARA, Section 311[b]) that EPA establish a program designed to accelerate the development, demonstration, acceptance, and use of promising alternative or innovative technologies targeted to meet the objectives of the overall Superfund Program.

Two categories of technologies are recognized in the SITE Program: (1) treatment technologies that may serve as alternatives to land disposal of hazardous waste, and (2) monitoring and measurement technologies for identifying contaminants. Monitoring and measurement technologies that are accepted into the SITE Program are evaluated as part of the Monitoring and Measurement Technologies Program (MMTP). Under the SITE Program, the MMTP is administered by the EPA Office of Modeling, Monitoring Systems and Quality Assurance (OMMSQA) through the Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV). The Bruker MEM was demonstrated under the MMTP.

The primary purpose of the MMTP is to provide developers with the means to demonstrate innovative technologies that could be used as alternatives to the current systems of detecting and assessing the extent of pollutants at hazardous waste sites. The focus of these demonstrations is to evaluate fully-developed technologies, thereby making performance and cost effectiveness data available to interested parties. Superfund decision makers will thus have the information that is necessary to consider whether or not these technologies are of potential use in future site characterization or remediation projects. The developers of the monitoring and measurement technologies are identified from as many sources as possible, including solicitations in relevant trade journals, periodicals, seminars, and professional conferences. Once the developers reply to a solicitation, the SITE Program representatives begin an evaluation process to determine the feasibility, utility, and need for each technology.

Bruker Instruments, Inc., of Billerica, Massachusetts, responded to one of these solicitations and its MEM was identified by EPA as a promising candidate for a field demonstration under the MMTP. The MEM, designed for the on-site analysis of organic contaminants, is a mobile mass spectrometer (MMS), optionally coupled to a gas chromatograph (GC) or a thermal desorption

sampling probe. Currently, full-size (therefore, nonmobile) laboratory gas chromatography/mass spectrometry (GC/MS) has been the preferred EPA approach to identifying and quantifying organic contaminants at Superfund sites. This technology analyzes compounds on the basis of the molecular weight, retention time, and characteristic fragmentation patterns of their chemical components. The primary disadvantages of conventional GC/MS systems are instrument size, power demand, and sensitivity to external factors (e.g., temperature, humidity, and vibration). The development of an MMS rugged enough to withstand a variety of field conditions is of considerable interest to parties responsible for contaminant monitoring and for remediation of Superfund sites. Newly developed mobile systems, such as the Bruker MEM, appear to have attained satisfactory levels of stability, power usage, and compactness for field applications.

MEM SITE DEMONSTRATION

The purpose of the demonstration was to evaluate the ability of the MEM to analyze polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs) in soils and to analyze volatile organic compounds (VOCs) in water, under field conditions at Superfund sites. The demonstration focused on the capability of the instrument to generate rapid, cost-effective, and reliable PCB, PAH, and VOC data from real-world samples. The demonstration was used to compare MEM performance to similar analytical method performance as required under the EPA Contract Laboratory Program (CLP) or the Resource Conservation Recovery Act (RCRA). Detailed project and quality assurance plans were prepared which defined the sampling and analysis protocols, the experimental design, the quality assurance and quality control (QA/QC) requirements, the data base management system, the health and safety considerations, and proposed data analysis and evaluation methods.

For this demonstration, real-world samples were collected from two National Priorities List (NPL) sites in Massachusetts (EPA Region 1). These sites were selected on the basis of documented (Record of Decision) presence of analytes of interest: e.g., PCBs in soil and VOCs in ground water at one site and PAHs in soil at the other. A screening analysis by the MEM identified the collection points (i.e., low, medium, and high concentration levels) for five samples in each compound class (PCB, PAH, VOC). Bulk samples were collected, homogenized, and split (bottled) into replicates. For each compound class, each of the five distinct samples was split into seven replicates for analysis on site (or near site) by the MEM, and off site by standard EPA methods. In addition, standard reference materials (SRMs), and blank samples were sent to all analysis locations for variability, detection, and other data quality assessments. This process worked well for the PCB and PAH soil samples; however, remediation activities at the chosen site precluded the collection of VOC-contaminated ground-water samples. Instead, surface water collected from the other site was spiked with different concentrations of VOCs.

ANALYSIS METHODS

The MEM analytical methodologies for field analysis were developed by the Trace Analytical Chemistry Laboratory of Tufts University. The off-site confirmatory laboratories used EPA-approved methods for analyzing demonstration samples. This process minimized intermethod biases because the EPA methods were chosen for their similarity to the MEM field methods. A brief overview of each method is provided below.

PAHs in soils: For the MEM, soils were first extracted with methylene chloride. The extracts were then thermally desorbed onto a 3-m chromatography column interfaced with the mass spectrometer. The data were collected and interpreted in a manner similar to that used for EPA methods. For the off-site laboratory, samples were first extracted by RCRA Method 3550 (methylene chloride, sonication extraction). The extracts were then analyzed by RCRA Method 8270 (GC/MS analysis for semivolatile organic compounds).

VOCs in water: For the MEM, analytes were purged from the samples onto Tenex tubes. The tubes were thermally desorbed onto a 30-m fused silica capillary column for compound separation. Compound identification and quantification were performed using quadrapole MS. The off-site laboratory employed RCRA Method 8260 (capillary column GC/MS for volatile organic compounds).

PCBs in soil: For the MEM, soils were first extracted with hexane. The extracts were then thermally desorbed onto a 3-m chromatography column connected to the mass spectrometer; the final concentrations were calculated by quantitating individual chlorination levels (mono- through octachlorobiphenyl, only). For the off-site laboratory, samples were first extracted according to RCRA Method 3550 followed by GC/MS analysis in concordance with the CLP high-concentration protocol. Like the MEM method, congener counting was used in sample quantification. RCRA Method 3640 (gel permeation chromatography cleanup) was used when necessary for high-concentration samples. (NOTE: The conventional GC method for PCB analysis was not used; this method measures arochlors and, thus, would not have provided proper intermethod comparison.)

MEM EVALUATION

Data Analysis: The data from all analysis sites were compiled into one fully documented data base. Data were then subjected to a detailed verification process. Following

verification, a variety of data analyses were performed, including intermethod comparisons (between the MEM and the off-site laboratory results), reproducibilty estimates (from replicate analyses on the same instrument), and the evaluation of data quality indicators. Direct comparison plots and a variety of statistical routines were used to interpret the data. Figure 1 and Table 1 represent selected demonstration results. Figure 1 presents the comparisons of real-world and SRM samples for the PCB trichlorbiphenyl congener. Table 1 presents precision, accuracy, and bias information for PAHs based on SRM analyses by the MEM and by the off-site laboratories.

Figure 1. Linear regression of trichlorobiphenyl.

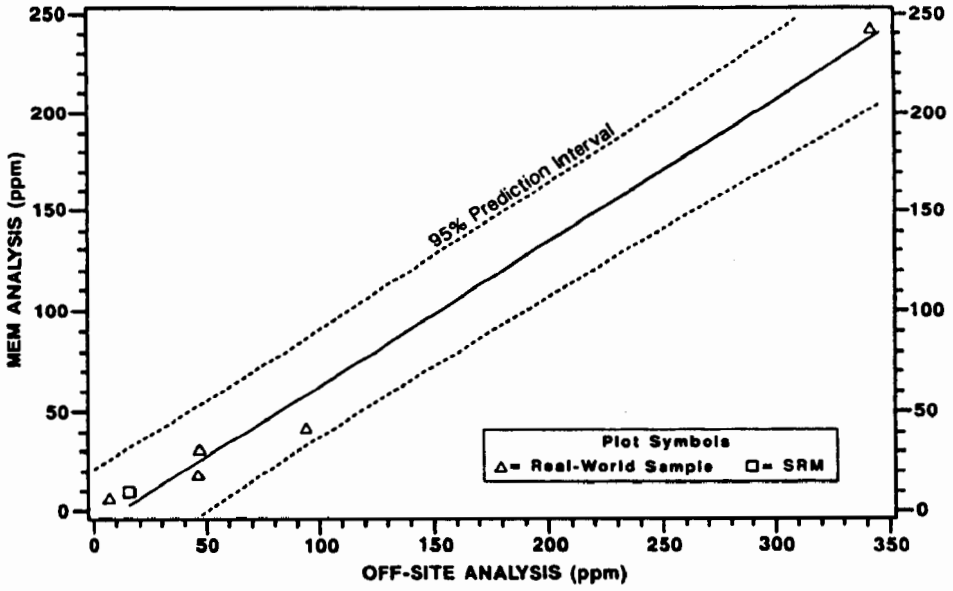

Table 1. Precision and accuracy data for PAHs based on SRM analysis.

Analyte (Theoretical SRM Value)	Lab	Mean[a]	%RSD	%Bias from Theoretical Value	%Bias from Off-Site Value	%Bias from EMSL-LV Value
Naphthalene (50.7)	MEM	28.6	55.1	-44.8	-15.2	-6.7
	Off-Site	32.8	11.3	-34.9	–	+10.0
	EMSL-LV	29.7	18.5	-40.8	-9.1	–
Acenaphthylene (46.4)	MEM	10.9	39.1	-76.3	-45.0	-56.0
	Off-Site	20.4	11.9	-56.9	–	-20.0
	EMSL-LV	24.6	20.1	-46.1	+25.0	–
Fluorene (45.9)	MEM	29.2	25.1	-36.8	-6.5	+3.6
	Off-Site	31.1	8.0	-32.5	–	+10.7
	EMSL-LV	28.0	19.6	-39.0	-9.7	–
Pyrene (50.6)	MEM	40.7	16.2	-19.0	+17.1	+28.1
	Off-Site	34.6	9.6	-30.8	–	+9.4
	EMSL-LV	32.4	23.4	-36.8	-8.6	–
Chrysene + Benzo(a)anthracene (97.9)	MEM	86.8	26.5	-11.1	+31.8	+35.9
	Off-Site	66.1	9.0	-32.6	–	+3.1
	EMSL-LV	63.3	23.5	-34.6	-3.0	–

[a]Means based on analysis of: 40 replicates for MEM; 30 replicates for off-site; 7 replicates for EMSL-LV. Units are in ppm.
%RSD = percent relative standard deviation
SRM = Standard Reference Material
EMSL-LV = Environmental Monitoring Systems Laboratory, Las Vegas, Nevada
MEM = Mobile Environmental Monitor

Instrument Characteristics: The primary advantages of the MEM are its portability and ruggedness. Rechargeable batteries supply all power required by the MEM, and logistical requirements are minimal and easily fulfilled. The use of purified ambient air as the carrier gas eliminates the need to transport compressed gas cylinders. The demonstration plan called for the analysis of 13 samples per day; the analysis team had difficulty meeting this sample throughput requirement. Although the MEM is easy to operate under normal conditions, a skilled operator is required to correctly diagnose and repair malfunctions.

FUTURE MOBILE GC/MS WORK IN THE SITE PROGRAM

On the basis of data collected and observations made during this demonstration, several issues have been identified that must be addressed before the MEM or other MMS instruments can be employed in Superfund site monitoring, characterization, and remediation activities. These issues include: (1) method development and procedural documentation, (2) development of standardized QA/QC requirements and limits, (3) development of data reporting standards for field analytical measurements, and (4) development of a detailed troubleshooting guides and training programs. These issues do not necessarily represent problems with the technology itself; several are external factors or policy issues that require attention before the EPA can use MMS instruments as reliable field analytical devices.

EPA is considering additional mobile mass spectrometer evaluations at EMSL-LV under the SITE Program. Future laboratory evaluations will concentrate on (1) separating variability associated with the instrument from variability associated with the method, (2) formalizing QA/QC procedures, and (3) establishing consistent data reporting procedures for field applications. Additional field demonstrations and evaluations will follow.

ACKNOWLEDGMENTS

The EPA would like to thank the following organizations for their participation in the demonstration and evaluation of the Bruker MEM under the SITE Program:

- EPA Region 1
- Bruker Instruments, Inc.
- Tufts University
- Lockheed Engineering & Sciences Company
- S-CUBED

THE DITAM ASSAY

A FAST, FIELDABLE METHOD TO DETECT HAZARDOUS WASTES, TOXIC CHEMICALS, AND DRUGS

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PURPOSE AND SCOPE OF ASSAY

The DITAM (Diffusion Through A Membrane) assay is fieldable, fast, extremely easy to use, inexpensive, and can be used to detect one or several substances simultaneously. The DITAM apparatus was developed along with the DITAM assay. This new assay is in the initial stages of development for the detection of several small molecular weight substances. Model systems have been tested for the detection of progesterone and *Ricinus communis,* a toxin. Based on the initial experimental results, it appears that the DITAM assay will be useful for the rapid detection of a wide variety of substances in the field. Examples of these substances include small molecular weight hazardous wastes, toxic chemicals, and drugs. Continuing research involves further modifications of this assay to enable the detection of large molecular weight substances such as proteins from infectious organisms and antibodies directed against these organisms.

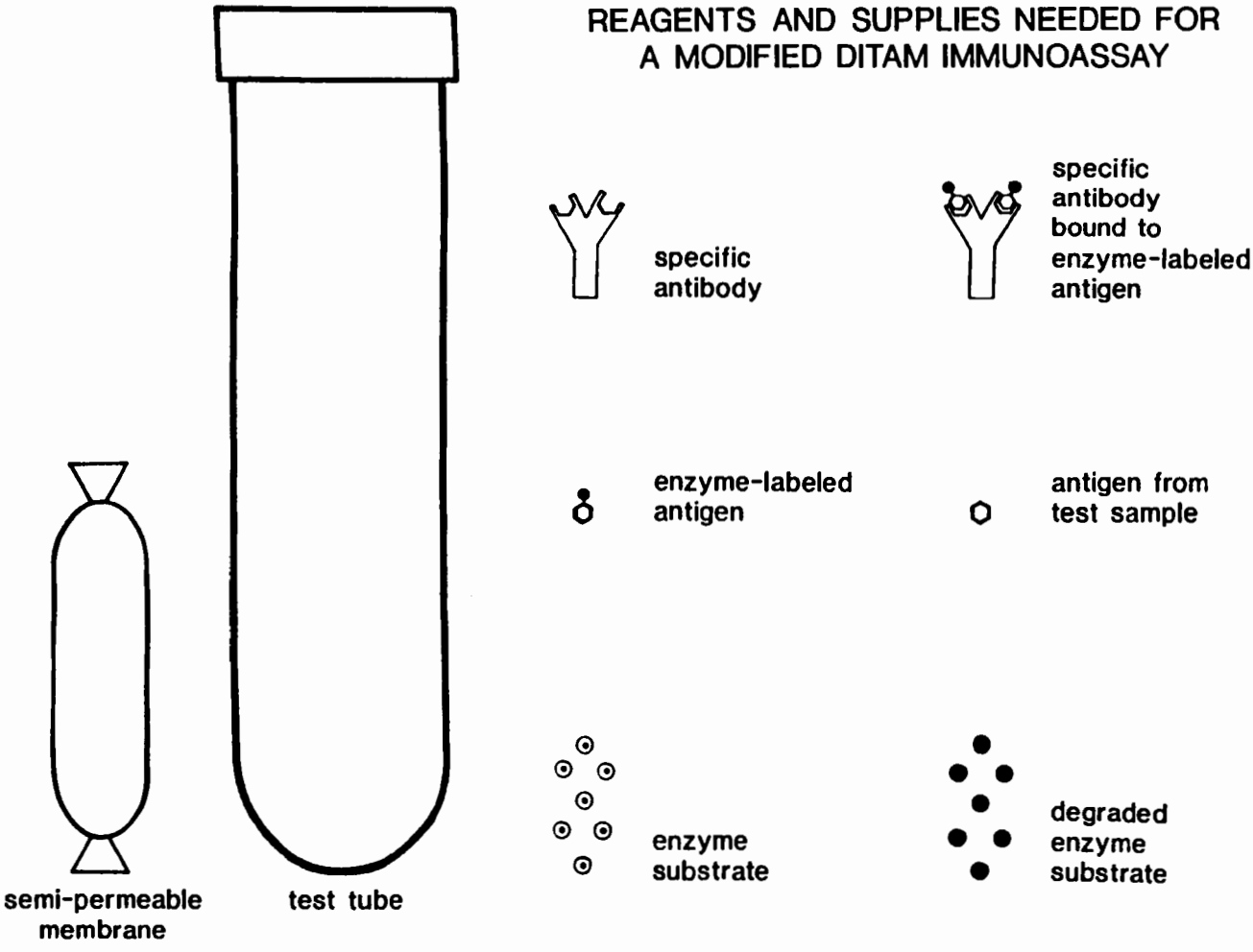
MATERIALS AND METHODS

There are two version of the DITAM assay and apparatus. The original DITAM apparatus consists of a hand-held polystyrene "box" with two to four chambers. The chambers are separated by semipermeable membranes. Because of the difficulty in producing these "boxes" in the laboratory, the design of the DITAM apparatus was modified. The modified version consists of a "bag" in a 12 x 75 mm capped test tube or an alternate pocket-sized vial. The "bag" is actually a cylindrical semipermeable membrane which is filled with reagents and tied or clamped at both ends. These reagents consist of specific antibodies, enzyme-labeled antigens, and a buffer solution. To date, several membrane types have been tested for their usefulness in this assay. The membranes must be flexible and have pores which allow molecules of a specific size to diffuse through easily and rapidly. The appropriate molecular weight cutoff of the membrane must be selected in order to retain the antibody molecules within the "bag" and enable the enzyme-labeled antigens and antigens in the test sample to pass through the "bag." All reagents and supplies needed for a modified DITAM assay are illustrated in the figure on the following page.

When performing a modified DITAM assay, an individual is supplied with a test tube which contains the reagent-filled "bag." To perform this assay in the field, an individual only needs to add the test sample to a fill line marked on the tube, shake the tube for approximately one to two minutes, add the enzyme substrate, shake the tube again, and observe the tube for a color change. All instructions can be printed on the tube.

The test sample can be liquid or solid. Solid test samples, such as dust particles, can be concentrated on cotton swabs and placed in test tubes along with a buffer solution.

The color of the reaction solution depends on the enzyme and the degraded enzyme substrate. When horseradish peroxidase is used to label the antigens and tetramethylbenzidine plus hydrogen peroxide is used as the enzyme substrate, a turquoise colored solution inicates a positive reaction and a clear solution indicates a negative reaction.



RESULTS AND CONCLUSIONS

Based on the initial experimental results, the modified DITAM assay can be completed in three to five minutes. Thus, it satisfies an initial requirement of speed in obtaining assay results. This assay is extremely easy to perform in both the field and in the laboratory. Since all of the assay instructions can be printed on the tube, little or no training is required in order to perform this assay.

In order to achieve the maximum contrast between the positive and negative reaction solution colors (turquoise for the former and clear for the latter), the appropriate concentration of reactants must be employed. The use of an inappropriate concentration of antibody molecules inside the "bag" can result in false positive reactions (darker blue coloring in negative test samples). Although there may be pale blue coloring in the negative samples due to background reactions, this can be kept to a minimum if the concentrations of reactants are carefully calibrated for the assay. This procedure is standard when developing any new immunoassay.

Due to the versatility of the assay, it can be developed for use by many government agencies and by the private sector as well. Possible future applications include the following: (1) detection of chemical warfare agents in the field and chemical warfare treaty verification, (2) detection of drugs in humans and animals, (3) protection of humans from environmental contaminants (i.e., pesticides and toxic chemicals in dust and water supplies), and (4) detection of hormones (i.e., determining levels in hospital patients and athletes). Continuing research and further modifications of the DITAM assay and apparatus should enable the detection of large molecular weight substances such as biological warfare agents and proteins from pathogenic organisms (i.e., in food, humans, and animals).

RAPID SCREENING OF GROUND WATER CONTAMINANTS USING INNOVATIVE FIELD INSTRUMENTATION

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With the increased use of on-site monitoring equipment at hazardous waste locations, an emphasis has been placed on development of rapid screening instruments designed specifically to provide quick and accurate ground water analysis.

Two instruments have been developed to accomodate those needs. The first one, the "TOP", provides quick assessments of total concentrations of volatile hydrocarbons in water. The second instrument, the AQUASCAN, provides an on-line analysis of individual volatile hydrocarbons in water.

The "TOP"

The "TOP" (Total Organic Purgables) is an instrument which monitors total concentrations of volatile hydrocarbons in water utilizing purge and trap technology. Figure 1 is a block diagram of the "TOP". The "TOP" is designed around an argon ionization detector (AID) and internal sample purge and trap system. A computerized control system activates an internal sample pump, drawing water into the purge cell. Argon gas is purged through the purge cell, stripping the purgable hydrocarbons from the water into the purge gas stream. The gas containing the purged hydrocarbons is routed through an adsorption trap, where the hydrocarbons are collected. Once collected, the trap is heated, desorbing the hydrocarbons into a blank capillary tube and into the AID chamber for quantification. The results are

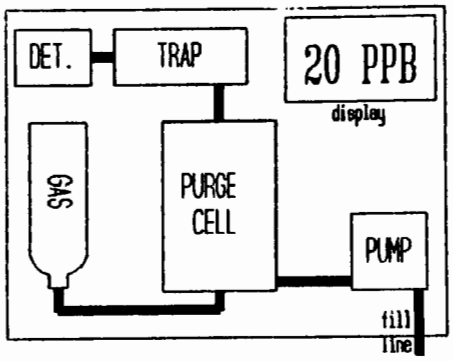

Figure 1. Block diagram of TOP instrument

automatically displayed on a LED screen and stored on a memory chip. This data can be transferred to a computer or a printer for a permanent record.

Calibration of the system is carried out by sampling a water sample containing known concentration levels of hydrocarbons. Figure 2 shows a typical trace of a total purgable run. The dashed line line is a calibration trace while the solid line is the analysis trace. The integrated area of the analysis is compared to that of the calibration, and a concentration value in the ppb or ppm level is automatically calculated and displayed on the LCD screen.

An AID is used because of its relative uniform response to a broad range of purgable hydrocarbons (Table 1.) This includes halomethanes and haloethanes which are not easily detected by other total hydrocarbon detectors, such as the photoionization detector (PID).

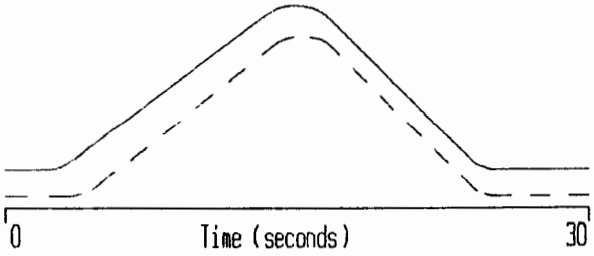

Figure 2. TOP concentration trace

	AID	PID
Ionizing Energy	11.6 eV	10.6 eV
Detected cmpds.	aliphatics aromatics halomethanes haloethanes	aliphatics aromatics
Relative response among detected cmpds.	1-10 times	1-1000 times

Table 1. Comparison of AID and PID

The more uniform response of the AID assures more accurate concentration readings regardless of the compounds chosen for calibration.

The AQUASCAN

The AQUASCAN is used for continuous monitoring of a water source or stream by purge and trap gas chromatography. The instrument consists of an on-line purge and trap sampling module attached to a gas chromatograph (GC) (Figure 3). The purge and trap module contains an internal pump to draw calibration, analysis, or clean water samples into the purge cell. The sample is then purged with inert gas with the resultant vapor swept into an adsorption tube. The trapped volatile organics are then thermally desorbed and injected into the GC column where they are separated. Each compound is then identified and quantified. The resultant chromatograph (Figure 4) is displayed on the computer screen and stored on disk for later review.

The AQUASCAN is automated so that a permanent operator is not needed. An internal modem allows for remote operation of the instrument.

Both of these instruments will aid in the screening and analysis of contaminated water sources. The "TOP" can rapidly and accurately determine total hydrocarbon values in water. The total

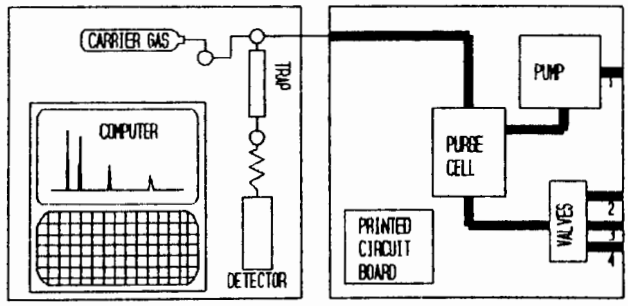

Figure 3. Block diagram of Aquascan; 1-drain; 2-rinse; 3-cal.; 4-anal.

analysis time from calibration to sample acquisition to concentration display is approximately two (2) minutes.

The AQUASCAN allows for complete, on-line, automated, and accurate chromatographic analysis of purgable hydrocarbons in water. Each component is accurately identified and quantified. The AQUASCAN can serve as a continuous monitoring system for traces of VOC's in water, such as waste water streams or water purification systems.

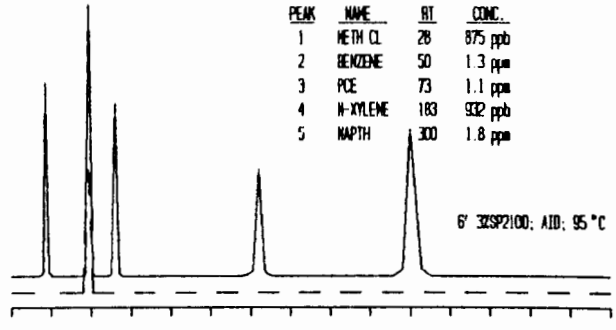

Figure 4. Aquascan chromatograph trace

IMPROVED DETECTION OF VOLATILE ORGANIC COMPOUNDS IN AIR BY ON-LINE SAMPLE CONCENTRATION IN A MICROCHIP GAS CHROMATOGRAPH

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Abstract

Pre-concentration of dilute gas samples was performed by adsorption on a 1.5" glass-lined stainless steel Tenax trap, interfaced on-line, in a Model 200 Portable Microchip Gas Analyzer (Microsensor Technology Inc., Fremont, California). Adsorption onto Tenax (2,6-diphenyl-p-phenylene oxide polymer) was achieved by passing 5 mL of dilute gas sample, at room temperature, through the trap placed between the sample loop (in a solid-state injector) and the switch valve. The adsorbed analytes were desorbed from the Tenax by rapid heating at 200°C followed by venting of the unconcentrated analytes to the atmosphere before injecting a concentrated plug of analytes into the analytical column. Concentration ratios of up to 30:1 were achieved for some analytes. Sample recovery was affected by several factors, such as, the amount of sample purged through the trap at room temperature, amount of sample injected, rate of desorption heating, final desorption and cooling temperatures of the trap, sample volatility. Sample recovery also varied according to whether the trap contained Tenax alone or Tenax with Spherocarb as the adsorbent.

Introduction

Throughout the history of modern chromatography, there has been a consistent trend to work with ever-decreasing amounts of analysed materials and at increasing demands on detection sensitivity. Only slowly has this direction been translated into smaller chromatographic columns and corresponding instrumentation (1). Difficulties are frequently encountered in attempting to directly analyze organic compounds of interest, which are often below the part per billion level. Despite the use of highly sensitive instruments, detection of trace amounts of substances in this range presents a technical challenge, especially as regards to the use of portable instruments (2). A good example is the analysis of volatiles from human expired air to seek distinctive differences between "normals" and those afflicted by disease. More recently, awareness has grown to the fact that minute concetrations of chemical pollutants can have far reaching effects as health hazards, further underscoring the need for reliable analytical techniques (3).

It is often stated that one of the possible applications of high speed gas chromatography (using a Microchip Gas Analyzer) is in the fields of breath gas analysis (4), and on-site analysis of hazardous volatile organic compounds (5). At the part per billion level, it has almost always been necessary to use some off-line cumulative or concentrating technique to obtain measurable amounts of sought-after compounds. Ideally, it is preferable to elliminate as much as possible, the unwanted background compounds (usually water and air) while accumulating the desired substances quantitatively. For most techniques, the result is a compromise between these two goals.

In off-line concentration applications with the Microchip Gas Analyzer, sample components trapped in a separate Tenax (a porous polymer of 2,6-diphenyl-p-phenylene oxide) concentrator are manually collected in a gas tight syringe and introduced to the Microchip Gas Analyzer for separation (6). This off-line technique is generally time consuming, operator-intensive, and difficult to automate. In our work, we sought to put the Tenax GC concentration trap on-line in a Microchip Gas

Analyzer, by placing it between the silicon injection wafer and the injection switch valve.

Experimental

GC System

This consisted of a model 200 Microchip Gas Analyzer (Microsensor Technology Inc., Fremont, CA) which was equipped with a solid-state sample injection system; two vacuum pumps connected in parallel; a 4 m long x 0.10 mm i.d x 0.4 μm phase thickness DB-1701 capillary column; a miniaturized thermal conductivity detector; and an apple computer, using M2001 software.

Zero helium was used as carrier gas at a column head pressure of 20 psi corresponding to a flowrate of 1 mL/min (an average velocity of about 36 cm/sec.). An isothermal column temperature of 40°C was used in our experiments.

Sample Mixture

100 ppmv mixture of n-propane to n-octane hydrocarbons in zero nitrogen.

1 ppmv mixture of acetone, benzene, toluene, chlorobenzene, and bromobenzene in zero nitrogen.

Traps

A 1.5" long x $\frac{1}{16}$" o.d.x 0.7 mm i.d. glass-lined stainless steel tube containing 2.0 mg Tenax GC, 60/80 mesh, Applied Science Laboratories Inc.,PA.

1.5" long x $\frac{1}{16}$" o.d.x 0.7 mm i.d. glass-lined stainless steel tube containing 1.5 mg of Tenax GC and 1.0 mg of Spherocarb 80/100 mesh, Analabs, Norwalk, CT.

Trap Loading and Sample Injection

Five mL of sample mixture was adsorbed onto the adsorbent in the trap by passing it through with the aid of two vacuum pumps using a sampling time of 140 seconds. This was followed by rapid heating of the trap to a temperature of 190°C for 90 seconds. With the trap at 190°C the switch valve was turned to the carrier gas position followed by venting of the the unconcentrated sample in the sample loop to the atmosphere through the sample valve and the injection valve opened for 200 msec., allowing about 0.2 μL of the concentrate to be injected into the analytical column. Delay times of 400 msec. were applied prior to venting and sample injection. After injection, the trap was prepared for the next sample by purging with carrier gas, while hot for two minutes and allowed to cool to room temperature with carrier gas purging continuing.

Results and Discussion

The main purpose of this work was to investigate the possibility of placing an on-line Tenax trap in a Microchip Gas Analyzer. For a glass-lined stainless steel trap with its many advantages, it has so far proved practically applicable (7).With a Tenax GC or Tenax / Spherocarb trap on-line, the two sample pumps were drawing the hydrocarbon sample at the rate of about 2.5 mL/min.

For a trapped sample volume of 5 mL, an injection volume of 0.2 μL (200 msec. injection time), and a 100 μm i.d. analytical column, concentration factors of 10 are quite common, depending on the amount of venting done before the injection. Concentration factors are dependent on the vent times used.

For a trapped volume of 5 mL on a Tenax adsorbent and an injection volume of 0.2 μL (200 msec. injection time), the following were some of the data obtained:

Cpd Name	Area	%RSD	Increase
Propane	Trace		
Butane	411813	2	4
Pentane	783870	11	5
Hexane	3164633	8	17
Heptane	7152900	2	Large
Octane	5451000	4	Large

For a trapped volume of 5 mL (the rest same as above):

Cpd Name	Area	%RSD	Increase
Acetone	2205500	5	2
Benzene	13518667	4	15
Toluene	7751567	7	41
Chlorobenzene	1760633	14	Large
Bromobenzene	3075167	17	5

Note: An increase of large implies that the compound was not detected before concentration

In general, the factors found to increase the concentration factor include: the use of an analytical column with an internal diameter larger than 100 μm i.d.; use of a higher desorption temperature (> 200°C); venting of an appropriate amount of dilute sample in front of the adsorbent in

amount of dilute sample in front of the adsorbent in the sample line; use of the fastest rate of desorption heating and use of an appropriate adsorbent for the group of compounds under investigation.The last factor which is still being optimized is very crucial more so for the lighter hydrocarbons which have a very low breakthrough volume in a Tenax trap as compared to Spherocarb.

Conclusions

Though still under investigation, our preliminary results, so far, have indicated that placing a Tenax or a Tenax / Spherocarb trap on-line in a Microchip Gas Analyzer can enhance the detectability of volatile organic compounds. However, for better reproducibility and quantitation, the stability of the trap heater still needs to be improved and also a better combination of adsorbents in the trap have to optimized for better concentration of all the analytes under investigation. According to Zlatkis et al, (2) Tenax, with a surface area of 18 m^2 g^{-1}, has a low retention for low molecular weight compounds, especially water. Higher molecular weight compounds with relatively low polarity can be trapped and thermally desorbed (at 300° C) at high efficiency. At this temperature Tenax does not contribute to detectable artifacts, due to its unusual thermal stability. Like any other chromatographic stationary phase, the Tenax or Tenax / Spherocarb trap must be evaluated as regards partitioning of a particular compound between adsorbent and carrier gas. As a consequence, our resuts apply to the specific amount of adsorbents employed in the trap. In this case, the beakthrough volumes for compounds of interest, which are proportional to the amount of adsorbent would have to be determined for a particular trap before it is put to use.

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ON-LINE SCREENING ANALYZERS FOR TRACE ORGANICS UTILIZING A MEMBRANE EXTRACTION INTERFACE

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A unique membrane extraction interface has been developed which enables automatic extraction of selected trace organic compounds from aqueous streams and samples. By selecting the type of extractant flowing through the tubular silicone rubber membrane, various classes of organic compounds can be selectively extracted and concentrated, with the exclusion of others. In addition to the advantage of selectivity, the interface can be used for streams with high dissolved solids and particulate content. Several types of on-line monitors have been developed based on this interface which would be suitable for screening and analysis of wastewater, leachate, ground water and surface water.

The simplest membrane monitor is based on a flow injection system where the analyte, which is extracted from the injected sample by the membrane, flows directly to the detector. This approach is useful in screening for a major component or for the sum of a class of compounds. For complex samples the membrane/detector selectivity may not be sufficient to isolate the single component and additional separation is necessary. In one on-line application, low ppb levels of chlorophenols are determined by extraction through the membrane into a basic extractant. This extract is then injected into a LC system for analysis. In another application, a capillary gas chromatograph is used to determine low and sub-ppb levels of organic compounds extracted through the membrane into a hexane extractant. An automated large volume (25-250 μL) injection technique, which couples a retention gap with an air actuated rotary valve, was developed to make on-column injections.

Membrane. The membrane used in the systems described was SILASTIC brand medical grade tubing (Dow Corning, Midland, Michigan), a seamless silicone rubber tubing designed for clinical and laboratory applications. Silicone rubber is chemically and mechanically stable and has a high permeation rate for a large variety of organic compounds. A single membrane has been used in a continuous wastewater analyzer for over a year with no apparent change. Depending on the membrane size, pressures above 10-20 psi will cause the membrane to expand and possibly rupture. Tubing of various sizes can be obtained from medical supply houses. The two membrane sizes used were 0.013 inches I.D. by 0.025 inches O.D. (Dow Corning Catalog No. 602-105), and 0.020 inches I.D. by 0.030 inches O.D. (Dow Corning Catalog No. 602-135).

General principles of membrane extraction. The permeation of compounds through a nonporous polymer membrane occurs by a "solution-diffusion" mechanism. The term "permeation" designates the overall mass transport of the compound across the membrane, whereas the term "diffusion" designates only the movement of the penetrant molecules inside the polymer matrix. For the compounds we have worked with, the diffusion coefficients are similar and the solubility of the compound in the membrane and the extractant appears to be the major parameter for selection.(1,2) The three major steps in the process are:

1. The compound of interest in the sample contacts the membrane and, depending on the solubility parameters, extracts into the membrane.

2. A concentration gradient forms and the compound diffuses across the membrane.

3. When the compound contacts the extractant on the other side of the membrane, it partitions into the extractant depending on the solubility parameters.

Since the silicone rubber membrane has a similar solubility parameter as hexane, membrane extraction can be thought of as a combination of a two-step liquid-liquid extraction with hexane. However, because the organic phase is solid, many difficult extraction procedures are now possible:

1. Samples which form emulsions can be extracted.

2. Very small volume organic/sample extractions can be performed.

3. Solvents such as acetonitrile, acetone, isopropanol and methanol, which would normally be miscible with the aqueous sample matrix, can be used as extractants.

4. Automated on-line extractions interfaced with analytical instrumentation can be developed more easily.

Membrane/Flow Injection Analysis. This is the simplest of the membrane systems. The detailed parameters of this system have been reported (2,3) and a brief description is given below.

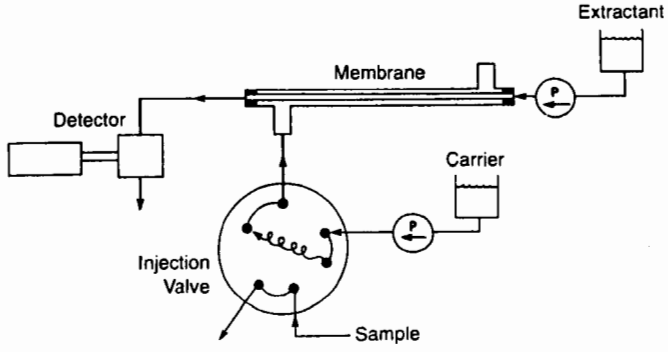

FIGURE 1. Membrane/Flow Injection System

In the Membrane/FIA system the membrane is connected directly to an LC detector (Figure 1). The membrane is contained in a glass flow-through cell. For determination of phenol, a dilute caustic solution is pumped through the tubular silicone rubber membrane and water or a buffered carrier solution is pumped around the outside of the membrane. The sample loop is filled with sample and when the valve is rotated, the sample is carried past the membrane. Some of the phenol in the sample permeates the membrane and forms a phenate salt when it reaches the caustic. The phenate salt is no longer soluble in the membrane and concentrates in the caustic. The carrier flows the extracted phenol to the detector where it is detected as a peak. Selectivity depends on the membrane parameters and the detector response. Since many neutral and basic compounds are not very soluble in the caustic solution, they prefer to remain in the membrane. Selectivity can also be obtained between phenols if their pKa values differ by 2 units or more. By making the sample a pH of 9, phenol (pKa=10) will extract while phenols with a pKa of less than 8 will show very little extraction. By using a basic carrier and an organic extractant such as methanol or acetonitrile, neutral compounds are extracted with the exclusion of phenolics. Therefore, by adjusting the pH of the sample and the composition and pH of the extractant, the membrane acts like a "chemical switch" which can select various chemical classes.

Membrane/Liquid Chromatography. Although the Membrane/FIA system will work in many situations, complex samples require more selectivity. The Membrane/LC system (1) is similar in principle to the FIA system except the extract flows into a sample loop of an LC valve as shown in Figure 2. The contents of the loop are then injected into the LC system where the extracted components are separated and detected. Higher concentration factors can be obtained by using a stop-flow extraction technique. If the stop-flow valve shown in FIGURE 2 is rotated, the extractant is trapped in the membrane and analyte continues to permeate and concentrate. When the valve is rotated to the initial position, the concentrated extract flows to the LC sample loop. Phenols and neutral compounds can be determined at low and sub-ppb levels using this technique.

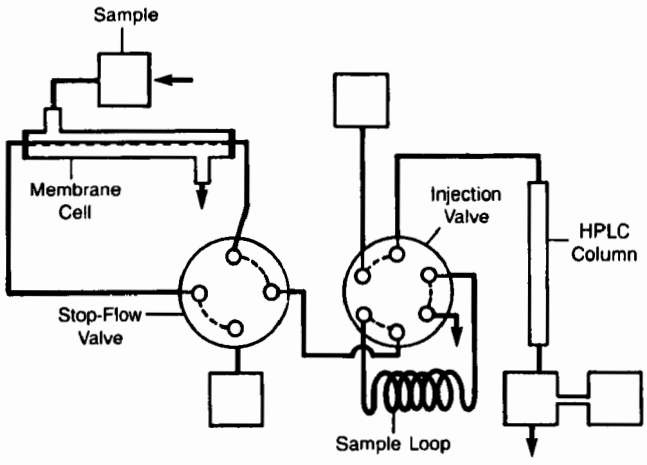

FIGURE 2. MEMBRANE/LC SYSTEM WITH A STOP-FLOW VALVE.

Another Membrane/LC has been developed (4,5) which uses only one pump and only one solution that serves as both the extractant and the LC eluent. An eight-port valve is used to isolate the membrane from the back pressure of the LC column and it is rotated for a short period to allow the concentrated extract to flow to a sample loop connected to the same valve. Although this system is not as versatile, its simplicity makes it useful for dedicated, on-line analyzers.

Membrane/Gas Chromatography. The Membrane/GC systems use the same type of membrane, however, the cell design is modified to allow for the swelling of the membrane when extractants such as hexane are use. Two types of Membrane/GC systems have been developed.(6)

One design, shown in FIGURE 3., combines membrane cell technology with a pneumatically operated pressurized injection valve (POPSI). A hexane extractant flows through the tubular membrane and extracts permeated compounds. This concentrate then flows to the injection valve with an internal 1-3 μL sample slot. When the valve is rotated, a short burst of pressure is applied and the entire contents of the slot is injected on-column into a capillary GC column. The system was evaluated using chlorinated aromatic compounds and pesticides.(7) These compounds were successfully extracted and determined in water in the part-per-trillion to part-per-billion range.

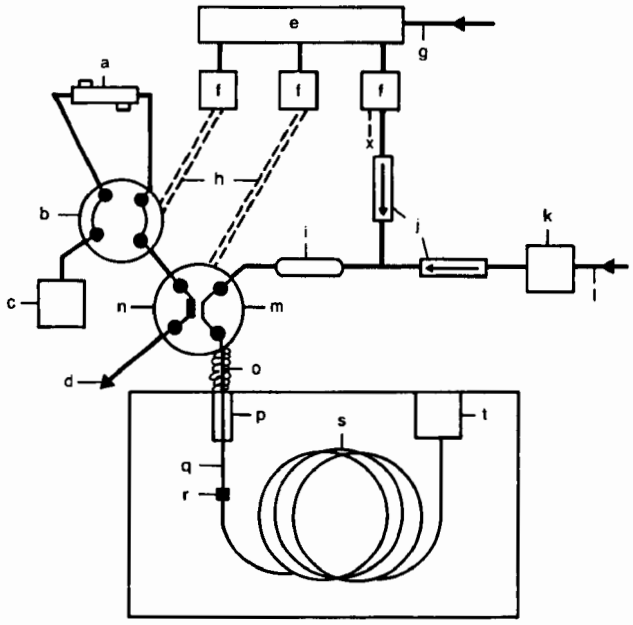

FIGURE 3. MEMBRANE/GAS CHROMATOGRAPHIC SYSTEM: (a) membrane; (b) extractant stop-flow valve; (c) extractant pump; (d) extractant waste; (e) soleniod controller; (f) soleniods; (g) 100 psi N_2 or He; (h) valve actuator lines; (i) charcoal trap; (j) check valves; (k) flow controller; (l) 30 psi He; (m) injection valve; (n) internal slot sample loop; (o) rentention gap capillary covered with glass wool; (p) injection port; (q) 0.3-M retention gap; (r) capillary connector; (s) capillary column; (t) electron capture detector.

The second system (6), shown in FIGURE 4, achieves high sensitivity by using an external sample loop and injecting a large volume of hexane extractant (25 to 250 μL) directly on-column using a retention gap connected to a capillary GC column (8,9). This system has been used on-line for the determination of semi-volatile organics in a waste stream down to the 1 to 2 ppb level with a flame ionization detector (FID).

Conclusions. The membrane interface can be used to greatly facilitate the use of analytical instrumentation for on-line applications. The membrane produces a clean, particulate-free extract of aqueous samples with no pre-treatment that can be injected and analyzed directly. The membrane can be used to select certain chemical classes and concentrate extracted compounds 200 times or greater.

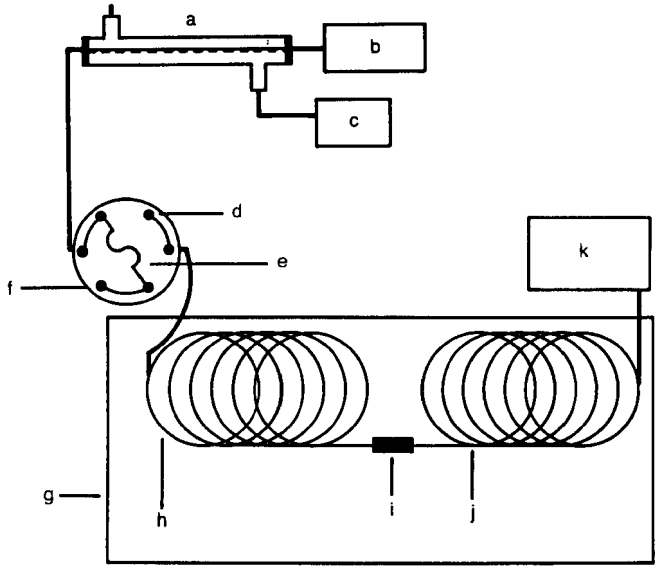

FIGURE 4. MEMBRANE/GC LARGE VOLUME ON-COLUMN INJECTION:(a) membrane cell; (b) extractant pump; (c) sample pump; (d) carrier gas inlet; (e) sample loop; (f) extractant waste; (g) oven; (h) retention gap; (i) capillary union; (j) capillary analytical column; (k) detector.

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Candidate Protocols for Sampling and Analysis of Chemicals from the Clean Air Act List

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Clean Air Act (CAA) amendments of 1990 renew and intensify national efforts to reduce air pollution. Title III of the Amendments lists 189 hazardous air pollutants (HAPs) and requires the Environmental Protection Agency (EPA) to promulgate new control standards for the principal sources of such emissions. The 189 HAPs are chemicals not previously regulated under the National Ambient Air Quality Standards. These HAPs listed in the CAA are not expected to be found in a large number of areas nor in large quantities. However, health effects may occur at low concentrations because of their high acute or chronic toxicity. Measurement of pre- and post-control emissions from a wide variety of stationary sources will be required in order to determine success in reducing emissions. Prior to testing at a source, however, a written sampling and analytical protocol must be available to ensure that data acquired during source testing are accurate and of known quality. In order to optimize the yield of information from any given field effort, the sampling and analytical methodologies which are selected should be applicable to the broadest possible range of compounds. Some sacrifice of accuracy and precision of the methodology may be necessary to extend the range of applicability. This study reports the results of a review and evaluation of existing information on sampling and analytical methods presently and potentially applicable to toxic air pollutants. Generic Methods which simultaneously yield information for a large number of HAP compounds have been emphasized. The goal of using methods which cover a broad range of compounds may initially require the sacrifice of some method accuracy. Many analytes have been assigned to generic methods on the basis of physical properties since individual compound validation data are often not available. Such validation data must come from well designed programs using data obtained by techniques such as dynamic spiking of isotopically-labeled compound analogs while sampling operating sources. Extension of an existing methodology is completely valid only when the applicability of both the sampling and analytical methodology to the specific analyte has been established. If complete field method validation has not been performed, it is possible that the compound can be analyzed using the analytical methodology but not collected quantitatively, or vice versa.

Some of the methods cited are written specifically to address gaseous emissions from stationary sources. Sampling and analytical methods may be divided into combustion and noncombustion stack methods, since CAA requirements will cover both types of stationary sources. For a stationary source not related to a combustion process, sampling and analytical methodology used for ambient air monitoring may be applicable. For some of the compounds listed as HAPs, there is a choice of methodology. Generic methods have been emphasized. Specialized sampling/analytical methodology for individual compounds or classes of compounds has also been summarized when it was available.

The following methods were selected as having the broadest possible range of application:

Volatile Organic Sampling Train (VOST) Methodology[1]

The VOST methodology is described in OSW-SW846 Method 0030 for sampling and Methods 5040 and 5041 for analysis. Samples in the field are taken using a specialized sampling train to collect volatile organic compounds on a sorbent. The sorbent sampling tubes are then returned to the laboratory for thermal desorption through water, collection and concentration of the vapors, and ultimate analysis by gas chromatography/mass spectrometry. The sampling methodology specifies that organic compounds with boiling points between 30° and 100°C may be sampled with the methodology. Compounds with boiling points below 30°C may be sampled using special care, and selected compounds with boiling points above 100°C may also be sampled in carefully selected situations. Polar, water-soluble compounds represent specific problems with this methodology. The literature presents a method for optimizing recovery of such compounds[2], but even with the optimized methodology, many problems remain.

Semivolatile Organic Sampling Train (SemiVOST) Methodology[1]

The SemiVOST methodology is describe in OSW-SW846 Method 0010 for sampling and Method 8270 for analysis. Samples in the field are taken using a specialized sampling train with sorbent to collect a range of semivolatile organic compounds. The train is recovered and components of the train are returned to the laboratory for extraction, concentration of the extract, and analysis using gas chromatography/mass spectrometry. The sampling methodology specifies only that it is applicable to compounds with boiling points above 100°C. Although no upper limit on boiling point is posed, the method is limited to compounds which can be solvent extracted and analyzed by GC/MS. Semivolatile organic HAPs in the CAA Amendments constitute an extensive list, including single entries that are groups of compounds. Some members of these groups will be observed with the SemiVOST analytical methodology with poor detection limits, but if higher specificity or accuracy is required for polychlorinated biphenyls or polycyclic organic material, there are specialized applications of the SemiVOST methodology available. Also, since the range of compounds on the CAA is so wide, the sample preparation methodology will not be optimum for all of the compounds simultaneously. The broad range of the method must yield to specific optimization of the methodology for a particular class of compounds, such as derivatization for carboxylic acids, or adjustment of pH during extraction to optimize recoveries of particular classes of compounds.

Multi-Metal Sampling Train[1]

The multi-metal sampling and analytical protocol is described in OSW-SW846 Method 0012 for sampling and analysis. The methodology for the determination of multiple metals incorporates a stack sampling train using specialized aqueous solutions, with ultimate analysis according to a series of digestion and analytical methods which include final quantitation with either atomic absorption spectroscopy or inductively coupled argon plasma spectroscopy. The source samples are withdrawn isokinetically from the stack through a heated probe, with particulate emissions collected on a filter in a heated filter holder located outside the stack and after the probe of the sampling train. The analytical methodology detects and quantifies metal ions, so an inorganic compound is not detected as a molecular species. For example, titanium tetrachloride would be detected as titanium; no identity of the molecule would be retained in the acidic digestion process by which the sample is prepared for analysis.

Aldehyde/Ketone Sampling Methodology

Sampling and analytical methodology for a variety of aldehydes and ketones is described in OSW-846 draft Method 0011 and Method 8315. Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenylhydrazine (DNPH) solution. Aldehydes and ketones present in the emissions react with DNPH to form a dinitrophenylhydrazone derivative which is extracted, concentrated, solvent-exchanged, and then analyzed by high performance liquid chromatography.

The sampling and analytical methods described above will provide a means of sampling and analyzing approximately 80-90 percent of the entries on the CAA List. However, for many of the compounds listed, a field test under controlled conditions has not been performed to demonstrate and evaluate the combined sampling and analytical methodology. Demonstration tests need to be performed to determine recoveries of the compounds from stationary source emissions exhibiting various matrix conditions, which will cause the performance of the methods to vary. However, a relatively broad coverage of compounds can be achieved with these generic methods, saving the expense of applying individual methods but potentially losing some of the specificity and sensitivity of individual methods.

Some of the entries on the Clean Air Act List will require specialized methodology because of problems with reactivity or other difficulties. For these compounds, some potentially applicable methodologies are:

- acetonitrile by Method 18 (GC/NPD),
- bis(chloromethyl) ether by Method 18,
- 1,3-butadiene by Method 18,
- carbaryl, by Method 0010 and Method 632,
- carbonyl sulfide, by Method 15,
- chloramben, by Method 0010 and Method 515/615,
- 2,4-D salts and esters, Method 0010 and Method 515/615,
- dimethyl carbamoyl chloride, by Method 0010 and Method 531,
- 4,6-dinitro-o-cresol and salts, Method 0010 and Methods 8270 and 515/615,
- ethylene oxide, CARB Method 431,
- hexamethylphosphoramide, Method 0010 and Method 632,
- hydrazine by Method 18,
- methanol by Method 18,
- propoxur by Method 0010 and Method 632,
- 2,3,7,8-tetrachlorodibenzodioxin by Method 23,
- asbestos by CARB Method 427,
- chlorine by modified Method 26 and OSHA Method ID-101,
- coke oven emissions, Method 0010 and Method 8310,
- cyanide compounds, by modified Method 6 and NIOSH Method 7904,
- hydrochloric acid by Method 26,
- hydrogen fluoride by Method 13A or 13B,
- mineral fibers by CARB Method 427,
- polycyclic organic matter by CARB Method 429 or Method 5 G,
- radionuclides, by Method 114.

Many of these entries on the CAA list represent a very broad category, and no single analytical methodology will be equally effective for all possible members of the category. Some of the categories are undefined or poorly defined. In such cases, the analytical methodology specified will serve for some representative members of the category.

No applicable sampling and analytical methods could be found for the following Clean Air Act List entries:

- diazomethane,
- phosgene,
- calcium cyanamide.

Many of the entries on the CAA List are extremely reactive. Because of physical properties such as boiling point, these entries may be initially assigned to a specific methodology. However, testing will be required to demonstrate that the compound can exist without serious decomposition under the conditions of heat, high water content, and possibly acid content which may exist in a stack. Also, a given compound may react completely when it is present in emissions at trace levels, but significant amounts may survive to be sampled and analyzed if the compound is present at levels of parts per million in the emissions.

Most of the numbered Methods incorporate specific guidance for quality control (QC) and quality assurance (QA) to ensure that data obtained are of known quality. Those who wish to apply the methodology must establish their capability and continuously train staff and demonstrate the quality of their results. Most of the guidance in the areas of method performance relates to requirements that the users of the methods:

- perform an initial demonstration of capability with the method and conduct ongoing demonstrations of capability,

- maintain accurate records, follow Chain of Custody procedures,
- demonstrate control of instrument parameters,
- demonstrate that equipment is not contaminated prior to use,
- perform appropriate QC daily for all instrumentation,
- establish the ability to generate acceptable accuracy and precision,
- locate/correct any problems in instrument operation,
- design and execute an appropriate scheme of blanks of various types, duplicates, matrix spikes, and matrix spike duplicates,
- determine the accuracy and precision of the methodology,
- qualify all data appropriately when QC criteria not met and,
- participate in performance evaluation studies, as available.

If the stationary source is not a combustion source, useful data can usually be obtained from stack methodologies, but methodologies originally developed for ambient monitoring[3] may also be useful, with appropriate allowance for the fact that emissions from a stationary source may contain significantly different matrices and higher than ambient levels.

Selection of sampling and analytical methods is governed by many considerations. Regulatory requirements dictate the selection in many instances. The detection limits which are required for the analytical methodology dictate a selection in many instances. Cost is frequently a major factor in determining which methodology will be used. Depending upon cost considerations, for example, it may be feasible to add an air toxics component to a source test program with a different primary mission. Selection of the best applicable methodology from a wide variety of potentially applicable methods is a very difficult choice.

Disclaimer

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THE INVESTIGATION OF SOIL SAMPLING DEVICES AND SHIPPING AND HOLDING TIME EFFECTS ON SOIL VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

Volatile organic compounds (VOCs) are the most often encountered class of compounds at Superfund and other hazardous waste sites. Many VOCs are considered hazardous because they are mutagenic, carcinogenic, or teratogenic and commonly are the controlling contaminants in site remediation projects. Because decisions regarding the extent of contamination and the degree of cleanup have far-reaching effects, it is essential that these decisions be based on accurate measurements of the VOC concentrations present. VOCs, however, present sampling, sample handling, and analytical difficulties, especially when encountered in soils and other solid matrices. Sample collection and handling activities can often introduce large sources of random and systematic errors compared to the analysis itself. Negative bias (i.e., measured value less than true value) is perhaps the most significant and most difficult error to delineate and control. This error is primarily caused by volatilization losses during soil sample collection, storage, and handling. Currently, no standardized procedures exist for sampling soils for VOC analysis. Several different samplers are available for collecting intact and disturbed samples. Samples are usually removed from the sampler, which often disturbs intact samples. Samples are then placed in glass jars or vials and sealed with Teflon-lined caps. Practical experience and recent field and laboratory research, however, suggests that procedures such as these may lead to significant loss of VOCs (1,2).

EXPERIMENTAL FEATURES

Experiments were conducted to evaluate sampling and sample handling techniques for the collection of soil for volatile organic analyses (VOA). Because natural soil systems can be extremely heterogeneous, experiments were performed by using large (18 in. i.d.) reconstituted soil columns. The soil was contaminated by the upward diffusion of VOCs from a glass-bead layer beneath the soil. This approach produced very homogeneous material for the evaluation of sampling devices and various sample handling scenarios. Figure 1 shows the horizontal and vertical homogeneity in bulk density and moisture content obtained by this column packing procedure.

Four different sampling devices (treatments) were evaluated: (1) acetate liner (4 cm i.d.) the contents of which were emptied out and disturbed, (2) split-spoon sampler with a brass liner (4 cm i.d.), (3) acetate liner (4 cm i.d.), and (4) acetate liner (2.5 cm i.d.). Samples from each device were placed in either a 40-mL VOA vial or a 125-mL wide-mouth jar.

Treatment 1 (disturbed vial sample) exhibited the largest VOC concentrations (Figure 2). The disturbance resulted in a homogenized material that had a higher concentration than the original sample because the shallow, low-VOC-level soil was combined with the deep, high-VOC-level soil. A vertical concentration gradient in the soil column was the cause of the elevated VOC levels in the disturbed sample. The vial-held disturbed sample yielded greater VOC concentrations than the jar-held disturbed samples, which indicates that VOC losses occurred during the homogenization and separation into aliquots as specified in EPA Method 8240. Of the undisturbed samples, the jar-held samples collected with larger diameter samplers (brass or acetate liner) exhibited higher VOC concentrations than the jar-held samples collected with the small-diameter, acetate-lined sampler. Samples collected from the large and small diameter intact cores, using a subcorer, yielded essentially the same VOC levels. Collection of a small sample from an intact core with a subcorer and extrusion into a 40-mL VOA vial maintained the integrity of VOCs better than jar-held samples. The vertical concentration gradient, however,

made direct comparisons difficult. Differences between jar-held and vial-held samples were probably caused by sample pretreatment rather than by leakage of VOCs from the containers.

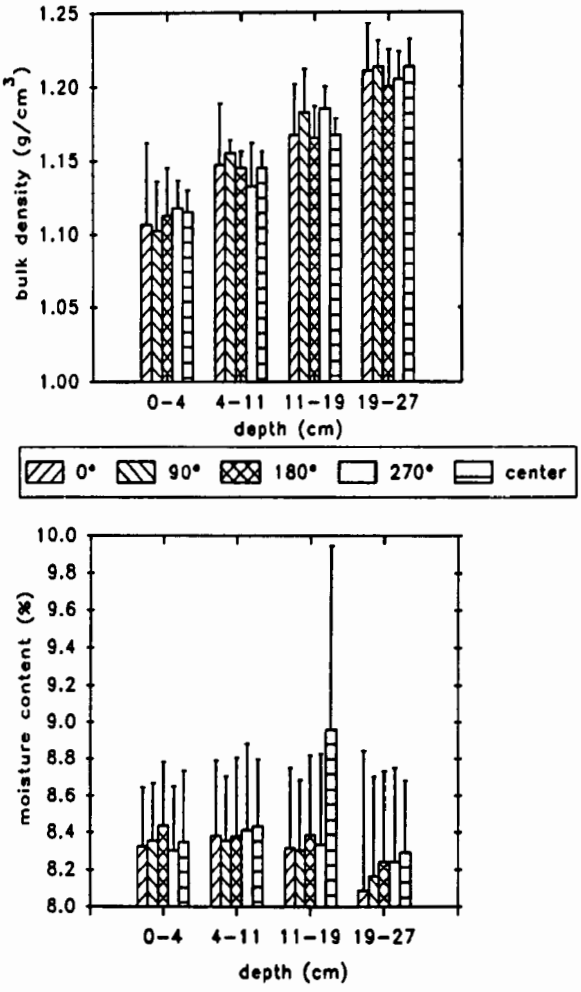

Figure 1. Horizontal and bulk density and moisture content obtained by column packing procedure.

Air shipment of soil samples held in commercially available sample containers was investigated. Samples shipped by different air carriers underwent changes in pressure and temperature. The results of pressure and temperature monitoring on three commercial air carriers are presented in Figure 3. This is obviously a small sampling of the environmental conditions that occur in aircraft cargo holds. These conditions will vary with the type of aircraft, the altitude at which the aircraft flies, and the time of year. The shipment container the monitoring devices were housed in was not insulated, so the observed pressures and temperatures are the actual ambient conditions inside the cargo hold. In-flight intervals are indicated by negative spikes in pressure. A pressure differential of as much as 2 psi was exerted upon sample containers. The integrity of VOC soil samples may be jeopardized when subjected to decreased pressures in the cargo holds of aircraft.

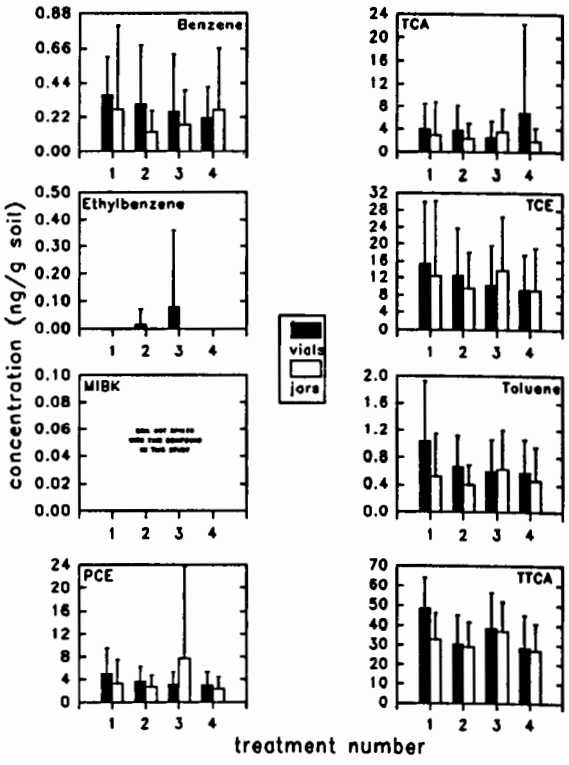

Figure 2. VOC concentrations in vial-held and jar-held samples collected with four different sampling devices.

The objective of the shipping effects study was to evaluate the stability of VOC in soil samples shipped and held in various commercially available containers. Five soil columns were reconstituted and samples from each column were taken in the following manner:

Treatment #1 - A 1-5 g aliquot was extruded into a tared 40-mL I-CHEM amber-glass VOA vial and sealed with a Teflon-lined septum cap.

Treatment #2 - A 1-5 g aliquot was extruded into a tared 40-mL I-CHEM amber-glass VOA vial and sealed with a modified purge-and-trap cap (Associated Design & Manufacturing Co., Alexandria, VA -- ADMC). Prior to analysis the sample with an ADMC cap was attached directly to the purge-and-trap unit by pushing the sparger tube into the cap thus dislodging the Teflon boiling ball lodged in the bottom of the cap into the vial.

Thus the sample was exposed to the atmosphere for only fractions of a second.

Treatment #3 - A 1-5 g soil was extruded into a tared 40-mL QORPAK amber-glass VOA vial and sealed with a Teflon-lined septum cap.

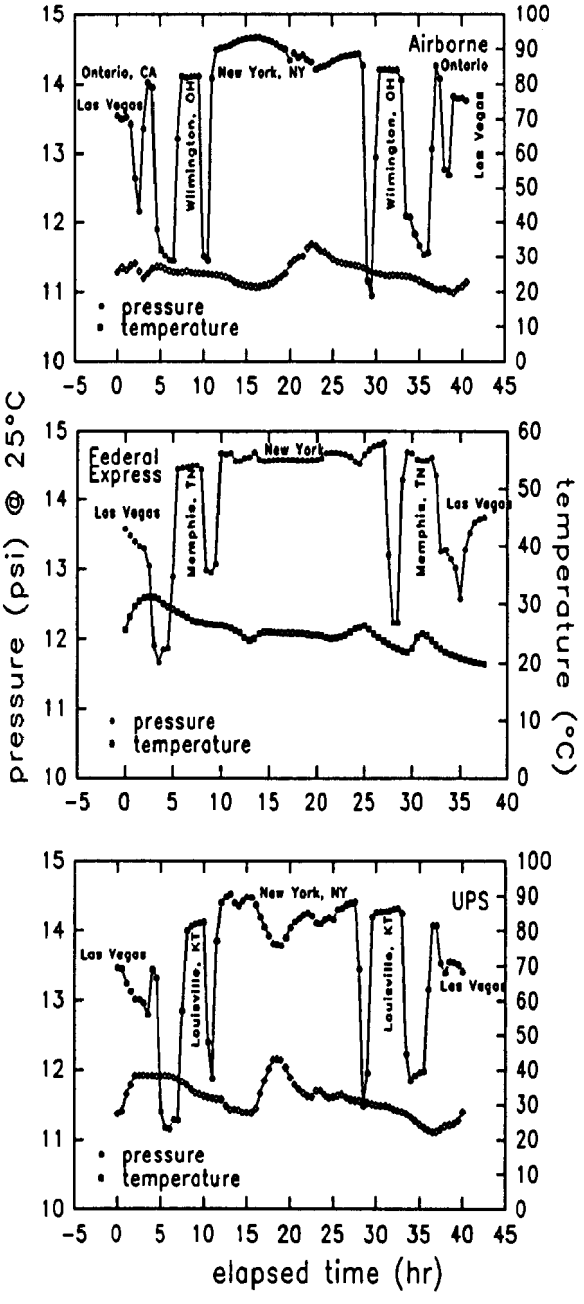

Figure 3. Preliminary pressure and temperature measurements.

Treatment #4 - A 1-5 g soil was extruded into a tared 40-mL QORPAK amber-glass VOA vial and sealed with an ADMC cap.

Treatment #5 - the entire contents of the middle liner section was extruded directly into an Eagle-Pitcher 125-mL wide-mouth jar (Eagle Pitcher Industries, Inc.) and sealed with a solid phenolic cap lined with Teflon. (Prior to GC analysis the contents of the jar samples were prepared as per EPA Method 8240 specifications.)

Treatment #6 - the entire contents of the middle liner section was extruded directly into an Eagle-Pitcher 125-mL wide-mouth jar (Eagle Pitcher Industries, Inc.) and sealed with a solid phenolic cap lined with Teflon.

For the shipping effects study one set of duplicates was placed in an ice chest and held in the laboratory. Another set of treatment duplicates was placed in an ice chest with several Freeze Gel packs and shipped on Federal Express. When samples returned to Las Vegas, NV, after two days, both held and shipped samples were removed from the ice chests and placed in the freezer until analysis.

All the containers evaluated adequately withstood the negative pressure differentials exerted by air shipment (Figure 4). Jars and vials may be equally suitable for shipping samples via air carrier. The greatest VOC loss occurred when soil samples were transferred from the sampling device to the container and when the samples were prepared in the laboratory for purge-and-trap analysis.

SUMMARY

The optimum soil sampling procedure reduces VOC losses by minimizing sample disturbance during collection and transfer to a container. The optimum scenario for maintaining the integrity of VOCs in a sample was found to be collection of an undisturbed sample with a tube-type sampler (split-spoon or zero contamination sampler) that has a precut liner. The soil in the middle liner section was used for sample collection because it represented the least disturbed material. A 2-g aliquot was taken from the center of the exposed soil surface in the liner by using a subcorer. The contents of the subcorer were extruded directly into a tared 40-mL VOA vial and the vial was sealed with a modified purge-and-trap cap. The vial was connected to the purge-and-trap unit without exposing the sample to the atmosphere.

ACKNOWLEDGMENTS

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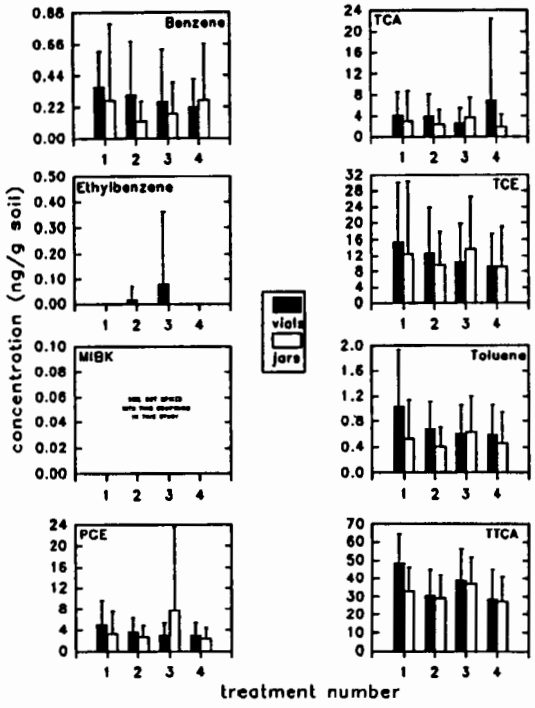

Figure 4. Shipping effects in containerized samples.

Malley, Mark Sweeney, and Heath Havey for sampling support; and Dick Hannah for supplying the pressure transducer used in these experiments. We thank to Roger Shura of EPA EMSL-LV for instrumental support during the shipping experiments, and we thank Bill Ahlert of Lawler, Matusky, and Skelly Engineers for receiving and returning air-shipped samples.

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NOTICE

Although the research described herein has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract No. 68-03-3249 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

DEVELOPMENTAL LOGIC FOR ROBOTIC SAMPLING OPERATIONS

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In the past decade great strides have been made in the application of remotely controlled mobile robots. Uses for one type of mobile robot known as a sampling robot has been successfully demonstrated in the nuclear and space industries. Two examples of successful applications of sampling robots are the Remote Core Sampler used at Three Mile Island to determine the depth and severity of radioactive contamination in containment walls and the Viking explorer which took and analyzed soil samples from the surface of Mars. Both of these applications had very similar developmental driving forces: the cost of performing the operations with humans was prohibitive and the environments were too hazardous to even consider it. In the case of the TMI robot, existing technologies were utilized in a cost effective manner to perform required operations while for Viking, new technologies were developed especially for the mission. In both cases, however, the beneficial returns outweighed initial development costs.

The most important factors to consider when undertaking the development of robotic equipment for sampling operations for field screening of hazardous wastes and toxic chemicals are cost, options, and the scope of the applications.

The primary factors that have an impact on the development of robotic sampling operations include:

- Does a robotic system yield an obvious advantage?
- What are the specific tasks the robotic sampling system must perform?
- Is it possible to perform these tasks with one transporter equipped for bolt-on tooling?
- Where will controls be located? Is portability an issue?
- What other tasks could the robotic sampling system perform, or support through reconfiguration, which would yield positive benefits?
- What unique or unevaluated conditions will be encountered which may require engineering evaluations, materials or component testing, or safety systems? Who will put together the expertise to properly address these issues?
- How will the robotic system be integrated into operations? Who will provide overall project management, design and fabrication and training of operators?
- What precautions must be taken to control contamination encountered by the robotic device?

The answers to these questions will begin to put the major scope of operation into perspective. However, there are many other items that will require attention both throughout the evolution of the operation and afterwards.

Cost Considerations

Cost must be evaluated thoroughly. The amount of money saved through the elimination of protective clothing, the improvement of worker safety, the reduction of manual staffing requirements, and the reduction of waste generated can rapidly reduce the initial estimates of the cost of a robotic operation. Conversely, application of new technology may be hindered by the unanticipated behavior of materials in untested environments, the failure to adequately research known limitations of existing technology, and uncalibrated engineering solutions to assure satisfactory performance. Any one of these factors can drive the cost beyond acceptable limits. In some cases, however, cost is not a factor. For example, when a particular operation is required and there are no existing methods to perform that operation, cost may cease to be a primary factor in the decision making.

Technological Options

One of the first decision points in the development process is whether to use existing technology or

techniques or to develop new technology for the application. This decision must be made in light of the capabilities of the available technology, whether existing equipment or techniques could be modified to accomplish the task, the projected capability and cost of new technology, and the risk of developing the new technology.

The primary objective of most operations is to accomplish a task reliably, safely, on schedule, and within budget. The confidence in the capabilities of the equipment and techniques to be used typically drives the time and budget projections. The sensitivities of budget and schedule make the technology development decision particularly difficult. In some cases, a competitive advantage in the marketplace can be established with the development of a new technology, offsetting the initial development costs. However, when the use of existing techniques is possible and feasible with respect to budget and schedule projections, it is difficult and risky to choose to develop a new technology and place the operational goals at risk. The development of new technology becomes an attractive alternative when the costs for existing techniques are exorbitant, the available technology is insufficient for the task, or a competitive advantage can be established in the marketplace.

Development Strategies

There are two strategies available when introducing new technologies: the ideal strategy and the pragmatic strategy. The ideal strategy presents the opportunity to develop the application of a new technology in parallel with the application of a proven technology. In this case, the application of the new technology is gradually phased into operations without creating disruption or putting objectives at risk. With time, the new technology permits the operation to become more effective and increases the competitive position of developers, rewarding them for their patience and vision through economic savings and gain.

Operational reality is more pragmatic. New technology should be seriously considered when necessary operations cannot be completed with available technology, when the necessary operational risk poses safety concerns that cannot be overcome, or when regulatory agencies prohibit the use of personnel or current equipment. Thus the developers of successful technologies are rewarded for their risk and vision through completion of operational needs often preventing economic penalties and potential losses. This defines the pragmatic strategy for introducing a new technology. Note that the results achieved by the two strategies are similar.

Development Approach

Idealistic and pragmatic development strategies require different approaches. In the idealistic scenario, the development should attempt to provide the greatest possible gain with the least risk to the operation. For example, a manufacturing operation that has several similar plants located in key geographic areas should attempt to identify problem areas in all plants, then develop and prove robotic technology in one plant. After the technology has been proven it may be applied in other plants with much less risk and a greater potential for gain. Each of the plants could be selected to develop one application of new technology thoroughly, then introduce it to the other plants and staff, achieving rapid improvements in productivity.

Pragmatic development approaches generally do not require extensive evaluation to determine the most immediate area of need. For example, at Chernobyl, an operation was required to move unshielded nuclear fuel from the roof of one facility into the void left by the disaster at an adjacent facility. Similarly, at Three Mile Island, there was a need to remove the damaged core and radioactive sediments from within the reactor facility. At both of these accident sites, the operation staff knew exactly what needed to be accomplished, the question was how it could be accomplished.

A potential disadvantage of the pragmatic approach, and of the development of new technology/equipment in general, is the lack of clearly defined, ongoing objectives for the new equipment. All too often, new technology or equipment is developed for a very specific, one-time operation without planning for other applications. Developers should always look beyond the immediate operational needs and attempt to tailor the development process so that the new technology or equipment can be easily reconfigured to meet future operational needs.

An example of this development foresight is provided by Niagara Mohawk Power Corporation. This New York electric utility recently developed a robotic device to disassemble a conveyer system and to clean an area where equipment malfunction resulted in stored radioactive materials which could not be easily retrieved by plant personnel. Although it was possible but undesirable to utilize personnel to perform this task, the developer decided to develop a specialized robotic system to accomplish the task. They required that the design of the device be reconfigurable to accomplish both the specific task at hand and additional future operations. The result of this endeavor is that the robotic device has successfully completed the specific work required, and will later perform several other planned tasks. This example illustrates how a pragmatic situation was used

as an opportunity to develop robotic equipment and technology which achieved the immediate objective and will provide ongoing benefit to the utility through increased safety of their personnel, reduced requirement for protective devices, and improved operational effectiveness. (1)

Lessons from Experience

The design of robotic devices should incorporate functional requirements for all conditions that can reasonably be expected to be encountered during the deployment of the device. Any additional capabilities should be evaluated in light of their cost, the level to which they would enhance system performance, the extent to which the added capability would avert catastrophic system failure, and the potential cost of a catastrophic failure.

The following is an example of when enhanced performance was justified. In the design of the Remote Core Sampler, a break-off actuator was specified to assure safe return of the device and teleoperated transporter in the event the core did not break and the drill became embedded in the concrete. During sampling operations the drill was embedded in the wall at full depth, the core could not be broken, and the drill could not be removed. The break-off actuator allowed the retrieval of the robotic sampling device and the transporter without difficulty, effectively averting the catastrophic loss of the robot. This was a cost effective enhancement.

On another mobile robot developed for TMI, a 10 horsepower electric hydraulic pump powered the onboard systems. A redundant pump was specified to assure total operability in the event of pump failure. Only one fluid reservoir could be fitted into the space available. The redundant pump would also have been disabled in the event of a fluid loss from the primary system. A much smaller pump with a separate reservoir dedicated to the operation of the primary propulsion units at a reduced speed would have been a better choice.

The lesson from these examples is that redundant, or backup, systems may be very effective and actually salvage some operations and equipment. It is important to have operations personnel and designers work closely to achieve realistic functional requirements for the robotic equipment in light of the environment in which it will be deployed.

Another important lesson from our experience identifies the immense value of the use of transporters with bolt-on tooling instead of multiple dedicated tooling systems. The Remote Reconnaissance Vehicle (RRV), used during the clean-up of TMI was specifically designed and constructed to permit attachment and manipulation of teleoperated and robotic payloads to perform the entire scope of operations required for completion of the project. In addition, this equipment has general application to other future needs. (2)

Bolt-on tooling used with the RRV included:

- Radiation Survey Equipment
- Core Sampling Equipment
- Kraft Undersea Manipulator
- Sludge Sampling System
- Sludge Vacuuming and Pumping System
- High Pressure (Water) Flushing Equipment
- Ultra High Pressure (Water) Concrete Scarifier
- Abrasive Cut Off Wheels
- Rotary Impact Drills

It would have been impossible to equip the RRV with dedicated systems for each of these tooling functions. Given the performance record of the system, the transporter concept with bolt-on tooling was a valuable asset. We assert that the use of bolt-on tooling is also appropriate for field screening robots — making them capable, flexible, and reliable.

With a highly reliable transporter, the tooling does not have to be infallible. In the event of tooling malfunction, the transporter returns the equipment to a controlled area for decontamination, repair, or replacement. In the event that multiple sample types are required, tooling for each type of sample could be exchanged after completion of each sampling step and the program continued using the same transporter.

Requirements for Robotic Sampling

One of the most frequent problems observed which results in poor sample results has been the lack of attention to basic technique. Common examples of conditions which destroy the results of samples before they ever reach the laboratory are the collection of gas samples by vacuum pump into sealed vials not adjusted to standard temperature and pressure for analysis, the collection of soil samples which were deposited in the same pouch without being individually sealed, and the use of the same scoop for all samples collected.

To achieve accurate characterization of a site it is imperative that samples are taken under conditions that guarantee their integrity. This requires that individual containers be maintained clean prior to sample collection and be kept sealed with the contents isolated during

transportation and storage. Also, control samples must be taken frequently enough to verify the integrity of the sampling system and the identity of the samples and their location must be accurately maintained. This is a tall order for a robotic sampling system and requires intense attention to detail.

Some reliable techniques must be used to plot the exact location of the individual samples. For a specific site, position readings could be taken from fixed markers by camera, sonar, or laser technology. In a more sophisticated setting with larger distances needing evaluation by a mobile robotic device, location may be documented by satellite triangulation.

It is also critical that the robotic device does not cross contaminate the sampling site. Specifically, the tracking of surface materials from one location to another or the loss of sample materials during collection could potentially contaminate previously uncontaminated soil.

The specific contaminants to be investigated and the degree of their toxicity determine what support will be required. Some hazardous wastes and toxic chemicals may be evaluated in simple field facilities while others may require more sophisticated evaluation. The degree of hazard present, the ease of analysis, the number of samples to be analyzed, the requirements and cost for transportation, and the size and needs of the project are all factors which will determine support requirements.

Operational Safety

It is important to consider the safety of personnel in the proximity of robotic devices. The area should be restricted to exclude personnel not directly working with the equipment. However, since robotic devices often draw attention from admiring spectators, it should be expected that people not working directly with the robots will often be present. Measures must be undertaken to ensure the safety of all those present.

Summary

A decade ago several people were faced with a unique problem at the Three Mile Island reactor. They envisioned employing a mobile robot that would perform all of the operations necessary to solve the problem. It took three years to make that vision a reality. Similarly, last year a group of people at Niagara Mohawk envisioned using mobile robots to help solve some of the problems they had encountered. In this case it only took six months to transform that vision into reality.

The amount of time necessary to make a reality of such visions has decreased tremendously during the past decade. Not surprisingly, the technology available has had a tremendous increase during the same timespan. Relevant applications of such technology are increasing each day with the enforcement of more stringent regulations and with an increased public awareness of the effects of exposure to hazardous substances. Currently, the nuclear and space industries are at the forefront both of robotic technology and the applications of that technology. Robotic technology is now at a point where it can be effectively applied to the characterization and remediation of hazardous waste sites.

Applications with a greater volume of repetitive operations will be more effective than those which have a once and done scope. [3] The use of personnel involved in previous projects provides a continuity of experience which also increases effectiveness, even for the once and done applications.

For companies with several sites which require characterization, the greatest effectiveness of mobile robotic operations is projected through use of a dedicated team which provides management, supervision, and continuity of all sites from a central location.

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PRACTICAL PROBLEMS ENCOUNTERED IN REMOTE SENSING OF ATMOSPHERIC CONTAMINANTS

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Recent sensing technology is now ready and able to play a significant role in Environmental Protection Agency (EPA) programs. The U.S. Army Chemical, Research, and Development Center (CRDEC) has been involved in remote sensing of environmental contaminants since 1951. During this time much practical information has been gathered concerning designing, building, and testing remote sensing systems. This paper briefly examines the practical development of remote sensing systems which could benefit the EPA in its mission to detect potential environmental contaminants.

Perhaps the least exciting and most tedious of any remote detection program is data base development. But for an instrument which will be used to detect and discriminate thousands of specific chemical species among a plethora of natural and manmade interferents this is the most important first step in any standoff detection program. The detection and discrimination of environmental pollutants is an exceedingly difficult problem because a clear base line measurement is almost impossible to get. This makes a complete data base very important.

There are two types of data bases used in the research and development of any remote detection instrument. The initial working data base consists of spectra, interferents, and backgrounds acquired either from in-house laboratory spectrometers or purchased from spectral data base houses. The second type is an instrument specific data base developed with a first generation sensor (a crude, working instrument designed from first principles). The initial data base is used to determine the type of instrument, the spectral band in which this instrument will work, the spectral resolution and some initial detection and discrimination parameters. This data base need not be quantitative (i.e. calibrated to a specific instrument response) but quantitative data will save some steps in future development. The instrument database is used to fill in details of instrument development and "finetune" the instrument for the work for which it is being designed.

For the most part two categories of remote detectors exist, active and passive. Active systems are based on the LIght Detection And Ranging (LIDAR) concept. The detection scheme, whether it is differential absorption (DIAL) differential scattering (DISC), Raman, or laser induced fluorescence (LIF), is dependant on the detection

requirements of the system. The LIDAR emits LASER radiation, at frequencies appropriate for the chemical under investigation, and the radiation is scattered back through a telescope to the detector for analysis. Passive systems are based on either a grating or an interferometric spectrometer. Interferometric systems are usually employed for portable field instrumentation because of the size and weight advantage over grating systems of comparable sensitivity. Passive systems use the ambient radiation emitted or absorbed by the chemical vapor under investigation as the basis for detection. The detection analysis is similar to that used in a laboratory Fourier transform infrared (FTIR) spectrometer. The choice of either a passive or active system is a consequence of the spectral band of interest, resolution, physical state of the contaminate, and the use concept.

The selection of spectral band and resolution is, at least initially, a consequence of the chemical species you want to identify. In order to detect a specific chemical you must select a band and resolution which affords the best chance of identification of the chemical. You must also consider all possible interferents against all backgrounds you may encounter in your use concept. This a particularly important decision since all subsequent development will proceed from this decision point. You must also determine what resolution you require to completely discriminate the chemical among possible interferents encountered in your use concept.

We have used the phrase "use concept" twice in the above paragraph - what is use concept? Use concept is nothing more than a notion as how, where, and under what conditions you will use your remote sensor. You can make your initial conditions something along the line of; I want to use the detector everywhere, under any conditions, and operated by an untrained chimpanzee. You then use some computer modeling and knowledge of current technology to back away from this initial use concept. This is where a quantitative data base comes in handy. If you have absorptivity coefficients or scattering cross-sections available for your chemical species and interferents and spectral emissivities for the backgrounds then you may "build" computer models of detectors and estimate their sensitivities. Computer models are very convenient for estimating performance for instruments with widely different design concepts including changes in fields-of-view, detector element response, LASER power, LASER frequency agility, etc. The results of these models can then be incorporated into a first generation instrument which can be used to develop a database that is instrument specific.

Unless you have ample resources in electro-optics, opto-mechanics, optics and system integration you will run into some difficulty building your first instrument. You have four choices, design and fabricate the instrument in-house; design in-house, have the parts fabricated by contract and integrate the instrument in-house; design in-house but fabricate by contractor; or find a contractor to do the whole job. The first option requires considerable in-house expertise and fabrication facilities but usually very little money. The second option requires the same in-house expertise but almost no fabrication capability and only slightly more funds. The third option requires some in-house technical capability and more money and the last requires in-house technical capability, a good contracting officer and lots of money. For a research/development operation we suggest one of the first two options and of these we think that the second choice is the best. Our reasoning goes like this all of these options require at least some in-house technical knowledge and if you don't have any in-house fabrication capability then the only other requirement is some integration capability. In addition you can rely on some of

the expertise you will obtain from the various parts vendors. This integration capability can be initiated with a minimum of startup time and allows your in-house personnel to become intimately familiar with the instrument they are integrating. This intimacy will become vitally important in the later stages of development.

You've got your first instrument in-house and you've worked out most of the electronic and mechanical bugs. What's next? - calibration, characterization, and collection!

Calibration is a basic precept to understanding instrument response and most of the operational attributes of the instrument. An unknown instrument response hinders the ability to make any type of confident detection and completely destroys any discrimination capability. The initial calibration method is dependant on the type of instrument. For example most passive FTIR based instruments are calibrated against some reference source which, within some practical error, mimics a blackbody, this permits an understanding of total instrument response.

Instrument characterization is essentially a "calibration" taking into account use concept, optical parameters (i.e. field-of-view, field-of-regard, etc.), measurements against contaminants and interferents in a controlled environment, and a measurement of how instrument response changes in the operating environment. These measurements permits the operator to gain a complete understanding of the instruments capabilities or lack of capabilities, the logistics of maintenance and operation, and its usefulness as a contaminate detector.

Data collection in order to define an instrument database is a time consuming, tedious, and expensive endeavor but is vitally important to complete instrument development. There are two stages of data collection, open air testing of interferents, simulants, and natural backgrounds and controlled chamber testing of obnoxious and dangerous contaminants. The chronological development of this instrumental database is of little technical importance and is based solely on an established or changing use concept. Chamber testing of the obnoxious contaminants is necessary to establish a sensitivity to known quantities and is performed in conjunction with simulant sensitivity measurements to corroborate instrument responses to open air tests. Open air testing of interferents, backgrounds, and simulants establishes instrument performance in the operating environment.

Although detection and discrimination have distinctly different definitions in theory they are practically impossible to separate in practice. They are intimately linked simply because you cannot make a proper detection of any contaminate without the ability to discriminate it from background clutter, for this reason we will discuss them together.

The initial ability to detect and discriminate particular contaminants or class of contaminants rests solely on the human perception. The operator must separate the contaminate from the interferents and backgrounds based on the use concept, the operator's knowledge base, the depth of the database, and the operator's ability to understand and adapt to changing environmental conditions. By the time instrument development reaches this point the use concept has, hopefully, been established and this leaves us with the task of developing some type of detection and discrimination algorithm based on the remaining parameters. You can, given an infinite amount time, money and manpower, develop an empirical solution to this problem. For all practical purposes this is impossible, and any solution based on a subset of parameters has at best a very limited success rate. Then what is your alternative? Statistics! The saviour of the

working scientist and the bane of the absolutists. Unfortunately there is no single statistical method which defines every detection and discrimination problem - indeed there are as many methods as there are problems. The method is defined by all of the ingredients in the development recipe, the use concept, instrument type, knowledge base, and database. It is just a matter of finding a method that fits (e.g. filtering, database matching, etc.) or developing a new method from a combination of previously defined methods. What ever your choice we strongly urge you employ the services of an experienced statistician from the beginning of your development effort. It will save you considerable time and frustration.

There you have it. A practical, albeit brief, recipe for the practical problems encountered in the development of remote sensing instrumentation. CRDEC has developed several remote sensors since 1951, some have successfully managed the development cycle and some have not. But despite all the requirement and funding vagaries, CRDEC has acquired an extensive in-house capability based on years of practical experience. This experience and capability is available to the EPA for its own detection programs.

A SI/LI BASED HIGH RESOLUTION PORTABLE X-RAY ANALYZER FOR FIELD SCREENING OF HAZARDOUS WASTE

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INTRODUCTION

Only four years have passed since the first publication describing the application of a portable x-ray analyzer, (XRF), for on-site chemical characterization of contaminated soil [1].

During that period, field portable x-ray fluorescence (FPXRF) has established itself as the most useful technique for a broad range of environmental applications. Its well known attributes such as ruggedness, nondestructiveness, minimal sample preparation and speed of analysis are indisputably the factors contributing to its growing success. However, it was technological advances in the proportional detector (high resolution) and in microprocessor technology (computing power and portable architecture) which really made feasible a small, truly portable, battery operated device with analytical capabilities similar to the laboratory XRF systems.

FPXRF ANALYZER CONCEPT

The most successful implementation of the FPXRF for the on-site screening and analysis of inorganics in hazardous waste is based on the aforementioned microprocessor controlled analyzer connected to a hand-held probe.
The probe contains an x-ray source(s), a detector and a means of reproducible presentation of the sample for measurement. The electronic unit accepts the signal from the probe, processes it and displays the result. It also contains power supplies and interfaces for communicatiion with the operator and peripheral devices.

A sealed radioisotope capsule emitting x-ray or low energy gamma rays is a preferred source of primary radiation for portable instruments. Such sources are rugged, compact, light weight and drift free.

A high resolution, gas filled proportional detector has been for years an integral part of the most successful FPXRF analyzer available, the X-MET 880. Its much improved energy resolution of 10 to 12% as compared with conventional proportional counters (20%), made possible abandonment of mechanical means of element separation (so called nondispersive XRF, using a pair of balanced filter for each measured element) in favor of energy

dispersive XRF, based on electronic separation of elements according to their characteristic x-ray energies. More recently, the probe of the analyzer has been modified to accept two excitation sources and thus has extended the range of elemental analysis of the probe.

Fig. 1. FPXRF Analyzer X-MET 880 with a gas filled detector probe.

QUANTITATIVE ANALYSIS

Quantitative analysis is accomplished by employing empirical calibration methods. Usually a set of 15 to 20 samples is required to develop calibration curves for up to six analytes per calibration program (model). The instrument can quantify six elements in each of its 32 calibrationh models. Availability of calibration samples may pose a problem especially in situations where not much is known about the site to be analyzed. Since XRF technique, it is important that the calibration samples match in matrix composition the unknown samples to be analyzed. This condition can rarely be met, although the most accurate results have always been obtained when the analyzer was calibrated with CLP analyzed samples collected on the site to be investigated (so called site specific calibration samples). An alternative solution is calibration of the analyzer with a set of spiked soil samples, so called site typical samples [2]. This approach results usually in a systematic error (bias) in the XRF measurements. However, it can be easily corrected as it is a common practice to submit 10 to 20% of all samples measured on the site with the FPXRF for verification by contract laboratory program (CLP) analysis. By correlating the XRF with the CLP results one is able to correct for the bias in the remainder of the XRF results.
This approach has been successfully used for screening and preliminary evaluation of levels of contaminats on a number of sites where FPXRF could be accepted as a Level I analytical method (that is inaccuracy up to +/- 50% relative and precision up to +/- 10% relative) [3].

HIGH RESOLUTION SI/LI PROBE

While the FPXRF analyzer configuration, described above enables one to reach detection limits down to 100 to 200 mg/kg for elements such as Cu, Zn, Pb, As, etc. [2], it has demanding calibration requirements when handling the diverse sample matrices common in analysis of hazardous waste. To address this problem a new, Si/Li based, hand-held probe was designed. The probe combines unsurpassed energy resolution with portability and ease of operation.

The heart of the probe is a Si/Li detector featuring 30 mm^2 active area and an energy resolution better than 170 eV for the K-alpha line of manganese at 1000 cps.
The detector is cooled by a small

LN_2 capacity with a holding time of 8 hours. Dewar construction enables operation of the probe in <u>any</u> position making it truly portable. There were no adverse effects observed due to thermal cycling of the probe. The probe can accommodate two radioisotope sources to cover the elemental range from K to U.

Fig. 2. A prototype Si/Li probe.

The probe is equipped with interlock mechanisms which prevent source exposure and high voltage supply to the detector, whenever the amount of LN_2 in a dewar is not sufficient. The probe can be easily set-up directly on the soil surface for true in-situ measurements, or it can be, after turning it over, used as a sample probe to measure samples presented in cups.

Perhaps the most important feature of the probe is that it can be used directly with the existing population of X-MET 880's. The Si/Li probe is therefore a useful addition to the many types that already are used with this analyzer.

Fig. 2 shows a photograph of the prototype Si/Li probe.

PROBE PERFORMANCE

The advantage of the state-of-the-art energy resolution of the probe can be seen in Fig. 3. The figure shows two simulated spectra as would be generated in a sample with Cr to Fe concentration ratio of 1 to 20.

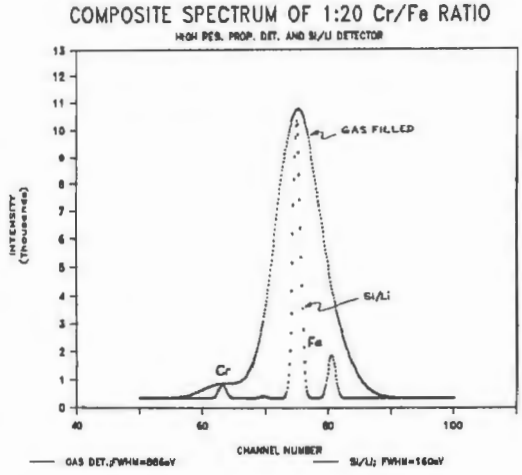

Fig. 3. Comparison of detector resolution.

It is clear that with a Si/Li detector it is possible to distinguish a minor Cr peak from a massive Fe peak, whereas even with a high resolution proportional detector such a faint Cr peak can hardly be seen.

Fig. 4 illustrates a typical soil spectrum excited with a Cd-109 source and collected with the Si/Li probe connected to the X-MET 880 FPXRF analyzer.

As expected, all peaks are clearly resolved except for the notorious pair of As K-alpha and Pb L-alpha. However, it is important to note that the resolution of the detector is not the only parameter determining its overall performance. For example, a gas proportional detector has much higher detection efficiency than a small Si/Li diode. This is due to the fact that a typical proportional counter collects radiation from a much larger solid angle than a typical Si/Li detector. However, a

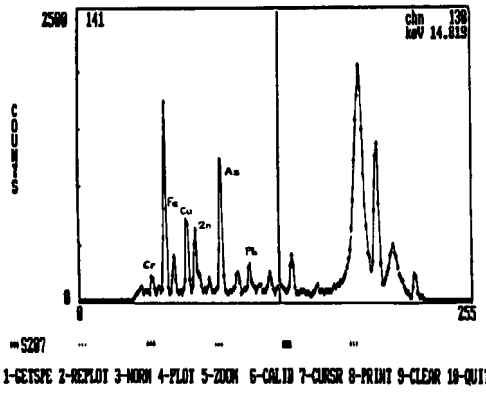

Fig. 4. Spectrum of soil sample.

proportional counter will usually exhibit also a higher background which somewhat offsets its efficiency advantage. The improvement in sensitivity and detection limits achievable with a Si/Li detector comes mainly from the low background of this detector.

Although the proportional detector exhibits excellent performance with conditions of optimal separation of more than Z+2 atomic number spread, when adjacent elements (or overlapping spectral lines) are present, enhanced resolution is of importance. In such cases of severe spectral overlap and unfavorable ratio of analyte concentration to interfering matrix element the resolution factor plays a critical role.

Another important implication of superb energy resolution is the ability to separate coherent and incoherent backscatter peaks of primary radiation. This enables one to implement a more sophisticated data treatment, such as those based on a fundamental parameters approach, which can better handle a diversity of sample matrices.

At present, the Si/Li probe can be used directly with the X-MET 880 in an empirical calibration mode. An extensive development program is being completed to implement a fundamental parameters based mode, initially in a PC connected to the FPXRF analyzer via its serial port.

Typical detection limits obtained with a Si/Li probe for a multielement matrix such as Cu, Zn, As, Pb are on the order of 30 to 80 mg/kg as opposed to a 100 to 200 mg/kg with a gas filled proportional detector.
Further work is in progress to further refine the final probe design and mathematical algorithms for data treatment. These results will be reported in the near future.

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Measurement and Analysis of Adsistor and Figaro Gas Sensors Used for Underground Storage Tank Leak Detection

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ABSTRACT

Gas sensor properties are measured with the purpose of comparing two sensor technologies used for underground storage tank leak detection. Four types of Figaro gas sensors and the Adsistor gas sensor were tested in simulated underground storage tank environments using the Carnegie Mellon Research Institute (CMRI) automated gas testing facilities. This automated system monitored the sensors' responses while dynamically exposing them to various mixtures of methane, butane and xylene. The sensors were also tested to determine the effects of humidity on their responses. Sensor responses were characterized by sensitivity, selectivity, and speed of response and recovery to selected test concentrations of methane, butane and xylene. The test results are presented as a list of sensor specifications to allow the potential end user a direct comparison of these two different types of sensors.

INTRODUCTION

This study was initiated to help the users of underground storage tank (UST) vapor phase product leak detectors to better understand the capabilities and limitations of commercial vapor sensors. The study was limited to characterizing two types of commercial vapor sensors, the Figaro [1] sensor and the Adsistor [2] sensor.

Four types of Figaro gas sensors, models number 812, 813, 822, 823, and the Adsistor gas sensor were tested in simulated UST environments using the CMRI automated gas testing facilities. The characterization of these sensors resulted in a set of specifications that allows direct comparison between the different sensor types. The Figaro sensors are metal oxide semiconductor devices that operate at elevated temperature [1]. The Adsistor sensor operates at ambient temperature and it works on the principle of gas adsorption [2] in a polymeric material.

The selection of test gases was based upon a study performed by Geoscience Consultants, Ltd in 1988 [3]. This study detailed the hydrocarbon vapor concentration at 27 gasoline service stations from three diverse geographic regions in the United States. Their findings indicated that:

- all the surveyed locations had some evidence of underground methane and gasoline vapor products.
- methane existed in high concentrations at many locations.
- tracking butane concentrations would be useful in detecting recent gasoline leaks or spills.
- m-xylene was a large component of gasoline product.

Based on this study, methane was chosen as a potential interference that may cause false alarms for UST monitors. Also iso-butane and m-xylene were chosen as tags because they represent major chemical constituents in gasoline.

The sensors were tested to determine their sensitivity and cross sensitivities to methane, butane, and xylene and humidity to help the UST leak detector manufacturers to better understand how to use these sensors. For example, 1) if a sensor responds to methane but the instrument's user is unaware of this sensitivity, then, this instrument placed in the field could produce false alarms due to methane interference. 2) The humidity level underground at UST sites is considered to be near saturation [4]. If a monitor is calibrated with dry gas, and the sensor is placed in the damp underground environment, this also could lead to false alarms, or worse, no alarm will be set when a real leak is occurring.

Response time is not a critical sensor parameter for this application since leaks in USTs generally occur slowly and site monitoring is done on time scales of days and not minutes. However, recovery time can be important in situations where an accidental spill

occurs. In this case, if a sensor takes too long to recover from the spill, the detection of a true leak could be masked.

Sensor responses were characterized by sensitivity, selectivity, and speed of response and recovery to selected test concentrations of methane, butane and xylene. The test results are presented as tables of sensor specifications to show the potential end user the advantages and disadvantages of using various sensor types for monitoring underground storage tanks.

EXPERIMENTAL

The data presented was collected using the CMRI automated gas sensor characterization facility. The facility has been designed to study the behavior of gas sensors and characterize their response in terms of sensitivity, selectivity, speed of response and recovery, and stability. A computer controlled gas delivery and data acquisition system (GDS) creates the test atmosphere in the sensor test chamber and records the corresponding sensor responses. The GDS controls and sets proper levels of oxygen, nitrogen, and water vapor to create a clean baseline environment through a network of mass flow dilution modules. This clean air can then be contaminated with up to five different vapor compounds. For this study, the facility was modified to independently set concentrations for methane, (CH_4), butane (C_4H_8), and m-xylene (C_8H_{10}). The GDS maintained a constant flow rate of 1 liter/minute.

A second gas system, delivering clean humidified air, was used to maintain the sensor atmosphere when the sensor chambers were not connected to the GDS.

An on-line gas chromatograph was used to verify the delivery of gases to the test chamber both during and in between tests.

Three test chambers were built to house the sensors. One chamber was built to test 9 Adsistor sensors and two chambers to house 12 Figaro sensors, 6 of each type. All the materials used in the construction of the chambers were chosen to minimize contaminating the test atmosphere. The chambers were built to power the sensors and monitor their responses in accordance with manufacture literature. The volume of each test chamber was 1.2 liters.

The test chamber temperatures were monitored during testing. The recorded room temperature and that of the Adsistor test chamber temperature was 22°C ± 1°C. The temperatures of the Figaro test chambers were 33°C ± 1°C.

TEST DESCRIPTIONS

Several types of tests were performed to characterize sensor response. These tests include:

- Gas concentration ramp tests to determine sensor sensitivity and selectivity to individual test gases.
- Target gas excursion test to determine sensor response to the presence of multiple test gases.
- Water vapor excursion tests to determine sensor humidity response in the presence of multiple test gases.
- Response and recovery time tests to determine how fast a sensor responds to changing concentrations of test gas.

Gas Concentration Ramp Test

Ramp tests expose the sensors to a single test gas at a time. The sensors are exposed to five different test gas concentrations for each test gas. The ranges were 50,150, 500, 1500, 5000 ppm for methane and butane and 10, 30, 100, 300, 1000 ppm for xylene. Each concentration was held for 30 minutes before preceding to the next level. The sensors were exposed to clean air for two hours between each ramp.

Each of the ramp tests was performed at two humidity levels. The first set was conducted at 15,000 ppm of water vapor. This level was chosen to represent the humidity present at underground storage sites (97% RH at 55 °F). The second set was done in dry air (less than 50 ppm water vapor) to simulate sensor response when exposed to dry calibration gases.

Target Gas Excursion Test

This test was designed to show sensor behavior in the presence of all three test gases. The sensors were exposed to relatively small concentrations of the three gases, as a background level. Then each gas was separately raised to 10 times its background level. The background gas concentration level was set to 500 ppm CH_4, 500 ppm C_4H_8, and 100 ppm C_8H_{10} in air containing 15,000 ppm of water vapor.

Water Vapor Excursion Tests

This test was designed to show how changes in humidity effect sensor response in the presence of all the three test gases. The background level used was the same as in the mixture excursion test. The water vapor concentration was then changed in thirty minute steps from 15000 ppm , to 5000 ppm, to 1667 ppm, to 0 ppm water vapor, and then set back to 15,000 ppm.

Response and Recovery Time Tests
These tests were performed to determine the speed of response and recovery to set levels of target gases. The tests were performed in air humidified to 15,000 ppm water vapor. The sensors were measured at one minute intervals during the test. The xylene concentration changed in thirty minute steps from 0 ppm, to 1000 ppm, to 100 ppm, to 1000 ppm and back to 0 ppm.

The response time is defined as the time from when the new gas concentration is first introduced into the chamber until the sensor reaches 95% of its final reading. The recovery time is defined as the time from when the new gas concentration is first introduced into the chamber until the sensor reaches 95% of the total change in the sensor reading. The final reading for both recovery time and response time is defined as 30 minutes after the new gas concentration has changed.

SENSOR MODEL EQUATIONS

To simplify direct comparison of these sensors, mathematical model's were used to convert sensor resistance (ohms) into gas concentration (ppm). The model chosen for the Adsistor is the one suggested by the manufacture [2]. The model selected for the Figaro sensors is commonly used in the literature [5].

Adsistor Sensor Model Equations
Adsistor data was collected by measuring the sensor electrical resistance. The resistance is related to concentration for most gas vapor concentrations by equation 1.

Eqn. 1 $R = R_b 10^{c/k}$

where R = Measured resistance R_b = Resistance in clean air, k = Gas constant at ambient temperature, and c = Gas concentration (ppm)

The Adsistor sensor resistance versus concentration is reported to be a straight line when plotted on a semi-log graph [2].

For this paper, because the sensors did not respond to the lower test concentration, a two point fit between the 100 and 1000 ppm xylene were used to determine R_b and k in equation 1. Solving equation 1 for c yields equation 2 which is used to translate the measured Adsistor resistance into a measured gas concentration.

Eqn. 2 $c = k \log10(R/R_b)$

Figaro Sensor Model Equations
Figaro sensor data was collected according to manufacturer's recommendations and converted to sensor resistance using equation 3.

Eqn. 3 $R = R_l (V_B - V_R)/V_R$

where R = Resistance (ohms), R_l = Load resistor (3920 ohms), V_B = Voltage bias (10 volts), and V_R = (10- V_B) = Sensor voltage

The resistance concentration curve was observed to be approximately linear on a log - log plot. Therefore a power law model was adopted for these sensors as seen in equation 4.

Eqn. 4 (a) $\text{Log}(R) - \log(Ro) = B\log(c)$

(b) $R/Ro = c^B$

where R = sensor resistance, c = gas concentration (ppm), B = power law slope, and R_o = sensor resistance when c=1

The two parameters R_o and B are determined by considering measurements taken at c =100, and c=1000 ppm for the gas in question. Once the parameters are determined, the sensor resistance is translated into concentration by inverting equation 5

Eqn. 5 $c = \frac{R}{R_o} c^{\frac{1}{B}}$

RESULTS and DISCUSSION

For this abstract only data comparing the Figaro 823 sensor and the Adsistor will be presented. The poster board data presented shows that the Figaro 812, 822, and 823 sensors all have comparable responses. The Figaro 813 sensor is more sensitive to methane than butane or xylene and is of questionable use for UST product monitoring.

The test results are presented in terms of sensor specifications related to sensitivity, selectivity, response time, and reproducibility. The data presented in this paper are shown in Tables 1-3. The data is the average of nine Adsistor sensors, and six Figaro 823 sensors. The data are reported as the average measured sensor response along with the standard and percent standard deviations.

Sensitivity
The ramp tests were used to determine the test gas to which the sensors were most sensitive. The sensors were then modeled for this target gas.

The Adsistor sensors and the Figaro 823 sensors were clearly more sensitive to xylene than either the methane or butane vapors. Thus, these sensors were all modeled and calibrated for xylene.

Selectivity

The Figaro 823 sensors respond to both butane and xylene, but are more sensitive to xylene that butane. The ramp and excursion tests indicate that these sensors are basically insensitive to methane at the levels tested.

The Adsistors are sensitive to xylene levels greater than 100 ppm. These sensors are basically insensitive to the tested levels of methane and butane.

Water Response

The response of Figaro 823 sensors is strongly affected by changes in humidity. Changes in reading of more than 50% were observed when the humidity varied from dry to wet conditions. This is seen both in the ramp tests and the water excursion tests.

The Adsistor sensors readings show little effect due to short term changes in humidity.

Speed of Response and Recovery

Both the Figaro 823 and Adsistor sensors respond and recover more quickly when changing from one xylene concentration to another than from clean air to a xylene concentration level.

Reproducibility

All the Figaro 823 sensors tested in this study showed wide variations in the sensor parameters and responses. The spread in response ranged from 15% to 100% of each other.

The Adsistors sensors tested had model parameters and sensor responses with in 11% of each other.

CONCLUSIONS

Sensor specifications for direct comparisons of the two different sensor types, the Figaro MOS sensor and the Adsistor adsorption sensor, has been presented.

Both sensor types appear to have sufficient properties to be used for UST leak detection. Both respond well to xylene, with the Figaro sensor being more sensitive to lower levels than the Adsistor. Both sensor types are relatively insensitive to methane, which is the primary interfering compound underground. The observed butane response for the Figaro sensor is not a serious problem since butane is also a component of gasoline. The Adsistors as a group were more reproducible, and had a much smaller humidity interference in comparison to the Figaro sensors. These two properties make the Adsistor easier to calibrate and work with from an instrumentation point of view. However, the Adsistors were observed to have longer xylene recovery times than the Figaro sensor.

Stability is a major sensor specification not yet studied. It plays an important role in determining how a sensor is employed in UST monitoring. If a sensor changes with time, independent of the actual conditions, it could lead to false alarms and/or not being able to detect a leak. It is recommended that stability test be undertaken to determine the calibration periods of the sensors and how their characteristics change with time.

ACKNOWLEDGEMENTS

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Table #1: Figaro 823 Sensor Specifications

Model Parameters [Calibrated @15K ppm H2O]

	Average	Std. Dev.	% Dev.
B	0.56	0.12	21.4%
Ro	9.1E+04	3.6E+04	39.6%

Xylene Readings (ppm) @ 15K ppm H2O
Calibrated at 100 and 1000 ppm Xylene

Actual Conc	Average	Std. Dev.	% Dev.
10	10.7	5.8	53.8%
30	43.5	10.0	23.0%
100	100.0	0.0	0.0%
300	239.9	36.1	15.0%
1000	1000.0	0.0	0.0%

Xylene Readings (ppm) @ 0 ppm H2O

Actual Conc	Average	Std. Dev.	% Dev.
10	0.2	0.3	141.3%
30	1.4	1.4	100.0%
100	5.9	4.5	75.0%
300	38.8	21.5	55.4%
1000	437.8	136.7	31.2%

Cross Sensitivity (ppm Xylene) @15K ppm H2O

	Average	Std. Dev.	% Dev.
Methane 5000 ppm	23.5	8.6	36.6%
Butane 5000 ppm	793.4	792.9	99.9%

95% Response Time (Minutes) @ 15K ppm H2O

	Average	Std. Dev.	% Dev.
0 to 1000 ppm	15.30	6.7	42.3%
100 to 1000 ppm	10.18	7.4	68.7%

95% Recovery Time (Minutes) @ 15K ppm H2O

	Average	Std. Dev.	% Dev.
1000 to 100 ppm	3.33	1.0	31.0%
1000 to 0 ppm	4.08	0.9	23.1%

Table #2: Adsistor Sensor Specifications

Model Parameters [Calibrated @ 15K ppm H2O]

	Average	Std. Dev.	% Dev.
K	2987.72	308.26	10.3%
Rb	3.5E+02	3.5E+01	10.0%

Xylene Readings (ppm) @ 15K ppm H2O
Calibrated at 100 and 1000 ppm Xylene

Actual Conc	Average	Std. Dev.	% Dev.
10	61.5	2.8	4.6%
30	67.9	2.3	3.4%
100	100.0	0.0	0.0%
300	233.3	3.7	1.6%
1000	1000.0	0.0	0.0%

Xylene Readings (ppm) @ 0 ppm H2O

Actual Conc	Average	Std. Dev.	% Dev.
10	118.9	13.1	11.1%
30	126.4	12.5	9.9%
100	139.0	12.1	8.7%
300	251.3	10.7	4.3%
1000	997.6	9.7	1.0%

Cross Sensitivity (ppm Xylene) @15K ppm H2O

	Average	Std. Dev.	% Dev.
Methane 5000 ppm	62.9	4.0	6.3%
Butane 5000 ppm	61.8	3.2	5.2%

95% Response Time (Minutes) @ 15K ppm H2O

	Average	Std. Dev.	% Dev.
0 to 1000 ppm	7.29	1.5	18.6%
100 to 1000 ppm	7.86	1.8	20.5%

95% Recovery Time (Minutes) @ 15K ppm H2O

	Average	Std. Dev.	% Dev.
1000 to 100 ppm	> 30	0.0	0.0%
1000 to 0 ppm	> 30	0.0	0.0%

Table #3: Figaro 823 and Adsistor Sensor Response to Target Gas Excursion Test and Water Vapor Excursion Test
Calibrated for Xylene @ 15 K ppm H2O

Actual H2O (ppm)	Actual Methane (ppm)	Actual Butane (ppm)	Actual Xylene (ppm)	Figaro 823 Average	Figaro 823 Std. Dev.	Figaro 823 % Dev.	Adsistors Average	Adsistors Std. Dev.	Adsistors % Dev.
15002	500	500	100	306.7	219.2	71.5%	141.2	8.3	5.9%
15002	**4999**	500	100	321.2	234.9	73.1%	142.2	8.6	6.1%
15002	500	**4999**	100	1042.6	1086.7	104.2%	142.3	8.5	6.0%
15002	500	500	**1000**	1720.5	696.1	40.5%	940.6	10.3	1.1%
15002	500	500	100	284.7	223.5	78.5%	213.4	12.1	5.7%
15002	500	500	100	272.8	186.2	68.3%	134.4	11.1	8.3%
4999	500	500	100	157.4	102.4	65.0%	137.1	13.0	9.5%
1667	500	500	100	100.1	59.3	59.3%	131.0	13.9	10.6%
0	500	500	100	57.6	30.3	52.7%	127.1	14.5	11.4%
15002	500	500	100	318.0	247.0	77.7%	111.3	10.8	9.7%

Extraction Disks for Spectroscopic Field Screening Applications

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Introduction

Field screening methods for hazardous waste site investigations need to be rapid and low cost to support on-site monitoring and characterization activities. The challenges are enormous because of the number and variety of chemicals that could be encountered. Detecting and monitoring contamination of water is one scenario which could benefit from the availability of a relatively simple field screening method. The data could be used to decide whether to apply more rigorous analytical methods in the field and/or to send samples back to the laboratory.

The research results described in this paper bring out the potential of utilizing solid phase extraction membranes as part of a field screening method.

Concept Description

The idea involves using commercially available solid phase extraction membranes to preconcentrate pollutants onto the membrane by sorption from aqueous solution followed by nondestructive spectroscopic measurements on site using man portable or fieldable instruments. Depending on the analytes being sought and the systems' parameters, the measurements could involve ultraviolet/visible luminescence directly, colorimetry/fluorometry with appropriate reagents, X-ray fluorescence analysis, and/or radioactivity determination.

The solid phase extraction membranes normally serve as alternatives to column chromatography in preconcentrating analytes from dilute solution. The use of solid-phase extraction techniques to replace conventional liquid-liquid extraction for isolating analytes has gained much popularity. Two reviews on water analysis cite various examples (1, 2). The usual approach is to use short columns or cartriges containing various solid sorbents. Such columns are prepacked and readily available from a number of manufacturers. The use of solid phase extraction membranes for preconcentrating analytes is also gaining popularity. The type of sorbent used to concentrate trace materials can vary widely depending on the analyte and the medium. The sorption theory behind the process relates to removal of components from both gases and liquids.

Organic analytes preconcentrated on the supports are usually extracted with an appropriate solvent. The extract is then analyzed using an appropriate laboratory method such as gas chromatography (GC), liquid chromatography (LC) or some hyphenated technique, e.g., GC-mass spectrometry (MS). *The concept pointed out in this paper involves examining the extraction membrane directly using solid state spectroscopy.* Laboratory analysis would be an available option after field screening.

Method Description

A variety of information is available in the literature on solid phase extraction methodology. For example, the use of solid phase membranes in the form of 25- or 47- mm disks for the extraction of pesticides, polychlorinated biphenyls (PCBs), and phthalates at the microgram per liter level was reported recently (3). The purpose of the work was to replace liquid-liquid extraction with a more rapid and less labor intensive technique. Standard filtration equipment (a laboratory suction flask) was utilized. Groundwater, surface water, and laboratory tap water were used for pesticide, PCB, and phthalate analysis, respectively. Adsorbed organic species were eluted from the disks with a small volume of an

appropriate solvent for subsequent chromatographic separation. Recoveries usually exceeding 80 to 90% were obtained for the classes of compounds examined. The membranes were obtained from Analytichem International under the trademark Empore with a typical composition of 90% (by weight) of octyl (C8)- or octadecyl (C18)- bonded silica particles and 10% polytetrafluoroethylene (PTFE).

The concept described in the present paper extends the application described above by examining the solid phase extraction disks in a nondestructive manner utilizing solid state spectroscopy *before the elution step*. Sufficient information may be obtained from the spectroscopic examination to often eliminate the need for any further work thus saving additional time and resources.

Further savings of time and costs are possible if the filtration step was also eliminated. For example, the solid phase extraction disks could be used in a dip stick mode. Alternatively, tabs of the extraction disks could be placed into a sample of the water being examined.

The concept is illustrated in Figure 1. The surface of the tab, modified with long alkyl chains, attracts the analytes. After a specified amount of time the tab is removed, allowed to dry, and examined with an appropriate portable instrument such as a spectrofluorometer, depending on the analytes being sought

The use of solid phase extraction media in a static configuration in which the analytes must diffuse to the surface has not been reported previously. However, we have determined that this is not only feasible but can also provide semiquantitative information. An experiment is describe below which simulates scenarios in which a dip stick is used with a water sample or in which a tab is inserted into a well.

Experimental

C18 Empore (TM) solid phase extraction disks were examined for the sorption of anthracene from water and then analyzed nondestructively using solid-state fluorescence spectroscopy. Tabs (1 cm x 2 cm) were cut from the disks and suspended without stirring in 40 ml of aqueous solutions containing ppb concentrations of anthracene at room temperature. The tabs were alowed to stand in the solutions for given time intervals at different concentrations of anthracene. The tabs were then withdrawn, allowed to dry in air, and examined front surface using solid-state fluorescence spectroscopy. A Spex laboratory spectrofluorometer was utilized. Figure 2 shows a

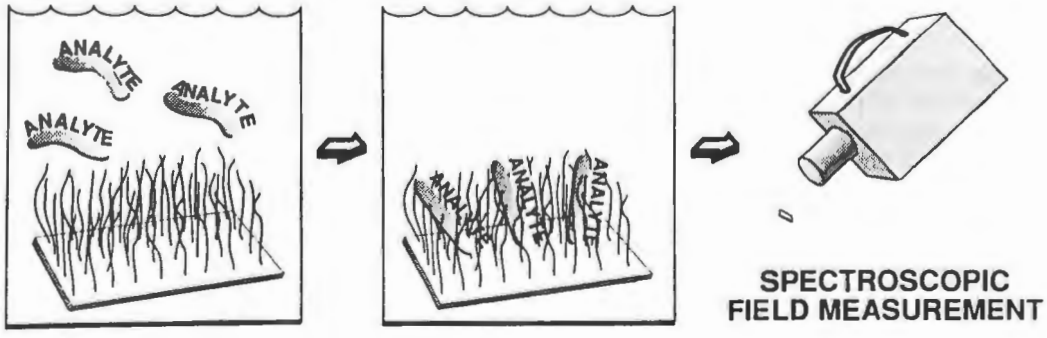

Figure 1. Illustration of the concept of using tabs from solid phase extraction disks to sorb analytes from aqueous solution followed by nondestructive solid state spectroscopic examination.

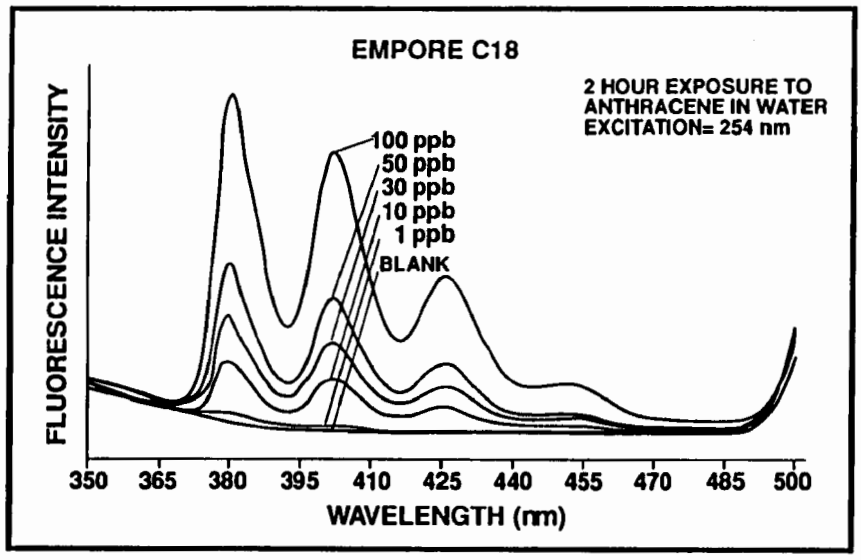

Figure 2. Solid-state fluorescence emission curves of Empore C18 tabs that had been allowed to stand for two hours in water containing 1-100 ppb of anthracene. (Excitation wavelength 254 nm; band passes 4 nm and 1 nm for the excitation and emission monochromators, respectively)

series of solid-state fluorescence curves of Empore C18 tabs that had been allowed to stand for two hours in water containing 1-100 ppb anthracene. The intensity of the emission peak at 380 nm versus anthracene concentration, was found to be linear. Various relationships were also found in other experiments, e.g., a linear increase in solid-state fluorescence intensity was observed of tabs taken at various time intervals (minutes to a day) from solutions containing 10 ppb of anthracene.

Discussion

Though the results reported in this paper are preliminary, the basic idea of using solid phase extraction disks in combination with solid-state spectroscopy is attractive to pursue for field screening applications. The individual technologies have strong scientific bases and do not need extensive development work, although the use of solid phase extraction membranes in a dip-stick mode is new.

Attractive features are listed below:

° The method is nondestructive.

° Extraction disks are commercially available.

° The potential exists for at least semi-quantitative analysis.

° The method is relatively simple.

° The opportunity exists for screening a variety of organic and inorganic compounds.

° The method is readily adaptable to decision-making in the field.

There are no apparent barriers to overcome in extending the techniques to environmental monitoring in aqueous media for a variety of analytes. Nevertheless, the combination of extraction and nondestructive spectroscopic analysis

using solid phase membranes has not been examined sufficiently to allow limitations to be defined thoroughly.

Future studies will focus on concept validation. Various analytes (organic and inorganic) will be examined using solid phase extraction disks/membranes both in dip-stick and filtration modes.

Notice

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FIELD ANALYTICAL SUPPORT PROJECT (FASP) DEVELOPMENT OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) TECHNIQUES FOR ON-SITE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AT PREREMEDIAL SUPERFUND SITES

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INTRODUCTION

Active and inactive woodtreating facilities employing creosote are one of the classes of industry most often investigated during the preremedial or site assessment phase of hazardous waste investigations and cleanups in the Pacific Northwest. Creosote is composed almost exclusively of polycyclic aromatic hydrocarbons (PAHs). This group of organic compounds is listed in the U.S. Environmental Protection Agency (EPA) Target Compound List (TCL), and significant numbers of samples are submitted annually to the CLP for semivolatile (GC/MS) analysis, which includes the PAH fraction. Turnaround time between sample collection and receipt of validated data is generally 7 to 9 weeks.

The Field Analytical Support Project (FASP) program developed by Ecology and Environment, Inc. (E & E) is utilized when project data quality objectives (DQOs) include any of the following as goals:

- Rapid turnaround of data results;
- Extensive sampling for site characterization;
- Optimization of sampling location selection while investigators are on-site; and/or
- Prioritization of samples for more expensive CLP analyses.

FASP data are utilized routinely to supplement and enhance the more rigorously analyzed CLP results. Use of FASP during site investigation activities has been demonstrated to provide both significant project cost savings and improved descriptions of contaminant distribution.

E & E's previously developed gas chromatographic method with flame ionization detection (GC/FID) for analyses of PAHs in contaminated soil has been demonstrated to provide results of good comparability with samples analyzed through the CLP. However, high performance liquid chromatography (HPLC) with in series ultraviolet/visible (UV/Vis) and fluorescence detectors offers numerous advantages over early FASP methodologies:

- HPLC instrumentation requires fewer gases for field analysis;
- Two detectors provide real-time confirmation of target analytes;
- HPLC allows injection of larger sample volumes, yielding lower method quantitation limits; and
- HPLC methodology provides better resolution than the GC methodology for comparable analysis times.

The HPLC method developed for analysis of PAHs in contaminated soil utilizes small volumes of sample and solvents, and disposable glassware to minimize the generation of investigation-derived waste in the field laboratory. Rapid extraction

and analysis techniques are employed to allow the shortest possible turnaround time for on-site samples.

SYSTEM SELECTION

Five commercial systems were evaluated for FASP use: Hewlett Packard, Shimadzu, Spectra-Physics, Dionex, and Waters. The primary considerations for purchase were ruggedness, size, and simplicity (ease of operation and maintenance). Secondary considerations were cost, warranty, compatibility with Nelson analytical data processing system, and technical training/ support. Finally, potential future analytical uses of the system (other analytes of interest that may be analyzed with the chosen HPLC) were investigated.

The Spectra-Physics system was chosen as the most appropriate and cost-effective instrumentation for field applications. The physical space constraints for field laboratories are met by the system, and the components operate with standard 110v power. The system is equipped with a universal system organizer, which facilitates securing the instrumentation during mobilization for field use. All maintenance (except electrical) is performed through front entry into the pumps and detectors, which in E & E experience, is a critical necessity for field repair or maintenance. The Spectra-Physics SP8800 gradient pump is equipped with an automatic maintenance log, automatic cleanup cycle, and self-diagnostic information on electronics and flow performance. In a cost comparison of price quotations, the Spectra Physics system was the least expensive overall, with a total system cost of $30,399.00. The warranty on the Spectra-Physics pump and the UV/Vis detector is 5 years. Shimadzu, Dionex, and Waters each offered a 1-year warranty, and Hewlett Packard offered a 90-day warranty in the base purchase quote. The field technical representative for the Spectra-Physics system is based in Portland, Oregon; technical support is also available through an '800' telephone number. Technical support includes system installation and on-site training for all chemists. Specific applications support is also available. Finally, this system is currently in use at the National Oceanic and Atmospheric Administration and the Federal Drug Administration laboratories; both laboratories require instrumentation of rugged, durable quality.

EXTRACTION AND ANALYSIS

One ± .01 gram of soil was weighed into a 12 mL disposable culture tube. The sample was then extracted twice. Consecutive 5-mL volumes of acetonitrile were repipeted into the culture tube, vortexed 1 minute, centrifuged 10 minutes, and combined in a 10-mL graduated centrifuge tube. The sample extract was evaporated to 1 mL under a gentle stream of nitrogen. Aliquots of the concentrated extracts were injected into the HPLC column for analysis.

The PAHs were analyzed with a Spectra-Physics Gradient HPLC System equipped with in-series fluorescence and UV/Vis detectors. A stainless steel chromatography column (25 cm x 4.6 mm, 5 mm octadecylsilyl stationary phase) under isothermal conditions was employed. Analyte separation was achieved using an acetonitrile/ water mobile phase with initial flow conditions of 35:65 v/v acetonitrile:water for 2 minutes followed by a 14 minute linear gradient to 100% acetonitrile. The mobile phase composition was then held at 100% acetonitrile for 9 minutes. Flow rate during the analysis was 1.5 mL/min and the analytical run time was 25 minutes. Samples were quantitated based on a five-point initial external calibration of all target analytes. The linear regression coefficients of all analytes routinely exceeded .995. Samples with large interfering areas were diluted and re-analyzed. Samples were analyzed for the following PAHs:

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene

Dibenzo(a,h)anthracene
Indeno(1,2,3,-c,d)pyrene
Benzo(g,h,i)perylene

RESULTS AND DISCUSSION

Method quantitation limits for HPLC/UV and GC/FID are presented in Table 1. For routine use, HPLC/UV/Vis results were used for identification and quantitation of the PAHs; fluorescence detection allows practical quantitation limits approximately 10 times lower than the reported UV quantitation limits, and was used primarily for confirmatory analysis of the quantitative data.

For this study, a representative number of samples from a site previously investigated (and known to be contaminated with PAHs) were split for sample analysis, matrix spike analysis, and duplicate analysis, by both HPLC and GC methodologies in order to compare the analytical results.

HPLC sample results showed reasonable agreement with GC comparison analyses. HPLC data and GC data for three soil samples are presented in Table 2. Analytes listed in the method that are not reported in Table 1 were not detected above the method quantitation limits by either analytical system.

To illustrate the efficiency of the HPLC extraction technique, results from three matrix spike events are summarized in Table 3. Three aliquots of a PAH-free soil sample were spiked and subsequently analyzed by HPLC to generate the matrix spike recovery data.

HPLC matrix spike results showed consistently higher recoveries than the matrix spike analyzed by GC. This difference is probably due in part to the loss of analytes during the cleanup procedure performed as part of GC sample preparation.

Duplicate analysis results of three contaminated soil samples are reported in Table 4. Duplicate sample results from both HPLC and GC displayed substantial variability. This phenomenon was due primarily to the non-homogenous nature of the soil matrix at the site; the GC results from the initial site investigation also demonstrated this variability. Variability of the GC results also could be influenced by the cleanup step of the GC sample preparation.

CONCLUSION

Recent developments in HPLC, including gradient elution and dual in-series detectors, have been introduced into E & E's FASP arsenal of instruments and techniques. Chemists may now provide reliable data of known and documented quality on PAHs in a near real-time mode to site investigators. Use of multiple detectors provides supplemental information regarding the accuracy of both the qualitative identification and quantitative measurement of target analytes. The data presented in this study document the accuracy and precision of the method for both standards and real world samples. FASP analyses employing HPLC for PAH measurements are designed to meet the DQOs and data use guidelines for the needs of preremedial site investigators. With appropriate alterations, this method also can be an effective analytical option for other types of investigations involving screening activities.

A FIELD COMPARISON OF MONITORING METHODS FOR WASTE ANESTHETIC GASES AND ETHYLENE OXIDE

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Purpose and Objectives

Several electronic direct reading instruments, that have been or could be used for monitoring toxic gases and vapors in hospital environments, were evaluated by investigators from the National Institute for Occupational Safety and Health (NIOSH) in a series of three field studies. The selected instruments were used to measure waste anesthetic gases and vapors released during surgical procedures in operating rooms, and to monitor ethylene oxide (EtO) concentrations during the operation of gas sterilizers. Instrument readings were compared with results from conventional industrial hygiene air sampling methods. The objectives of these field studies were to: (1) compare calibration and operating techniques for several types of direct reading instruments, (2) compare instrument operational advantages and disadvantages during actual field survey applications and, (3) compare accuracy and precision of direct reading instruments to conventional air sampling methods. The locations chosen included two separate field surveys at a small community hospital, and a third, and more extensive survey at a large medical university teaching hospital.

Methods and Procedures

Battery powered air sampling pumps, configured with bag filling outlet ports, and 40 Liter (L) Tedlar® sampling bags were used to collect air samples. The bagged air samples were then comparatively analyzed by direct reading instruments and conventional sampling and analytical methods. Sampling pumps modified for bag filling were typically set to a 1 liter per minute (Lpm) flow rate. During actual surgical procedures, breathing zone air samples were collected either from the "Scrub Nurse" or from the anesthetic cart. Samples were collected through vinyl plastic tubes connected to air sampling pump and bag assemblies. Area air samples were collected near the operating room exhaust vents.

Sterilization gas samples were also collected in 40L and 50L Tedlar® bags using bag filling sampling pumps. Air samples were collected from several points near EtO gas sterilizers during gas purge cycles and after hospital personnel cracked open sterilizer doors to dissipate residual gas before removing a load to an aeration chamber. Other air samples were collected from inside mechanical enclosures and near floor drains. Air samples collected in Tedlar® bags were then analyzed on-site using the selected direct reading instruments. Direct reading instruments were also used for continuous and sequential real-time monitoring of EtO and Freon 12 (dichloro-difluoromethane) during purge cycle operations and during unloading of EtO sterilizers.

Where sufficient sample remained in sample bags, and after direct analysis with instruments showed measurable concentrations of either halogenated anesthetics (isoflurane or halothane), EtO, or Freon 12; air samples were withdrawn from the bags using conventional NIOSH sampling and analytical methods[1-3] for the analytes of interest. To obtain analytical precision data, three samples from each selected bag were collected and subsequently analyzed by the NIOSH contract laboratory. A three-outlet manifold was connected to the bag valve and each outlet of the manifold was connected to the inlet of the appropriate sorbent tube. Known volumes of the sample were pulled from the bags through the sorbent tubes using pre-calibrated battery powered air sampling pumps. NIOSH recommended sampling rates were used. Based on results from direct reading measurements, sufficient air sample volumes were pulled from the bags to ensure the analytes collected on the sorbent

tubes were above the NIOSH published analytical limits of quantitation. Results from laboratory analyses of the air samples collected from air sample bags were compared to instrument readings from direct analyses of those same bag samples.

Direct Reading Instruments Tested

Real-time instruments evaluated were the Brüel & Kjaer (B & K) Multi-gas Monitor Type 1302, the Miran 103 Specific Vapor analyzer and Miran 1B2 Portable Ambient Air Analyzer manufactured by The Foxboro Company, the Photovac Model 10S50 Portable Gas Chromatograph (GC), and the Summit Interests, Model SIP-1000 Portable GC.

The Brüel and Kjaer (B & K) Model 1302 gas monitor uses a photoacoustic spectroscopy detection technique to measure simultaneously up to five gases or vapors, plus water vapor, down to the part-per-billion (ppb) range. Microprocessor control allows the instrument to compensate for water vapor and other gaseous interferences such as carbon dioxide. The photoacoustic spectroscopy technique uses an infrared (IR) light source focused through a chopper which pulses the IR light beam through one of six optical filters rotated into position on a filter carousel. Light transmitted by the optical filter at the predetermined wave length is selectively adsorbed by the gas being monitored. The gas sample analyzed is automatically pumped into a hermetically sealed analysis cell. The modulating expansion and contraction of the gas in the cell caused by heating and cooling of the gas as it is irradiated by the pulsed infrared light beam generates pressure waves in the cell that are detected by sensitive microphones mounted on opposite sides the cell. The amplitude of these pressure waves is proportional to the concentration of the measured gas. After the first analysis, the filter carousel turns to bring the next optical filter into position so that other gases in the cell which adsorb infrared light at different wavelengths can be subsequently analyzed. The 1302 is operated by using the push-buttons and the two-line digital display on its front panel. Measurement results are automatically stored in the instrument's "display memory" and can be permanently stored in one of ten "background memory" locations. Display memory data also can be transferred to a printer or personal computer.

The Miran 103 and Miran 1B2 analyzers are single-beam infrared spectrometers. The air sample analyzed is pumped through the analysis cell at a flow rate from 25-30 Lpm. Quantitative analysis of the gas in the cell is accomplished by electronically detecting and comparing the energy of an infrared light source with the energy of the light after passing through the gas in the cell. Infrared energy lost through absorption by the gas is proportional to concentration of the gas in the cell. The Miran 103 Specific Vapor Analyzer can monitor several gases and vapors. However, to change from one gas or vapor to another, a different filter and meter scale must be installed. The use of the Miran 103 for monitoring nitrous oxide has long been the established sampling and analytical method used by NIOSH investigators.[4] The Miran 1B2 Portable Ambient Air Analyzer is a portable microprocessor-controlled infrared spectrometer configured with an internal library of 116 precalibrated compounds and ten user selected compounds. It uses interactive programming to prompt the operator through available choices and functions.

Both the Summit and Photovac portable GCs use a photoionization detector, and each was equipped with a Carobopak BHT packed column. The carrier gas used was ultrapure air. Both GC columns were operated at ambient temperature. Samples and calibrations standards were injected using gas-tight syringes. Injection volumes ranged from 10 to 500 microliters. Gas concentrations were detected by measuring the peak height of an injected sample from a recorder output, and comparing the result to a calibration curve. Standards were periodically injected between sample injections.

During the surveys all instruments were subjected to many span calibrations using known concentrations of the gases measured. The B & K 1302 was configured with filters to measure Freon 12, halothane, isoflurane, ethylene oxide, nitrous oxide, carbon dioxide, and water vapor. Before use, the B & K 1302 was zero calibrated and humidity interference calibrated according to manufacturers recommendations. The 1302 was then subjected to a single point span and cross-interference calibration for each gas or vapor to be measured before each series of sample measurements were made. The Miran 1B2 user library parameters for nitrous oxide, EtO, or isoflurane were used to set up the instrument. To optimize accuracy of the 1B2 and 103 when monitoring EtO or nitrous oxide, a five-point span calibration was performed using a closed-loop calibration system. Pre-calibration data stored in the user library of the 1B2 was used for measuring isoflurane concentrations in spiked samples. Calibration of Photovac and Summit portable GCs was done through microliter injections of known concentrations. Throughout the surveys, considerable time and effort was devoted to calibrating and verifying instrument accuracy through testing of prepared standards. Nitrous Oxide, EtO and Freon standards were prepared from dilutions of pure gases mixed with clean air or nitrogen in gas sampling bags. A purchased cylinder containing 9.8 ppm EtO in nitrogen was also used. Halogenated anesthetic

standards were prepared from liquid anesthetic agents supplied by the hospitals surveyed. Measured amounts of liquids were injected into gas sampling bags and mixed with metered volumes of clean air or nitrogen to prepare standards that were then diluted to the desired concentrations. A mixed Standard of 9.8 ppm EtO and 30 ppm Freon 12 was also used to test instrument accuracy when measuring EtO in the presence of Freon 12.

Using the appropriate concentrations for performing span calibrations was critical for obtaining accurate results when measuring EtO with the 1302. Freon interference over compensated EtO readings when the instrument was span calibrated with a 1 ppm EtO standard. B & K recommends using a span calibration standard of at least 100 times the detection limit, which for EtO is 0.2 ppm. When the 1302 was recalibrated using a 20 ppm EtO standard, over compensation effects were eliminated. When calibrating for analytes that are CO_2 compensated, room air could not be used for preparing standards because of CO_2 build-up in indoor air. Although the Miran 1B2 can measure both isoflurane and nitrous oxide, to switch from one gas to the other required time-consuming rezeroing of the instrument. The relatively large volume of air sample required for analysis by the Miran 103 and 1B2 (about 20L) permitted only one measurement from each sample bag. It was therefore not possible to measure both halogenated anesthetic and nitrous oxide concentrations from the same bag sample using the Miran 1B2 or 103. To allow both the 103 and 1B2 to obtain a reading from the same sample bag, a tube from the sampling outlet of the 1B2 was connected to the inlet of the 103. Of all the instruments evaluated, the only instrument tested that could make simultaneous measurements of more than one gas or vapor from the same sample bag was the 1302. Neither the Photovac nor Summit GCs would respond to samples containing halogenated anesthetics, and the Summit GC would not detect nitrous oxide. Difficulty identifying the EtO peak detected on the Photovac GC rendered all EtO readings from this instrument invalid. An interference peak from Freon 12 or some other source made quantitative analysis of low-level EtO concentrations difficult with the Summit GC.

Measurement Results

Nitrous Oxide

All the instruments used for measuring nitrous oxide, which included the B & K 1302, Miran 1B2, Miran 103, and Photovac GC, gave similar readings. For nitrous oxide concentrations above 10 ppm, instrument responses relative to Miran 103 readings were within ± 5% for all instruments used. At concentrations below 10 ppm, nitrous oxide readings on the 1302 averaged 1.82 times higher than Miran 103 readings. Photovac readings were within ± 25% of readings obtained on the Miran 103 for concentrations ranging from 5-110 ppm. The Miran 1B2 did not detect nitrous oxide in sample bags containing Miran 103-detectable concentrations of less than 10 ppm.

Halogenated Anesthetics

Laboratory results from nine isoflurane samples collected during surgical procedures ranged from 0.09 to 0.95 ppm. B & K 1302 results from gas bag samples collected side-by-side with charcoal tube samples were within ± 0.3 ppm of the lab results. The average relative response of the B & K 1302 when compared to the average laboratory results was 0.98. B & K 1302 readings from two sample bags spiked with isoflurane averaged 0.16 ppm higher than laboratory analysis of those same samples. Miran 1B2 readings average 0.23 ppm lower than the laboratory results. More comparisons made from two gas-bag collected samples on a follow-up survey at another hospital showed B & K 1302 readings averaging 0.13 ppm lower than the laboratory results. Less satisfactory results were obtained for halothane when comparing B & K 1302 readings with laboratory results. The average response from the B & K 1302 analysis of three sample bags was 3.8 times lower than the laboratory results. Laboratory results ranging from 1.1 to 1.5 ppm halothane ranged from 0.3 to 0.5 ppm on the B & K 1302. No other direct readings for halothane were measured or detected on the other instruments.

EtO/Freon 12

The Miran 1B2 and 103 EtO readings from gas bag samples collected near operating gas sterilizers were consistently higher than the EtO readings from the B & K 1302, Summit GC, and analytical laboratory. Of the nine bag samples collected, only four were subjected to follow-up laboratory analyses. Laboratory results for one of the four samples was 4.9 ppm EtO. Direct readings from analyses of this sample were 4.2 ppm for the B & K 1302, 5.3 ppm for the Summit GC, 11 ppm for the Miran 1B2, and 9.1 ppm for the Miran 103. The other three laboratory analyzed samples were compared only with the 1302 and the Summit. Average response to EtO for the 1302 and Summit relative to laboratory results was 1.2 and 1.1 respectively. The 1302 gave a 1.3 relative response to Freon 12 when compared to laboratory results for four samples ranging in concentration from about 1 to 80 ppm.

Concurrent monitoring of EtO and Freon 12 during real-time measurements and analyses from collected bag samples showed considerable EtO/Freon ratio variations in both analytical laboratory results and B & K 1302 readings. Although an 88/12 mixture contains a volume-to-volume ratio of 73% Freon 12 and 27%

EtO, only two of 23 samples tested came close to this ratio. Most samples showed the Freon component well above the expected 73% level. In two of the samples the EtO component was greater than 70% of the total mixture.

Conclusions

Any of the instruments tested will give satisfactory performance for monitoring nitrous oxide. Until additional field testing shows consistent accuracy and comparability with laboratory results, direct reading instruments may not yet be suitable for monitoring all halogenated anesthetic gases. Both the B & K 1302 and Summit GC gave satisfactory performance for the monitoring of both short term and long term exposures to EtO. The Photovac GC has been shown to give satisfactory performance for monitoring EtO,[5] but unknown operational problems caused the instrument to fail during this field testing. Freon 12 interferences from the 88/12 sterilization gas will likely give false positive EtO readings or readings with a high positive bias on IR spectrometers like the Miran 1B2 and 103. The considerable variation in EtO/Freon ratios noted from various locations near and during the operation of gas sterilizer equipment should prohibit the use of 88/12 sterilization gas as a calibration standard.

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On-Site and On-Line Spectroscopic Monitoring of Toxic Metal Ions Using Ultraviolet Absorption Spectrometry

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I. The need for on-line monitoring of heavy metals

Heavy metals are common by-products in industrial operations and can thus enter the environment from wastewater discharges or as leachate from industrial wastes.[1] Wastewater discharges from industrial operations must be periodically tested for compliance with permit requirements, including limits for several heavy metals.[2] Groundwater and drinking water quality testing also includes measurement of several heavy metals.[3,4]

Although Atomic Absorption Spectrometry is the standard method of analysis required for compliance reporting, it is not a method that is easily adapted for on-line monitoring in factory or field screening applications. Reliable and affordable methods are needed to detect and measure specific heavy metals in multi-constituent effluents and to detect specific heavy metals in surface or ground waters.

II. Detection of absorption spectra

Heavy metals tend to form anions that bond with water molecules into compounds known as ligands. These compounds contain bond structures where electrons can become excited upon exposure to electromagnetic energy of a specific frequency, resulting in absorption of light in the ultraviolet-visible wavelength range (200 nm to 800 nm).[5] Chemical analysis of liquids using uv-vis absorption spectra does not rely upon detection of a single peak wavelength as with other forms of spectroscopy, but instead makes use of an absorption signature across a range of wavelengths. This signature is a function of all absorbing components in the solution. Special apparatus and techniques are required to detect the spectra and interpret the information.

III. Apparatus required for detection of heavy metal spectra

Absorption spectra attributable to individual elements can be observed by recording the signature for the element dissolved in a transparent solvent, such as pure water. Spectra for metals such as chromium, copper, iron, mercury and zinc have been recorded for the applications discussed in this paper. Figure 1 represents the spectra for several concentrations of iron, ranging from 0.1 to 2.0 ppm (the actual spectra being mathematical values for absorption at numerous wavelength intervals). It is possible to characterize an unknown substance in pure water as iron if the absorption signature matches the pattern observed for iron. Furthermore, it is possible to estimate the concentration of iron by comparing the intensity of the signature for unknown concentrations to the relative intensity of the signatures for known concentrations.

The apparatus required to perform absorption spectroscopy in the laboratory is well known.[6] Basic elements include a light source for the wavelengths of interest, a transparent cell to hold the sample, a detector to measure the light remaining after transmission through the sample, and a means to process analysis models for interpretation of the detected information. Many simple laboratory analyzers such as colorimeters use an optical system that is limited to one or a few specific wavelengths, which limit the instrument to detection of a specific substance. Other laboratory instruments have a wider wavelength range, but only look at one or a few wavelengths at a time, requiring mechanical adjustment to the optics in order to step through a wide range of wavelengths. These instruments are slow and unsuited for use outside of the laboratory.

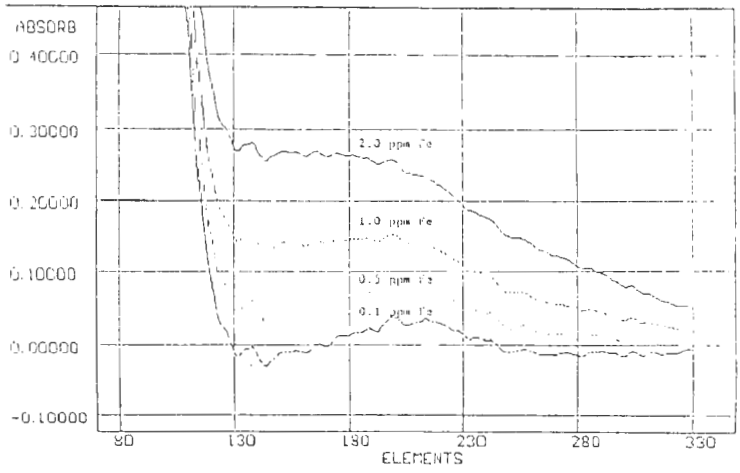

Figure 1. Iron in pure water.

IV. Technology advances for on-line absorption spectroscopy

On-line spectroscopy for field use must be able to rapidly detect a wide wavelength range in a flowing sample or in a dynamic environment. Several recent technology advances make this possible:

FIBER OPTICS make it possible for there to be distance between the analyzer and the liquid to be analyzed, with the light source and detector remaining in the analyzer. Transmission of light through the liquid occurs in a device known as an optrode, which may be immersed in a process tank or flow stream, or may be designed to permit a sample line to flow through a special optical cell.

ARRAY DETECTORS contain a series of photodiodes, each connected to its own storage capacitor. Each element in the detector is responsible for a specific wavelength interval, with as many as 1024 intervals possible in the most advanced version. A fixed grating is used to separate the detected light into wavelength intervals and to project to light onto the detector. The system used for ultraviolet-visible absorption spectroscopy (UVAS) can simultaneously scan 1024 intervals from 200 nm to 800 nm.

CHEMOMETRICS is the name collectively given to the statistical and mathematical models used for chemical analysis of multi-component liquids. These models make it possible to perform qualitative and quantitative analysis by establishing the contribution that an individual chemical constituent makes to the overall absorption spectra of the liquid.

V. Chemometric analysis of absorption spectra

Heavy metals must often be analyzed in waters that contain numerous components, resulting in overlapping or closely grouped spectra. The overall absorption spectra for the liquid is a smooth pattern that results from the effects of absorption by these individual components. There are three basic steps involved in the process of using absorption spectra for chemical analysis:

QUANTIFICATION involves converting detected spectra for calibration solutions and unknowns into numerical values that can be processed using mathematical and statistical procedures.

PREPROCESSING of raw data reduces the effects of noise and transforms absorption information into forms that permit more efficient analysis.

ANALYSIS of absorption values identifies individual components and calculates an estimate of their concentrations in the liquid.

These three steps are the result of a process that is performed at the beginning of a monitoring project to select the combination of wavelengths, preprocessing techniques and analysis models that are capable of providing the most accurate analysis of the analytes of interest in a specific application. This process uses information from several site specific samples that contain known concentrations of the target analytes. These samples, known as a "learning set" are used to perform a parallel calculations using combinations of techniques to find the model that produces the lowest error when actual and predicted values are compared. Several "test sets" are then processed to verify the model.

The quantification step is fairly straightforward. Absorption of light is governed by Beer's Law, which relates absorption to the absorptivity of the media, path length through the media, and concentration of the absorbing components within the solution. When all of the absorbing components in the media are known, total absorption at each wavelength is a function of the sums of all of the absorbing components. A series of simultaneous equations can be used to calculate absorption. Most often, however, all of the absorbing components are not known, in which case an inverse technique that defines concentration as a function of absorbance must be used.[7]

Preprocessing of spectra is often done for multi-component solutions or to adjust for noise or drift. Typical techniques include the use of first or second derivatives of the absorption spectrum, the use of Fourier or Walsh transformations, and the use of Principal Components Analysis (PCA). PCA uses statistically determined quantities to rotate the coordinate system such that the original information that may have been aligned on several axes becomes aligned on only a few axes. In effect, the variables that are highly correlated with one another can be treated as a single variable, thus simplifying the analysis.[8,9]

The analysis techniques currently used include multiple linear regressions (using least squares techniques) and discriminant analysis. Discriminant analysis is a clustering process which defines linear decision boundaries between information clusters for known concentrations of analytes, and assigns unknowns to an appropriate cluster based upon detection of significant characteristics for the unknown.[10]

Emerging techniques for analysis include experimental methods such as inductive learning and neural networks, especially for problems that cannot be simplified through principal components analysis. A technique that shows great promise is the Lattice-K Nearest Neighbor technique, where known values for variables are organized into the nodes of a lattice. Predicted values for an unknown are based upon relative distances of variables for the unknown with those of the nearest neighbors in the lattice.

VI. Application of Chemometrics for Analysis of Heavy Metals

Several recent applications have demonstrated the ability of ultraviolet-visible absorption spectroscopy (UVAS) to detect various heavy metals in multi-component solutions.

Industrial process (boiler) water was analyzed for the presence of iron and copper. Copper was detected over a range of 1.0 to 5.0 ppm with an error of 0.047 ppm, while iron was detected over a range of 0.5 to 10.0 ppm with an error of 0.014 ppm. These were the lowest errors achieved, using Walsh transformations and discriminant analysis.

Iron was analyzed over a range of 0.0 to 10.0 ppm in a complex nutrient solution containing random concentrations of copper, nitrates, phosphates, calcium, magnesium, sodium, chlorides and other compounds. Figure 2 shows several spectra for iron in the nutrient solutions. Figure 3 plots actual versus predicted iron values for 20 samples, using linear regression of untransformed absorbance values which produced an error of less than 0.03 ppm. Nitrates were also successfully analyzed for this application.

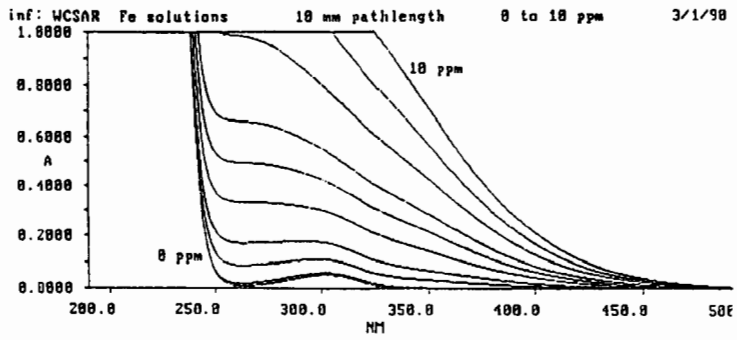

Figure 2. Iron in nutrient solutions.

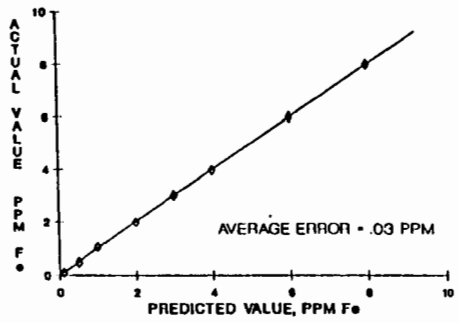

Figure 3. Actual vs. predicted iron values.

Other applications to date include trace levels of mercury in wastewater (range: 0.0001 to 0.01 ppm), molybdate in cooling water (range: 1.0 to 2.2 ppm), zinc in wastewater (range: 0.85 to 3.65 ppm), and chromium in wastewater (range: 0.85 to 4.45 ppm).

VII. Conclusion

Ultraviolet-visible absorption spectroscopy (UVAS) is an emerging technology that is currently being demonstrated for on-line analysis of heavy metals and other chemical substances to monitor water quality in complex multi-component solutions without the need to chemically alter samples prior to analysis.

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RAPID SCREENING OF SOIL SAMPLES FOR CHLORINATED ORGANIC COMPOUNDS

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Cleanup of an industrial site contaminated with chlorinated organic compounds requires methods for the rapid assessment of many soil samples. An estimate of soil content of chlorobenzenes, chlorophenols, and hexachlorocyclohexanes is the EOX value. This determination requires solvent extraction of the soil, which generally takes at least 2 h and is therefore too lengthy for the present purpose. In the present work we have compared this method with the following more rapid ones:

- Thermal desorption of organic compounds from soil, followed by combustion in an oxygen atmosphere (Organochlortest A-P-E; supplier: Burger)
- Measurement in the headspace over a soil sample with a photoionisation detector (supplier: TIS) test kit based on extraction and reduction of chlorinated compounds from soil ("Chlor-N-Soil"; supplier: Dexsil)

The main characteristics of these four methods were compared. Nine soils of different type and degree of contamination were examined with the results.

Our provisional method of thermal desorption, which is still under development, almost always yields higher values than the EOX method, even though the former have been corrected for ionic chloride in the soil. Possibly thermal desorption is more efficient than soxhlet extraction for the compounds in question. However, except for sample 92/03, both methods yield the same relative order for the degree of contamination. This result suggests that the thermal desorption method merits further development.

No such correlation was obtained for the PID. For the Chlor-N-Soil test kit, results were obtained for only three samples because of limited availability of reagent sets. In principle, this test appears to be applicable within the limited scope of its specification, but a correlation of the colour change (violet: "little", yellow-brown: "strong") with approximate contamination has yet to be established.

DEVELOPMENT OF A MICROBORE CAPILLARY COLUMN GC-FOCAL PLANE MASS SPECTROGRAPH WITH AN ARRAY DETECTOR FOR FIELD MEASUREMENTS

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A gas chromatograph-mass spectrograph (GC-MS) system using a microbore capillary column (50 μm i.d.), and a miniaturized focal plane mass spectrograph (Mattauch-Herzog type) with an array detector has been developed. The extremely small carrier gas flow rate (0.05 atm $cm^3 min^{-1}$ of helium) through the column permits its direct coupling to the ion source, and reduces the pumping needs of the MS. The mass spectrograph with an array detector measures the intensities of all masses simultaneously. Analysis of mixtures of compounds, each at a concentration of 1 ppmv has been performed with high signal-to-noise ratio. The minimum detectable quantity of benzene is determined to be 7.5×10^{-14} g which corresponds to a concentration of 40 ppb for an injected sample volume of 0.5 μl. Lower analyte concentration can be determined by increasing the sample volume and/or the signal integration time. The system is found to have a linear dynamic range of $>10^3$. Because of its low weight, power, and high sensitivity, the combination of a microbore GC column and a miniaturized plane mass spectrograph is uniquely suited for field analysis.

INTRODUCTION

The combination of a gas chromatograph with a mass spectrometer (GC-MS) is one of the most powerful instruments for the analysis for complex mixtures. GC-MS is eminently suited for the measurement of environmental pollutants. However, in its present form it has remained largely confined to the laboratory because of its mass and power requirements. Our own interest lies in the development of a field-portable GC-MS instrument. Such an instrument is much needed for the real-time, on-site measurement of pollutants, e.g., at toxic waste dump sites and for fugitive emissions from various sources. This instrument should also be fast and possess high efficiency and sensitivity in order to analyze compounds present at low concentration levels. In the hyphenated technique of GC-MS, the speed of analysis is determined by the GC separation time. Fast separation with high efficiency can be achieved by the use of a narrow-bore capillary column (e.g., 50 μm i.d.) of short length.[1-3] Also, the carrier gas flow rate through such a column is very low which offer the advantage of reducing the pump-size (often requiring large mass and power) needed to maintain the proper operating vacuum conditions in the MS.

Such microbore columns, however, put important restrictions on the sample size for analysis, and on the detector used for measuring the eluted compounds.[4,5] Extremely narrow and closed spaced peaks are produced from the use of microbore columns, particularly in the early part of the chromatogram. The detector must, therefore, have a high sensitivity and a low-time constant for signal measurement. To maintain the column efficiency, the dead volume needs to be minimized. These considerations have prohibited the application of columns of <100 μm i.d. in commercial GCs. The fast rate of data acquisitions needed to measure peaks from a microbore column makes it incompatible with a scanning type mass spectrometer.[4]

The aforementioned problems in exploiting the advantages of a microbore column can be overcome by the use of a mass spectrograph (non-scanning). The capability of a mass spectrograph for measuring the intensities of all masses at the same time confers on it an almost unlimited speed for obtaining mass

spectra. Its sensitivity also is inherently greater that of a scanning-type MS because the latter measures the signal at a given mass peak only for a short dwell time. However, in the past, the lack of a sensitive ion detector has been an important reason for not using a nonscanning MS for measurements that required high sensitivity. Recently, an array detector known as an electro-optical ion detector (EOID) has been developed in our laboratory for a focal plane mass spectrograph (Mattauch-Herzog type).[6,7] The EOID possesses the simultaneity of a photoplate (used in focal plane MS) and the high gain of an electron-multiplier. The EOID can integrate signals continuously for a wide range of time (25 ms - 30 s) and, by an appropriate selection of integration time, multiple mass spectra from transient samples (like a narrow GC peak) can be obtained without sacrificing sensitivity.

Our approach towards the development of a high performance field-portable GC-MS instrument consists of combining a short microbore column and a miniaturized focal plane mass spectrograph. In this paper, the new GC-MS system developed in our laboratory is described. Some of the results obtained on this system for the analysis of a mixture of priority pollutants are also reported.

II. EXPERIMENTAL

A. Gas Chromatograph

The experimental arrangement is shown schematically in Fig. 1. The fused silica microbore GC column (3.0 m, 50 μm i.d.) with a 0.2 μm bonded DB-5 stationary phase (J. & W. Scientific, Folsom, Ca.) was housed in a temperature programmable oven. The outlet end of the column was directly led into the ion source of that mass spectrograph. A sample injector valve (Valco Instruments) with an internal volume of 0.5 μl was used to inject the sample onto the column. A pneumatic actuator along with pilot valves and a digital valve interface[8] was incorporated into the sample injector for fast injection. Samples could thus be injected reproducibly in less than 14 ms. GC-grade helium was used as a carrier gas at a flow rate of 40 cm s^{-1}. Because of the small volume flow rate of the carrier gas (0.05 atm cm^3 min^{-1}), it was possible to connect the GC column and the MS without any interface. The direct inlet of the column effluents into the ion source eliminated the dead volume that usually arise from GC-MS interfaces and allowed for the complete utilization of the analyte sample.

B. Mass Spectrograph

Two miniaturized focal plane mass spectrographs, one with 2.0" long focal plane and the other with a 5.0" long focal plane have been designed and fabricated at JPL. The 2.0" focal plane covering a mass range of 40-250 amu is destined to be used for field measurements. A photograph of this MS is shown in Fig. 2a. The magnetic sector of this analyzer was fabricated from new magnetic materials having high energy product value, and high magnetic flux permeability for reducing the mass of this sector. The 5.0" focal plane MS covers a mass range of 28-500 amu.

C. Array Ion Detector

The details of the EOID have been reported previously.[6,7] In short, it consists of a microchannel electron multiplier array, a phosphor-coated (P-31) fiber optic window, and a photodiode array (PDA). In the EOID, an ion exiting the magnet impinges on the microchannel array and initiates an electron cascading process along the channel length. The electrons coming out at the other end of the channels produce photon images of their parent ions on the phosphor window (shown in Fig. 2b). The intensities of these images are then measured by the photodiode array (2.0" long active region) having a center-to-center distance of 25 μm between its two adjacent diodes.

The photodiodes are integrating detectors and accumulate the photon signal (proportional to the ion signal) for the desired period of integration. The position of the photodiode along the focal plane determines the mass of the ions producing the ion image at that location. The signal stored in the photodiodes are read (at a rate of 220 kHz) serially by a computer after a predetermined integration time. Each readout, called a frame, provides a mass spectrum of all the ions accumulated during the integration period. Each diode accumulates the signal continuously except for its read-out time (~4 μs) when it is reset and resumes signal integration. This allows for the complete mass spectral measurement of GC effluents at a high frequency without any loss of sensitivity in the process.

Both of the mass spectrographs described above are equipped with their own array detectors. The computer interface electronics for the small MS has not been completed at this time and, therefore, the results reported in the paper were obtained on the 5.0 in. focal plane MS. For laboratory measurements, this did not create any complications and demonstrated the analytical capability of the MS-EOID system.

Moreover, it is expected that the new 2.0-in. array detector will have better performance because of the minimization of the signal losses at the PDA-fiber-optic window interface in this design.

A mixture having a concentration of 1 ppmv in air of each of the compounds listed in Table 1 was prepared. The internal volume of the injector valve was filled with this mixture and injected on the GC column for analysis.

RESULTS AND DISCUSSIONS

The mass chromatogram of a mixture of the compounds listed in Table 1 is shown in Fig. 3. Each component in the mixture had a concentration of 1 ppmv in air. The GC column was maintained at the room temperature and a signal integration time of 250 ms for the array detector was used in the measurement. Complete mass spectra of the components eluting into the ions were recorded every 250 ms. In obtaining the mass chromatograph, the sum of the intensities of all masses (>45 amu) in each record (frame) is plotted against the corresponding frame member (time).
The chromatogram shows that the components (dichlorodifluoromethane, chloromethane, bromomethane and chloromethane) correspond to peaks 2-5 are narrow and closed spaced. For example, the peak-to-peak separation between 2 and 3 is less than 700 ms and the full width of peak 2 is about 300 ms. Quantitative measurement of such GC peaks are made possible by the simultaneous measurement of all ions and by the proper selection of the signal integration time.

The continuous measurement by the EOID with a short integration time (>25 ms) can be used to perform time-resolved mass spectral measurement and can be applied to resolve otherwise overlapping GC peaks. Figure 4 demonstrates the effect of measurement time on resolution of compounds by the microbore column. It is seen in Fig. 4a that bromomethane and chloromethane corresponding to frame numbers 89 and 95, respectively, are well separated when an integration time of 100 ms is used for their mass spectral measurement. For 250 ms integration time, the chromatographic separation is barely adequate (Fig. 4b) but the separation is lost when spectral measurements are made every 500 ms (Fig. 4c). The time resolution capabilities of the MS-EOID make it particularly useful for short columns of moderate resolving power. Their combination reduces the analysis time and renders it suitable for a field-portable GC-MS analyzer.

It should be noted that the quantitative nature of measurement is not compromised by the number of mass spectra (frames) obtained from a GC peak because of the continuous and simultaneous measurements of ion intensities. Figure 5 shows that some of the intensities contained in all the frames of a GC peak (corresponding to dichlorodifluoromethane) is independent of the integration time used in recording these frames. The sum of intensities determines the amount of the compound.

The mass chromatogram (Fig. 3) demonstrates that this GC-MS system can readily analyze mixtures of compounds present at the 1 ppmv level without preconcentration of the analytical sample. From these data, the minimum detectable quantity (MDQ) was calculated for each compounds. For benzene this amounts to 7.5×10^{-14} g, which corresponds to a concentration of 40 ppb for an injected volume of 0.5 μl (results of 100 ppb mixtures of benzene and chloroform are included in Fig. 6). Lower analyte concentrations (<40 ppb) can be determined by increasing the sample volume and/or the signal integration time. However, larger volumes (>2 μl) cannot be injected without degrading column resolution. The problem can be overcome by sweeping the sample from an injector valve and cryofocusing the volatile organic compounds at the head of the column, thus, removing the air. The temperature of the column can then be programmed for subsequent analysis.

A series of mixtures of chloroform and benzene of various concentrations (0.1 - 100 ppmv) in air was prepared to study the dependence of mass spectral intensity on concentration. These mixtures were injected onto the GC column and their mass spectra were measured. In Fig. 6, the sum of the intensities of a single mass (m/z = 83, characteristics of chloroform) and also of a group of masses (76-78 amu characteristics of benzene) contained in frames of the respective GC peaks have been plotted. The intensity is found to increase linearly with concentration showing a linear dynamic range of $>10^3$. This is the range with a constant integration time of 250 ms. It is possible to further extend the dynamic range by suitably adjusting the signal integration time. The straight lines in Fig. 6 are the least square fit through the data points. A linear-correlation coefficient equal to 0.99 is found for mass spectral measurement of benzene showing an excellent correlation between concentration and intensity.

CONCLUSIONS

A GC-MS system using a microbore column (50 μm i.d.) and a miniaturized mass spectrograph

with an array detector has been developed. The performance of this system in the analysis of mixture of priority pollutants has been demonstrated. A short microbore column (50 μm i.d., 3.0 in. long), when combined with the MS-EOID, resolves the early eluted gases satisfactorily. The GC-MS system described above possesses high sensitivity and a linear dynamic range of $>10^3$. The minimum detectable quantity (MDQ) for benzene is found to be 7.5×10^{-14}g which corresponds to a concentration of 40 ppmv in a sample volume of 0.5 μl. Larger sample volume can allow measurement of lower concentrations. The combination of a microbore column and a miniaturized focal plane MS is eminently suited for field measurements. The extremely small carrier gas flow rate drastically reduces the mass and power needs of the mass spectrograph.

ACKNOWLEDGMENTS

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TABLE 1

Compounds	Peak No. (Fig. 3)
air	1
dichlorodifluoromethane	2
chloromethane	3
bromomethane	4
chloroethane	5
dichloromethane	6
1, 1, 1 - trichloroethane	7
chloroform	8
benzene	9
trichloroethylene	10

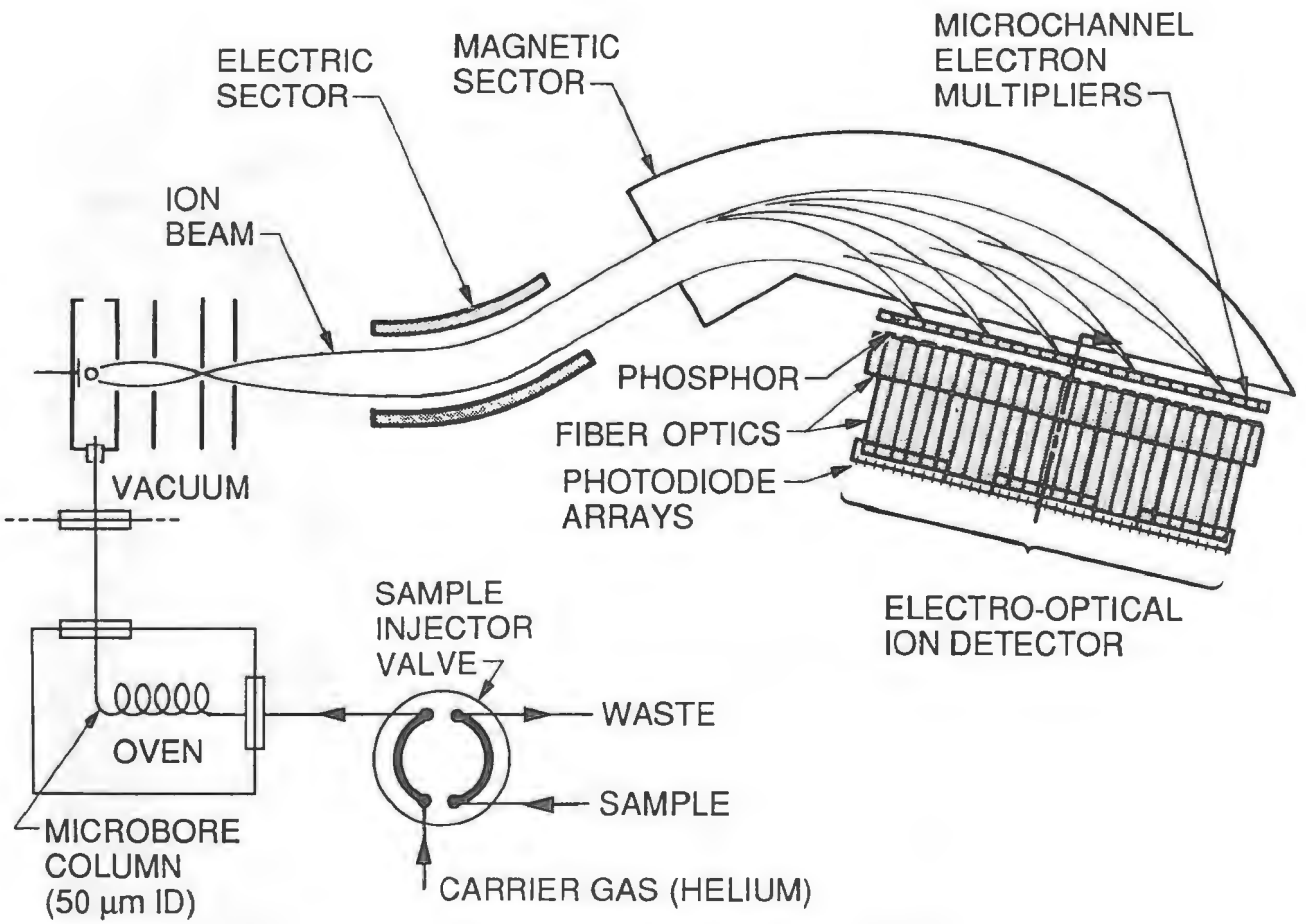

Fig. 1 Schematic of the microbore capillary column gas chromatorgraph and the focal plane mass spectrograph assembly. The sample injector is pneumatically actuated and is provided with pilot valves and a digital valve interface for fast sample injection.

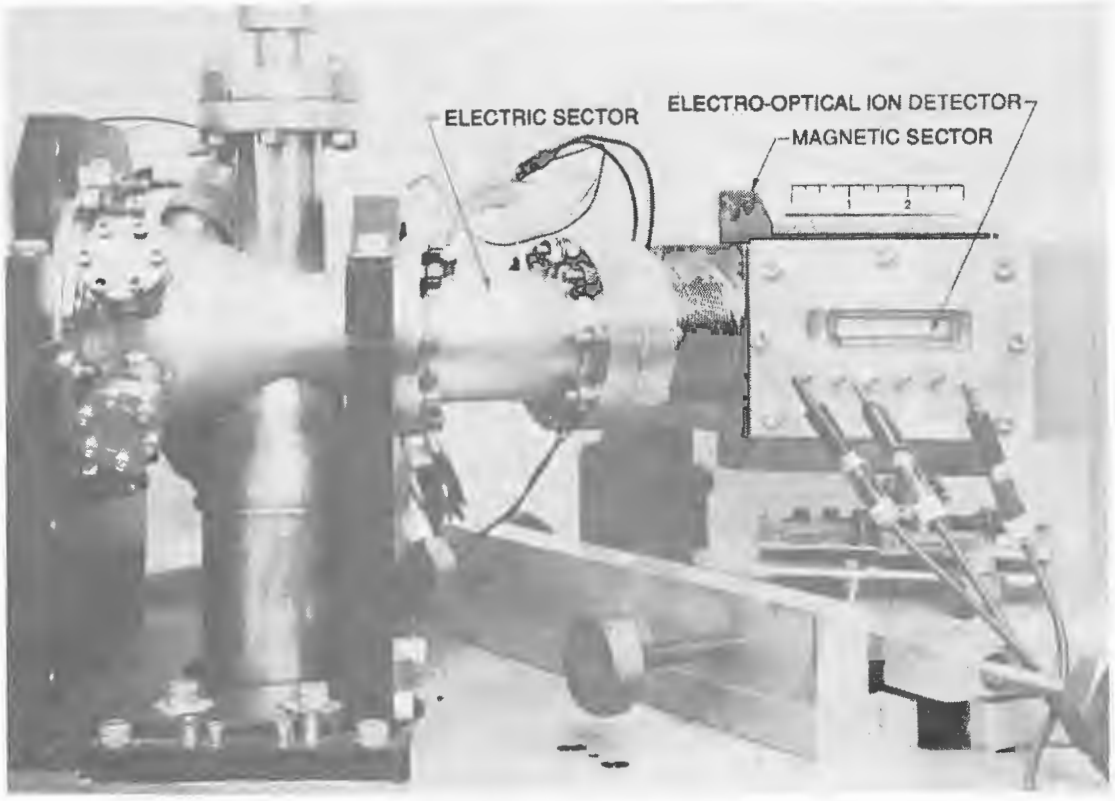

Fig. 2a: Photograph of the focal plane (2.0-in) mass spectrograph with an electro-optical ion detector.

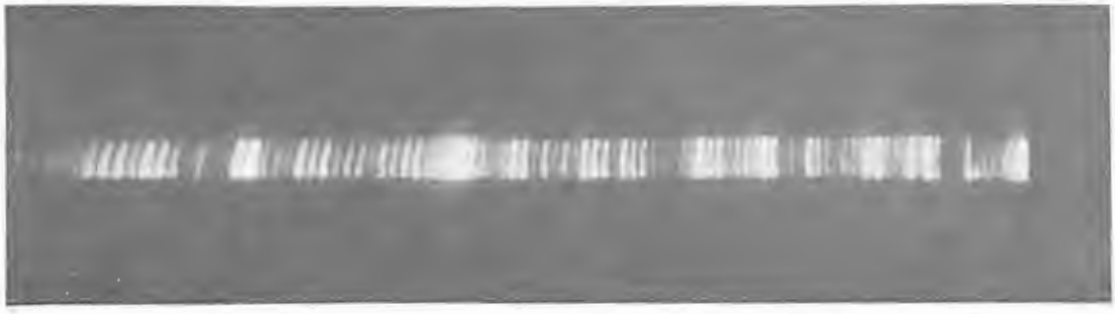

Fig. 2b: Photograph of ion images

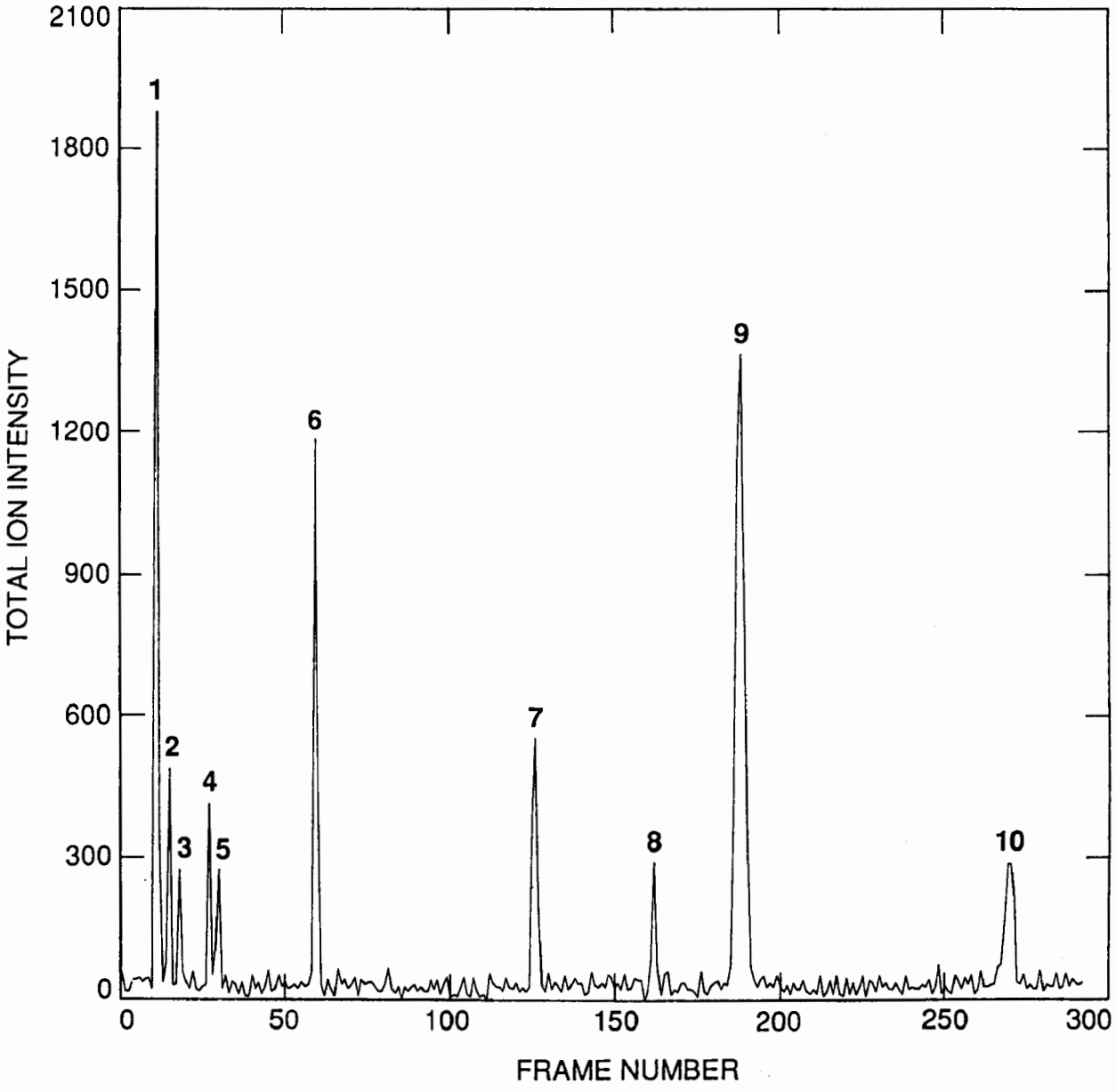

Fig. 3: Total ion chromatogram obtained from a mixture of compounds listed in Table 1. Each component in the mixture has a concentration of 1ppmv. A sample volume of 0.5 µ l was injected, and a signal integration time of 250 µs was used for each frame.

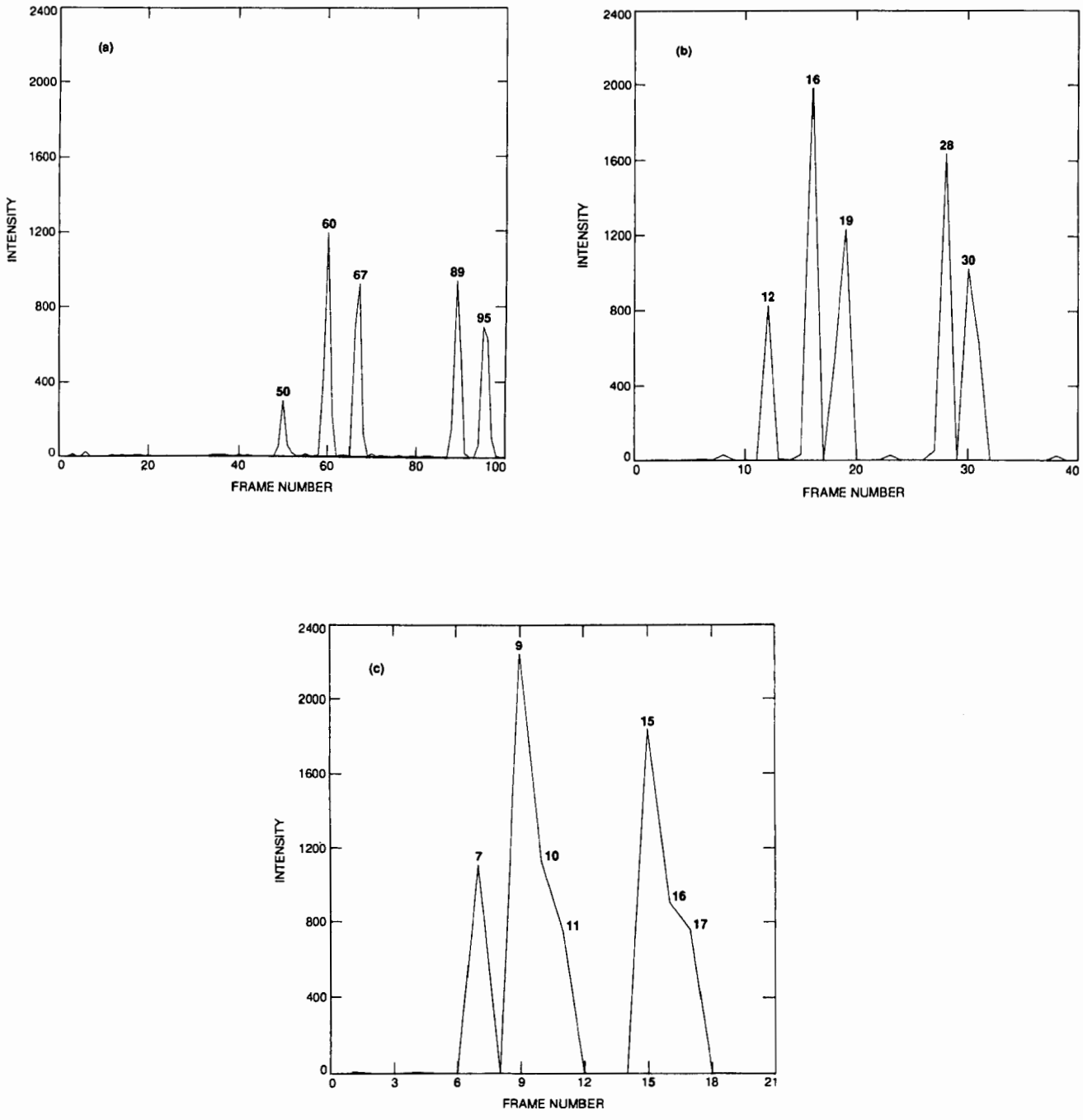

Fig. 4 Effect of signal integration time on resolution of GC peaks. Integration times of 100, 250, and 500 μs were used for a frame in (a), (b), and (c), respectively. The peaks corresponding to dichlorodifluoromethane and chloromethane, and bromomethane and chloroethane are not resolved with 500 μs integration time.

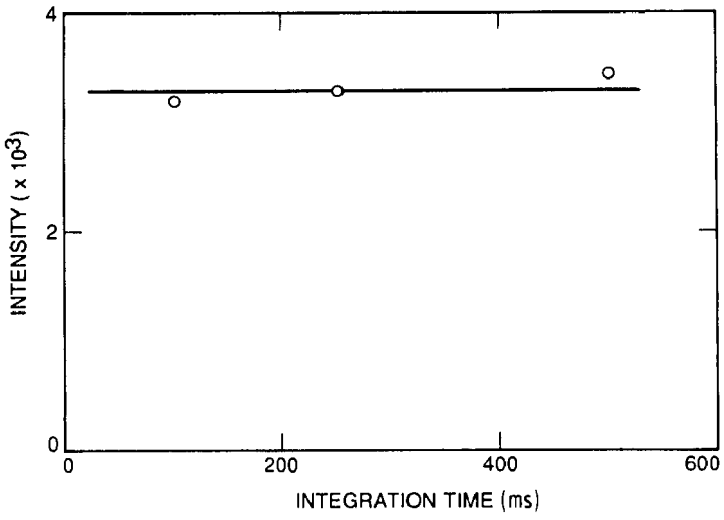

Fig. 5 Sum of the intensities of the frame comprising the last two peaks in Figs. 4 a, b, c are plotted against their frame integration time. The sum is found to be independent of the integration time.

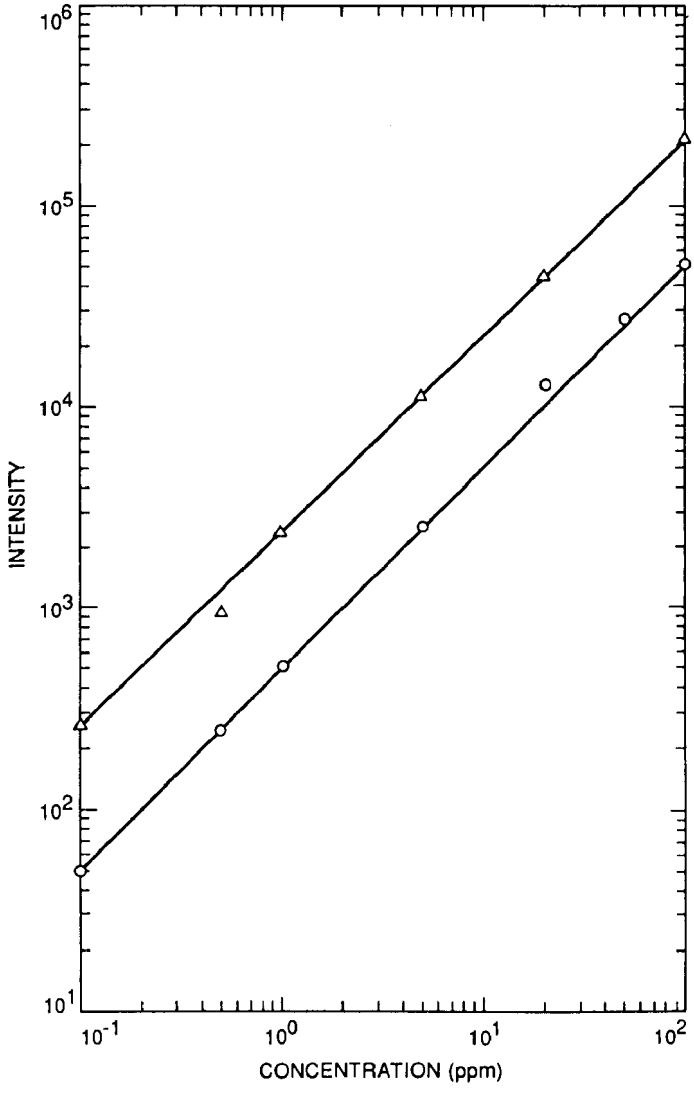

Fig. 6 The straight line plots show a linear dynamic range of $>10^3$ Os represent the sum of intensities in various frame of mass 83 (characteristic of chloroform) where as Δs represent the sum of intensities for a group of masses 76-78 (characteristic of benzene).

APPLICATION OF A RETENTION INDEX APPROACH USING INTERNAL STANDARDS TO A LINEAR REGRESSION MODEL FOR RETENTION TIME WINDOWS IN VOLATILE ORGANIC ANALYSIS

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The retention time (RT) of an analyte can be predicted by measuring its fractional distance between the RT of the internal standard (IS) eluting before the analyte and the RT of the IS eluting after the analyte. The development of RT windows using the retention index method involves calculation of a prediction interval that is derived using linear regression statistics. This approach can also be adapted to the relative retention time (RRT) method, which uses one rather than two internal standards to predict an analyte's RT. Linear regression equations were derived and software was developed for linked operation with a gas chromatography (GC) data system. RT windows were established to compare the performance of the RT index method versus the RRT and external standard techniques. Data sets were generated under a variety of conditions for purge and trap analysis of calibration standards using megabore capillary and packed columns with a dual detector system. RT windows generated using the RT index method were much narrower than those obtained using the RRT method in variable-temperature environments and slightly narrower than the RRT method in a controlled-temperature environment. The RRT and the RT index methods generated much narrower windows than the external standard method under all conditions. All methods were successful in terms of speed of calculation, minimal QC failures, and few interferences. Because the RT index method achieves the narrowest prediction windows of the three techniques, it offers increased specificity of analyte identification without changing the probability of missing an analyte that is present.

INTRODUCTION

When GC analysis is performed in a mobile laboratory, fluctuations in ambient temperature and other factors can cause greater variations in analyte RTs than under more controlled laboratory conditions. The use of ISs can improve the accuracy of RT predictions under such conditions. The RRT method successfully compensates for RT shifts when the analyte elutes very close (within ± 20 percent) to the IS but provides a less accurate estimation of RTs for analytes that elute farther away. Whereas the RRT method assumes that an analyte's RT will be increased or decreased in proportion to the ratio of the RTs of the IS in the sample divided by the standard, often analyte behavior is intermediate between a proportional RT shift and a constant, additive shift. The RT index method offers the advantage of compensating for either type of shift by means of a linear interpolation in the predicted magnitude of RT shifts in the region from the IS that elutes before the analyte to the IS following the analyte. If the general 2 parameter linear equation for prediction of RTs is employed ($IS_1 \cdot A + IS_2 \cdot B$ = predicted RT), then it can be shown that a range of predicted RTs will occur as the fitting parameters A and B are varied, with the predictions based upon the RRT method using the first IS (B = 0) or the second IS (A = 0) at either extreme and with the RT index method (having the side constraint A + B = 1) yielding a prediction that is intermediate between the two RRT methods. In addition, the RT index method is more practical than other enhanced prediction techniques. This is because it is only a one-parameter method and so does not require multiple calibration runs to compute the prediction coefficients as is necessary with the true two-parameter linear model referenced above.

GC conditions were selected for rapid and simultaneous separation and identification of 33 analytes using purge and trap sample preconcentration, DB-624 or 1% SP1000 analytical columns, and a PID/ECD dual detector system. Three IS reference peaks were used for each detector. Standard operating procedures (SOPs) and computer programs were written so that the width of the RT window for each analyte was computed as plus or minus the square root of the variance of the observed minus the predicted RTs within a set of standard analyses, multiplied by the student's t-value using a 99% confidence level. The width of RT windows calculated in this manner was considered valid for up to 60 days, as long as GC conditions remained constant. The center of each analyte's prediction window was calculated every day using the RTs from a single standard run in the 12-hour period prior to the sample. Predicted RTs were computed for all three techniques (external standard, RRT, and RT index). The RRT technique and the RT index technique were designated as the primary methods for analyte identification, with the external standard technique applicable only to those (rare) situations where interferences precluded the use of ISs for RT prediction.

The GC system was operated in the Region 3 EPA Field Investigation Team (FIT) mobile laboratory and also in the FIT base-support facility. The effect of ambient temperature fluctuations was investigated by analyzing a series of standards and calculating and plotting RT window widths under several different temperature conditions and environments. In addition to demonstrating the overall superiority of the RT index method over the RRT and external standard methods, this investigation provided insight into several factors that influence RT variance.

THEORY

All three RT prediction techniques discussed above utilize RT windows that are confidence intervals for the predicted minus the observed values of the retention time. The RT window width is computed as a 2-tailed 99% confidence interval using the t-distribution coefficient multiplied by the square root of the variance of the observed minus the predicted RT:

(1) $$\text{RT window} = \pm t_{0.995,df} \times \sqrt{\text{Var}(RT_{obs} - RT_{pred})}$$

The above equation is valid provided that the observed RTs exhibit constant variance and observed minus predicted RTs exhibit a normal distribution. These assumptions could not be strictly verified because of the small data sets (typically, n = 6 standards) employed to calculate the variance in each case; however, moderate departures from normality should still produce reasonable estimations.

The derivation of the variance of the observed minus the predicted RT is outlined below for the RT index method.(1) The variance for the RRT and the external standard methods can be derived in an analogous fashion.(2,3) The RT index prediction formula is as follows:

(2) $$\frac{C_X - I_{1X}}{I_{2X} - I_{1X}} = \frac{C_S - I_{1S}}{I_{2S} - I_{1S}}$$

Where X = sample, S = standard, C = the analyte, and I_1 and I_2 are the bracketing internal standards.

(3) Algebraic rearrangement of equation 2 leads to:

$$C_X = \left(\frac{I_{1X} + I_{2X}}{2}\right) + \left(\frac{I_{2X} - I_{1X}}{2}\right)\left[\frac{C_S - \left(\frac{I_{2S} + I_{1S}}{2}\right)}{\left(\frac{I_{2S} - I_{1S}}{2}\right)}\right]$$

(4) Introduce the change of variables Z_1 and Z_2:

$$Z_1 = \frac{I_1 + I_2}{2} \quad \text{and} \quad Z_2 = \frac{I_2 - I_1}{2}$$

(5) Substituting (4) into (3): $$C_X = Z_{1X} + Z_{2X}\left[\frac{C_S - Z_{1S}}{Z_{2S}}\right]$$

(6) Equation (5) happens to be the linear regression solution for the linear equation with one calibration run only: $C_X = Z_{1X} + Z_{2X} A$

(7) To derive the slope of the regression line (A), the sum of the square of the errors in the regression (observed minus predicted values) is minimized by taking the first derivative and setting this equation equal to zero. This yields:

$$A = \frac{\sum_{i=1}^{N_P} Z_{2i}(C_i - Z_{1i})}{\sum_{i=1}^{N_P} Z_{2i}^2}$$

Where N_P = no. of standards used to calculate "A."

(8) To derive the variance of the observed minus the predicted retention time, it is necessary to derive the variance of "A." This is illustrated in reference 1 and yields:

$$\text{Var}(A) = \frac{\text{Var}(C_i)}{\sum_{i=1}^{N_P} Z_{2i}^2}$$

(9) $$\text{Var}[RT_{obs} - RT_{pred}] = \text{Var}(C_i - Z_{1X} - Z_{2X} A)$$

(10) Because Z_{1X} and Z_{2X} are treated as constants:

$$\text{Var}[RT_{obs} - RT_{pred}] = \text{Var}(C_i) + Z_{2X}^2 \text{Var}(A)$$

(11) Substituting equation (8) into (10):

$$\text{Var}[RT_{obs} - RT_{pred}] = \left[1 + \frac{Z_{2X}^2}{\sum_{i=1}^{N_P} Z_{2i}^2}\right] \text{Var}(C_i)$$

(12) From chapter 11, section 11.3 of reference no. 2, the unbiased estimate of the variance of the observed (retention time) value about the regression is related to the sum of the residuals from the fitted regression by the following equation:

$$\text{Var}(C_i) = \frac{1}{N-1} \sum_{i=1}^{N} (RT_{C(i)} - RT_{pred})^2$$

In this case, the value of N - 1 is used because only one parameter ("A" from equation 7) is calculated from the data.

(13) When only one standard is used to predict the retention times for a sample, $N_P = 1$; whereas, the number of standards used to estimate the variance of the observed retention time does not equal 1. Making this substitution into equation (11) and substituting equation (12) into (11):

$$\text{Var}[RT_{obs} - RT_{pred}] = \left\{1 + \frac{Z_{2X}^2}{(Z_{2std})^2}\right\} \times 1/(N-1) \sum_{i=1}^{N} (RT_{C(i)} - RT_{pred})^2$$

(14) Substitution of the identities for Z_1 and Z_2 from equation (4) and "A" from equation (7) into equation (6) allows equation (6) to be substituted for the term "RT_{pred}" in equation (13). Simplification yields:

$$\text{Var}[RT_{obs} - RT_{pred}] = \left\{1 + \frac{(RT_{I2X} - RT_{I1X})^2}{(RT_{I2std} - RT_{I1std})^2}\right\} \times \frac{\sum_{i=1}^{N} \left(2 \times RT_{C(i)} - I_{1i} - I_{2i} - (I_{2i} - I_{1i}) A\right)^2}{2 \times (2N - 2)}$$

Where:

$$A = \frac{\sum_{i=1}^{N} (I_{2i} - I_{1i})(2 \times RT_{C(i)} - I_{1i} - I_{2i})}{\sum_{i=1}^{N} (I_{2i} - I_{1i})^2}$$

(15) Because one standard run is used to determine the center of the prediction window in a sample, equations (1) and (2) can be combined to yield the RT index prediction window as follows:

$$RT\,window = RT_{Ia(SPL)} + \frac{(RT_{Ib(SPL)} - RT_{Ia(SPL)})}{(RT_{Ib(STD)} - RT_{Ia(STD)})} \times (RT_{C(STD)} - RT_{Ia(STD)}) \pm t_{0.995,N-1}\sqrt{Var\,[RT_{obs} - RT_{pred}]}$$

Where:

$RT_{Ia(SPL)}$ = RT of IS eluting before C in sample.
$RT_{Ib(SPL)}$ = RT of IS eluting after C in sample.
$RT_{Ia(STD)}$ = RT of IS eluting before C in standard.
$RT_{Ib(STD)}$ = RT of IS eluting after C in standard.
$Var\,[RT_{obs} - RT_{pred}]$ = equation (14)

(16) For determination of the RT window width using the RRT method, the formula for the variance of the observed minus predicted (RT) value can be extracted from reference nos. 2 and 3, yielding:

$$Var\,[RT_{obs} - RT_{pred}] = \{1 + \frac{RT_{I(SPL)}^2}{RT_{I(STD)}^2}\} \times 1/(N-1) \sum_{i=1}^{N} (RT_{C(i)} - RT_{I(i)} \times M)^2$$

Where:

$$M = \frac{\sum_{i=1}^{N} (RT_{I(i)} \times RT_{C(i)})}{\sum_{i=1}^{N} (RT_{I(i)})^2}$$

N = number of standards in set used to determine RT window width

(17) The formula for the variance of the observed minus predicted (RT) value for the external standard method is also found in reference nos. 2 and 3:

$$Var\,[RT_{obs} - RT_{pred}] = 2/(N-1) \sum_{i=1}^{N} [RT_{C(i)} - 1/N \sum_{j=1}^{N} RT_{C(j)}]^2$$

Where: N = number of standards used to determine RT window width

$RT_{C(i)}$ = RT of C in standard i

EXPERIMENTAL SECTION

GC Configuration. A Varian 3300 gas chromatograph was equipped with a Tracor photoionization detector (PID) and a ^{63}Ni electron capture detector (ECD) arranged in series with a splitter mounted ahead of the ECD to shunt 97 to 99 percent of the PID effluent away from the ECD. The GC was connected to a Tekmar LSC 2000 sample concentrator for purge and trap analysis of soil or water. Data acquisition and reduction were accomplished through a Nelson Analytical PC Integrator System that consisted of an AT-compatible computer connected to a 10,000 data-point-capacity interface module.

Computer Programs. Nelson Analytical software (rev. 5.0) was used to tentatively identify peaks and for quantitation. In the first phase of this project, RT window widths were calculated using an HP-15c calculator program. This interim procedure was used while BASIC programs were developed for linked operation with the GC data system. The BASIC program developed to calculate the width of RT windows reads area/RT files created by the Nelson system for several standards run over a 7- to 12-hour period, calculates the width of RT windows using all 3 techniques (external standard, RRT method, and RT index method), and outputs these windows to a disc file. (This program also allows pooling of RT windows over several 12-hour periods.) For each sample, the Nelson software produces a disc file containing concentration results and tentative peak assignments. Next, the second BASIC program reads this sample file, the method file containing the daily standard RTs, and the RT window width file. Two standard outputs are produced: The first consists of compounds tentatively identified as present by the Nelson software and tabulates the observed minus predicted RTs versus the width of RT windows for all three techniques. The second printout lists all compounds present in the RT window file (not just "hits"), and a printout of predicted RTs and low and high limits of the RT prediction window is tabulated for each compound using all three techniques. This BASIC program substitutes a minimum RT window width if the width of the calculated window is less than a specified value. (This avoids use of RT windows that are narrower than the prediction error caused by the step size of the integrator.) For this work, the integrator step size was set to 0.01 minute, and the minimum allowable width was set (based upon worst-case scenarios) to 0.02 minute. This program also allows a constant to be added to the calculated width if two compounds co-elute in the standard and require a wider window to ensure detection of both components.

Analyte Selection and GC Separation. EPA Region 3's pre-remedial program required determination of analytes from the EPA Contract Laboratory Program's target compound list (TCL). All volatile TCL analytes except the four gases were included in the SOPs for analysis. GC conditions were optimized for the fastest analysis times that would not degrade resolution between adjacent analytes. For the capillary column, helium flow was 7 ml/min. The GC was held at 40°C for 7 minutes, followed by a 4°C per minute ramp to 75°C, followed by a 10°C per minute ramp to 138°C. For the packed column, helium flow was 40 ml/min. The GC was held at 45°C for 3 minutes, followed by an 8°C per minute ramp to 215°C. The ECD split ratio was about 65:1 in all cases.

Selection of Internal Standards. Three IS peaks were desired for each column and detector so that most analytes could be bracketed by IS peaks on either side. Based upon trial testing, a final set of ISs was selected for use on each column. These ISs are listed in table 1 along with target analyte RTs.

Table 1: Analyte and IS Retention Times

Compound	Capillary Column		Packed Column	
	PID	ECD	PID	ECD
(IS) 3-Cl-2-mepropene	7.42	---	---	---
(IS) 2-Br propene	---	---	11.98	---
(IS) BrCl methane	---	7.74	----	10.26
(IS) 2-Br-1-Cl propane	---	15.80	---	19.19
(IS) 4-Br butene	11.92	---	---	---
(IS) 1-Br butane	---	---	18.58	---
(IS) 1,3-Br_2-1-propene	20.54	20.83	---	---
(IS) 4-BrF benzene	---	---	30.21	---
(IS) 1-Br-3-Cl-2-mepropane	---	---	---	23.84
acetone	3.81	---	7.43	---
1,1-dichloroethene	3.81	4.08	9.59	9.80
carbon disulfide	4.13	---	8.42	---
methylene chloride	4.48	4.76	6.89	7.10
1,1-dichloroethane	---	5.88	---	11.06
trans-1,2-dichloroethene	4.88	---	11.53	11.73
2-butanone	5.73	---	12.67	---
cis-1,2-dichloroethene	6.88	---	11.53	11.73
vinyl acetate	6.88	---	14.53	---
chloroform	---	8.00	---	12.31
1,1,1-trichloroethane	---	8.45	---	14.32
carbon tetrachloride	---	8.88	---	14.70
1,2-dichloroethane	---	9.44	---	13.00
benzene	9.09	---	17.53	---
trichloroethene	10.95	11.22	17.05	17.26
1,2-dichloropropane	---	11.80	---	16.50
bromodichloromethane	---	12.67	---	15.18
cis-1,3-dichloropropene	13.73	14.01	16.53	16.73
4-methyl-2-pentanone	14.29	---	20.74	---
toluene	14.67	---	23.85	---
trans-1,3-dichloropropene	15.46	---	17.53	---
1,1,2-trichloroethane	---	16.23	---	17.93
tetrachloroethene	16.29	16.57	22.60	22.81
2-hexanone	16.81	---	22.24	---
dibromochloromethane	---	17.26	---	17.93
chlorobenzene	18.38	---	25.01	---
ethyl benzene	18.70	---	27.21	---
m-xylene	18.97	---	32.05	---
p-xylene	18.97	---	33.46	---
o-xylene	19.77	---	33.46	---
styrene	19.77	---	32.05	---
bromoform	---	20.34	---	20.57
1,1,2,2-tetrachloroethane	---	21.34	---	22.81

Retention Time QC. QC requirements were developed in SOP format by FIT for Region 3 EPA's pre-remedial program.(1) These SOPs required determination of external standard-type RT windows for IS monitoring each time analyte RT windows were computed. The standard run in the 12-hour period prior to each sample was used in conjunction with sample internal standard RTs, to predict the center of the RT window for each analyte. A second standard was run at the end of each 12-hour analysis period and was required to exhibit RTs for all analytes that were within the windows based upon the prior standard. In addition, ISs in all analytical runs were required to fall within RT windows. If IS RT window criteria were exceeded, the analyst was to check for co-eluting IS interferences via a decision scheme in the SOP. Co-elution problems required data evaluation using external standard quantitation or re-analysis on the second column. Conversely, re-analysis of the sample on the same column was required if there was no evidence of IS co-elution problems.

Method Evaluation. Base laboratory testing normally was done under a controlled temperature environment (± 2°C), although on one occasion, ambient temperatures were deliberately varied by 4°C to demonstrate the resulting effect on RT window width. In-field testing was conducted inside the FIT mobile laboratory. Ambient temperature control within the mobile laboratory was achieved via a central, ceiling-mounted HVAC unit that was manually operated. Monitoring of the ambient temperature surrounding the GC was accomplished via a thermometer mounted on the side of the GC, away from all heated zones and GC blower outputs. The GC was operated in the mobile laboratory under hot weather conditions in which the air conditioner had difficulty achieving temperatures less than 29°C. Operations were also conducted under cool weather conditions in which ambient temperature control was achievable but, because of the manual heater control, variable over a 21° to 25°C range over the course of a typical day.

RESULTS AND DISCUSSION

Table 2 indicates the various conditions under which RT windows were generated and references the figures that depict associated RT window performance. Each of these graphs illustrates the plus or minus width of RT windows for all three techniques, for each analyte, plotted against the mean RT for the analyte. The external standard method's RT window widths are represented by circled points on these plots and are generally greater than the RRT window widths (denoted with an asterisk) or the RT index window widths (represented by squares). Vertical lines are located at the elution times of each IS and are drawn with heights that indicate the width of IS RT windows (which are calculated using the external standard formula). The minimum allowable RT window width (set at 0.02 minute) is represented on these graphs by a horizontal line.

Table 2: Key to RT Window Figures

Figure No.	GC Column	Detector	Location	Ambient Temp. Range
1a	DB-624	PID	base lab	23 - 24.5°C
1b	DB-624	ECD	base lab	23 - 24.5°C
2a	DB-624	PID	mobile lab	24 - 29.5°C
2b	DB-624	ECD	mobile lab	24 - 29.5°C
3a	DB-624	PID	mobile lab	21.5 - 25°C
3b	DB-624	ECD	mobile lab	21.5 - 25°C
4a	1% SP1000	PID	base lab	20°C
4b	1% SP1000	ECD	base lab	20°C
5a	1% SP1000	PID	base lab	20 - 24°C
5b	1% SP1000	ECD	base lab	20 - 24°C

Figure nos. 1, 3, 4, and 5 each represent the RT windows from analysis of six standards on a given day, using a t-value with five degrees of freedom. Figure no. 2 was calculated with four degrees of freedom using pooled variances from standards run on two adjacent days. (This t-value is only 15 percent greater than that used in other figures.)

General Trends. Comparison of figure nos. 2 and 3 to figure no. 1 and comparison of figure no. 5 to figure no. 4 indicate that the width of RT windows for all three techniques increases substantially as the span of ambient temperatures increases. The level of significance of these comparisons is graphically illustrated by a plot of the square root of F-test

critical values (expressed as horizontal lines) superimposed over plots of the ratio of RT window widths obtained at variable versus controlled temperatures. Figure nos. 6, 7, and 8 compare the RT windows of figure no. 2 to figure no. 1, figure no. 3 to figure no. 1, and figure no. 5 to figure no. 4, respectively. (Critical values in figure no. 6 were corrected for the different t-values used.) The F-tests indicate that many analyte RT windows cannot be considered to be from populations having identical variance at a 10 percent level of significance. Therefore, RT windows obtained under controlled temperatures should not be applied to analytical runs under variable temperatures and vice versa.

Narrower RT windows, which indicate the superiority of the RT index method over the RRT method, are much more pronounced under the variable temperatures in figure nos. 2, 3, and 5 than under the controlled temperatures in figure nos. 1 and 4. Capillary column behavior under variable temperatures revealed that 94 percent of RRT windows were wider than corresponding RT index windows, with 56 percent displaying at least a factor of 2 ratio. Under controlled temperatures, capillary RRT windows were wider in 92 percent of cases, with 33 percent 2-fold wider. Packed column behavior under variable temperatures revealed that 83 percent of RRT windows were wider, with 46 percent 2-fold greater. Under controlled temperatures, packed column RRT windows were wider in 88 percent of cases, with only 8 percent 2-fold wider. In figure nos. 1 and 4, most of the RT prediction errors were on the same order as errors caused by the integrator's step size. This explains the noisy appearance of these RRT and RT index plots.

Capillary Column Trends. Under variable-temperature conditions (figure nos. 2 and 3), the RRT and RT index plots exhibit pronounced spikes at RTs that correlate with a one- to four-minute retention time region after the junction points where the GC program is changed. (At 7 minutes, the capillary column ramp begins, and at 15.75 minutes, the ramping rate shifts from 4 to 10°C per minute.) The fact that these spikes occurred at roughly the same RTs on the PID and ECD, despite the elution of the PID's middle IS nearly four minutes earlier than the middle IS used for the ECD, suggests that this phenomenon is not just a consequence of decreasing predictive ability (higher RT window width) as analytes elute farther away from the nearest IS. However, the adverse effects of a GC program's junction point may be partially offset if an IS elutes very close to the junction point. For example, the spikes at 16 minutes in the ECD plots in figure nos. 2b and 3b are relatively smaller than corresponding spikes in the PID plots in figure nos. 2a and 3a.

One feature unique to figure no. 2 was the unusually high values for RRT window width at the beginning of the PID and ECD plots. This is a consequence of high ambient temperatures adversely affecting the GC's ability to maintain precise control over the desired 40°C initial temperature. (A second unique feature of figure 2b was a bimodal distribution caused by inclusion of a separate analytical run containing only four analytes in the RT window plots.)

Packed Column Trends. Packed column RT windows generated under variable and controlled temperatures exhibited a range of values very similar in magnitude to those obtained on the capillary column. It is interesting that RT prediction errors are of similar magnitude because other properties of the packed column (namely resolution) are markedly inferior in comparison with capillary chromatography. Packed column behavior under variable-temperature conditions (figure no. 5) also revealed RRT and/or RT index plots with spikes at certain RTs. The RRT window spike between 13 and 14 minutes in the ECD plot (figure no. 5b) does not appear in the PID plot (figure no. 5a). This spike may be attributable to a relatively greater distance between these ECD analytes and the first IS. (Note that the RT index method's windows were nearly optimum throughout the region where this RRT spike occurred, resulting in windows that were narrower than the RRT method by up to a factor of six.) The RRT and the RT index method exhibited spikes of nearly equal height at elution times of 23 to 26 minutes in the PID plot in figure no. 5a. These spikes may be related to wide spacing between ISs and also to the third IS eluting in the final temperature hold zone that appears to be associated with higher RT variance for all compounds (as suggested by wider external standard RT windows). Because the third ECD IS eluted much earlier, this trend was not observed on the ECD.

CONCLUSIONS

The RT index method performed somewhat better than the RRT method under controlled-temperature environments. The variable-temperature environments afforded by the mobile laboratory resulted in wider windows for all three methods, but the RT index method showed more dramatic advantages over the RRT method under these conditions. The RT index method showed the greatest degree of superiority over the RRT method at elution times that were affected by GC program ramp shifting points and when analyte RTs were most distant from the nearest IS.

Because all three techniques generate RT windows that are sensitive to temperature fluctuations over the course of a day, ambient temperature monitoring in the vicinity of the GC is useful during RT window development to define the range of conditions over which the derived windows will be applicable. Precise temperature control over the laboratory environment is desirable in GC analysis; however, because mobile laboratory temperature control is rarely as good as that in a fixed laboratory, the use of the RT index method will greatly assist in achieving the most specific GC analysis possible. By using the RT index approach, mobile laboratory GC analysis can be performed in a manner that minimizes the chances of erroneous (false positive) identification of target analytes.

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ACKNOWLEDGEMENTS

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FIG.1a: RT WINDOWS FOR CAP.COL.,PID, AMBIENT TEMP 23-24.5°C

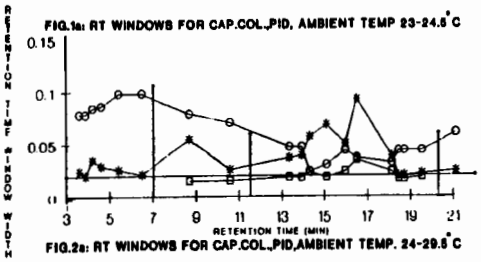


FIG.1b: RT WINDOWS FOR CAP.COL., ECD, AMBIENT TEMP 23-24.5°C

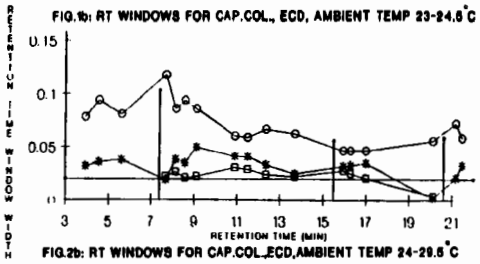


FIG.2a: RT WINDOWS FOR CAP.COL.,PID,AMBIENT TEMP. 24-29.5°C

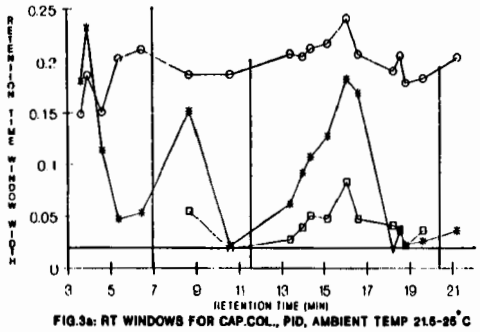


FIG.2b: RT WINDOWS FOR CAP.COL.,ECD,AMBIENT TEMP 24-29.5°C

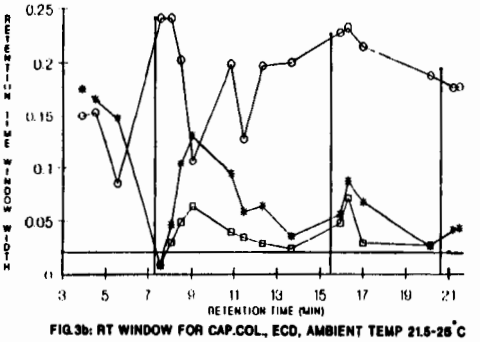


FIG.3a: RT WINDOWS FOR CAP.COL., PID, AMBIENT TEMP 21.5-25°C

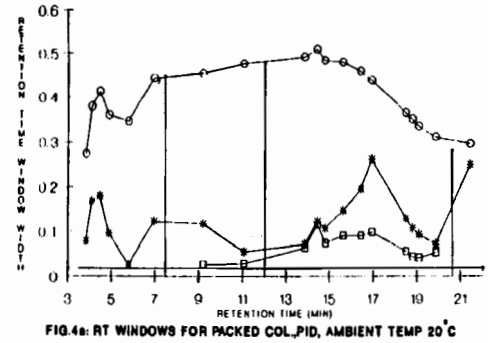


FIG.3b: RT WINDOW FOR CAP.COL., ECD, AMBIENT TEMP 21.5-25°C

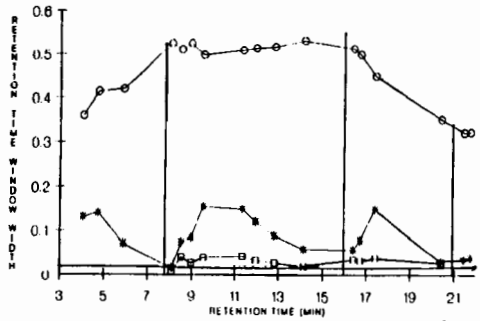


FIG.4a: RT WINDOWS FOR PACKED COL.,PID, AMBIENT TEMP 20°C

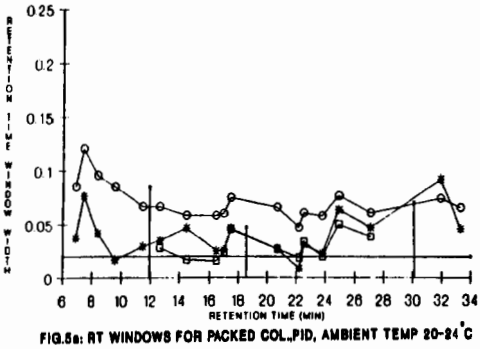


FIG.4b: RT WINDOWS FOR PACKED COL.,ECD, AMBIENT TEMP 20°C

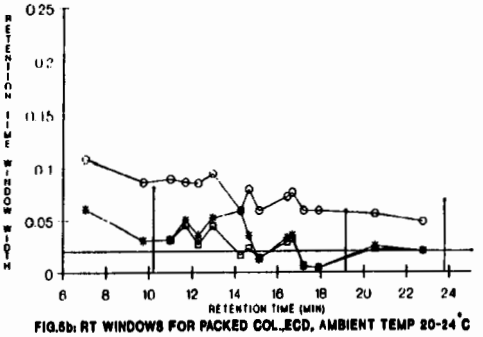


FIG.5a: RT WINDOWS FOR PACKED COL.,PID, AMBIENT TEMP 20-24°C

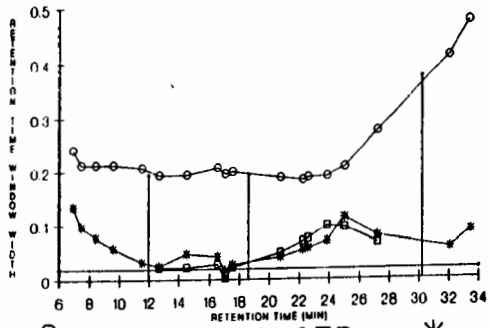
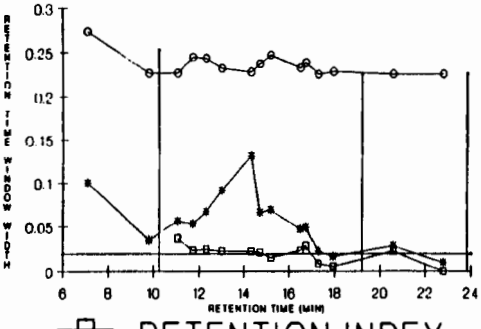


FIG.5b: RT WINDOWS FOR PACKED COL.,ECD, AMBIENT TEMP 20-24°C



EXTERNAL STD RELATIVE RT RETENTION INDEX

MIN ALLOWABLE INTERNAL STANDARDS

FIG.6a: RTW RATIOS ON CAP.COL.,PID,24-29.5°C vs. 23-24.5°C

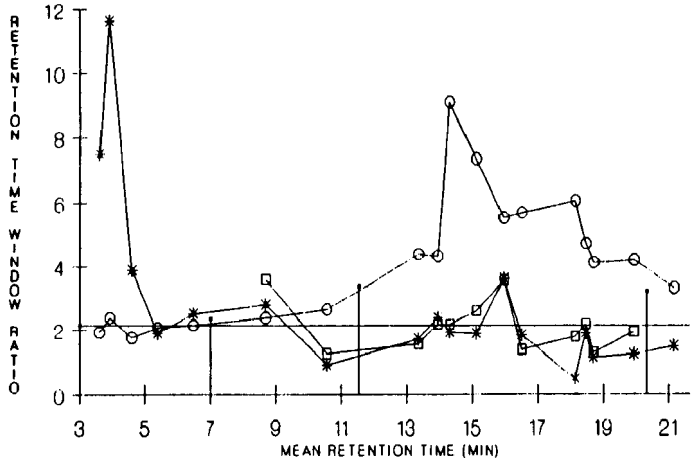


FIG.6b: RTW RATIOS ON CAP.COL.,ECD,24-29.5°C vs. 23-24.5°C

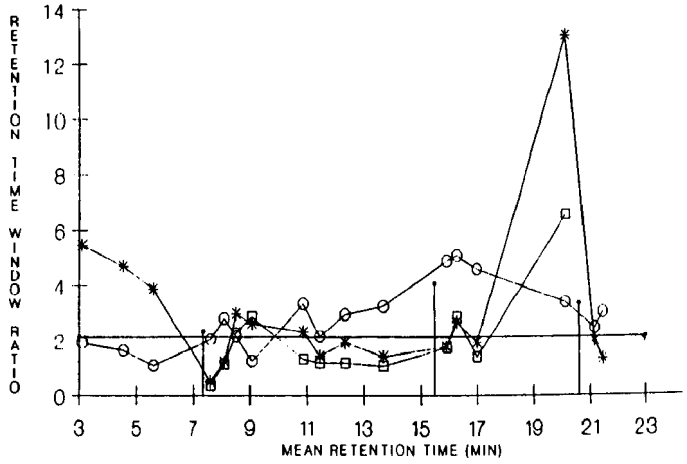


FIG.7a: RTW RATIOS ON CAP. COL.,PID, 21.5-25°C vs. 23-24.5°C

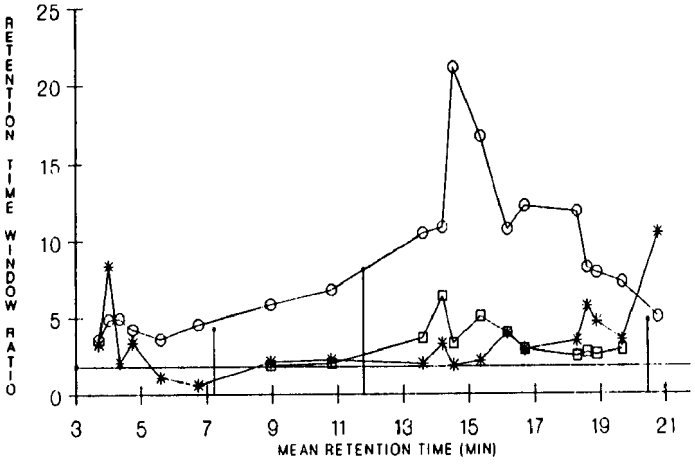


FIG.7b: RTW RATIOS ON CAP.COL., ECD, 21.5-25°C vs 23-24.5°C

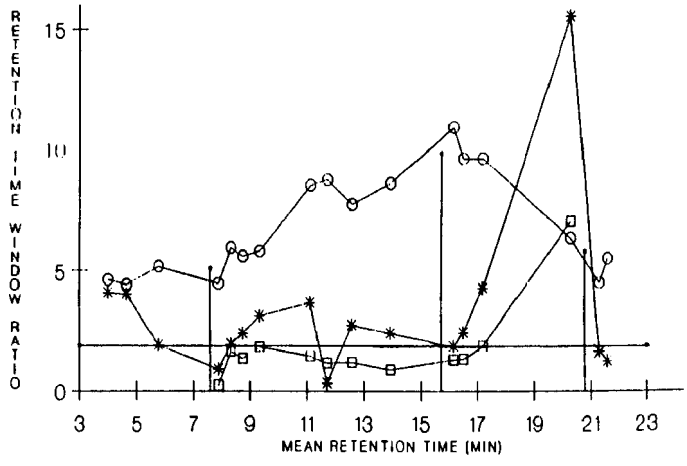


FIG.8a: RTW RATIOS ON PACKED COLUMN, PID, 20-24°C vs. 20°C

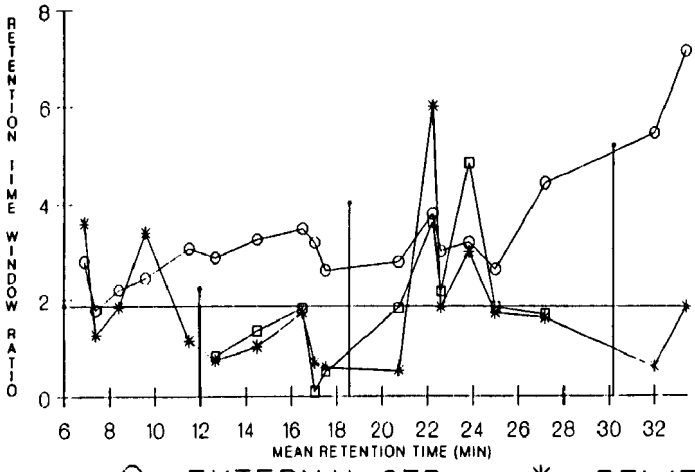
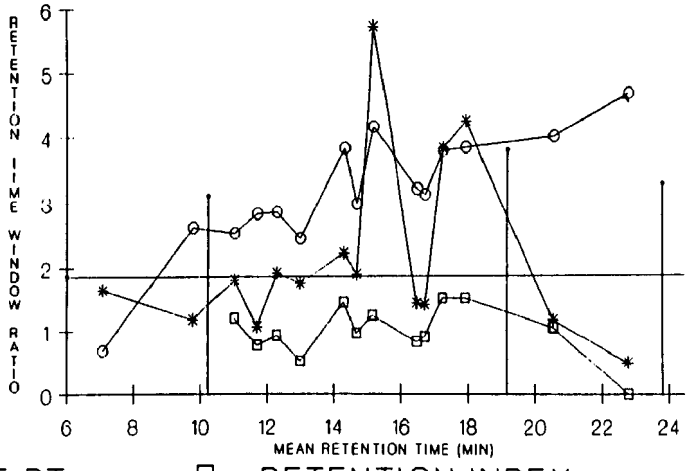
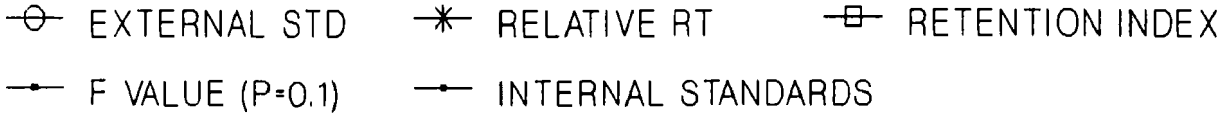


FIG.8b: RTW RATIO ON PACKED COLUMN, ECD, 20-24°C vs. 20°C





DETECTION OF AIRBORNE MICROORGANISMS USING A HAND-HELD ION MOBILITY SPECTROMETER

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Microorganism detection and identification challenge even the best microbiological, clinical and analytical instrumentation techniques. Analytical techniques such as gas chromatography of inherent volatiles, $^{14}CO_2$ radiometry, electrochemical measurement by molecular hydrogen and microcalorimetry have typical sensitivities and response times in the 10^6 cells/ml and 1.5 hr ranges, respectively. Colorimetric and fluorometric microbiological procedures fare much better and can be found in the 10^3-10^5 bacteria cells/ml and 0.25-4 hr time ranges.

The detection of fecal coliform bacteria (E. coli, Klebsiella, Citrobacter and Enterobacter) is of prime concern in water, wastewater and soil analysis and management. Since E. coli is found in 100-fold greater concentrations than the other bacteria, its detection can indicate the presence of pathogenic organisms. A Graseby-Ionics hand-held ion mobility spectrometry device was investigated for its potential in the detection and determination of microbial presence in both liquid suspension and aerosol form. A standard microbiological test that is used to detect the presence of total fecal coliforms is the extracellular enzyme reaction with that of ortho-nitrophenyl-galactopyranoside (ONPG). If these bacteria are present, the constitutive enzyme beta-D-galactosidase cleaves the colorless ONPG substrate to produce the galactosidase sugar and the yellow ortho-nitrophenol (ONP) products. Because of its relatively low melting point (45-46°C), ONP has a considerable vapor pressure (0.54 torr). This concept was exploited by the use of the ion mobility spectrometry analytical technique. Strips of filter paper were inoculated with microliter amounts of fecal coliform cells and the ONPG substrate, and the strip was then placed in a vial and stoppered. After 15 min, a clear ion mobility peak that matched that of pure ONP was registered when the hand-held unit was placed near the opening of the vial. With pure bacterial suspensions, approximately 300 cells of E. coli were detected in 15 minutes with ONPG and 1,000 cells of Bacillus subtilis were detected in 15 minutes with ONPG acetate. Indeed, the accumulated headspace vapor of the liberated ONP from the bacterial enzyme reaction was the source of the signal.

Under controlled (0.45 m^3 container) conditions, bacterial aerosols were collected by a four stage impactor and the filter paper strips from each stage were subsequently analyzed by IMS monitoring of the ONP vapor product. Positive responses were observed in the second and third stage of the impactor (corresponding to 2-4 microns) while the fourth stage (1 micron size) produced no signal.

These observations indicate the potential of ion mobility spectrometry in the detection of extremely complex analytes as that of living microorganisms under both suspension and aerosol conditions.

FIELD ANALYSIS FOR HEXAVALENT CHROME IN SOIL

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ABSTRACT

Hexavalent chromium [Cr(VI)] has a high aqueous solubility and has entered the groundwater at many hazardous waste sites. Chrome is present at over one hundred sites of concern nationally (1). Hexavalent chromium is environmentally significant. It moves rapidly from the soil through groundwater to receptors. Soils contaminated with hexavalent chromium are targeted frequently for removal and treatment.

Electroplating sites containing chromium are an important class of sites in Region 10 of the EPA. Region 10 has determined the extent of soil removal at sites by first determining the extent of leaching that corresponds to various levels of chrome in the soil. The cleanup criteria (concentration of Cr(VI) allowable in the soil) is then dictated from the desired groundwater quality. A field test procedure for the detection of chrome can then be applied to direct the soil removal effort.

The test method for defining the removal effort should be simple, field portable, quick and accurate in the parts per billion (ppb) range. X-ray fluorescence (XRF) is a proven and useful analytical tool for investigation and management of metals in soils. However, chromium is one of the heavy metals that has more than one oxidation state. Hexavalent chromium is the oxidation state of environmental concern. Hexavalent chromium can not be differentiated by the XRF. Another procedure must be used in conjunction with the XRF to establish hexavalent chromium levels in the soil. The HACH Company developed a field procedure for the analysis of hexavalent chromium in soils. The procedure reportedly permits the measurement of Cr(VI) in soil down to 250 ppb in less than 30 minutes.

HACH PROCEDURE (OUTLINE)

1) Preparation of sample:
   A) Dry sample
   B) Homogenize sample

2) Measure appropriate sample into Whirl-pak™ bag. The appropriate Sample Size is based on the Estimated Concentration in the soil.

Estimated Cr^{6+} Concentration	Sample Size
250-5000 ppb	20 g
0.50-10 ppm	20 g
2.50-50 ppm	20 g
50-1000 ppm	1 g
500-10000 ppm	1 g

3) Add extractant solution to Whirl-pak™ bag. Prepare the solution by adding one extractant pillow to 40 mLs of deionized water.

4) Extract the sample:
   Shake mixture for 15 seconds at two minute intervals. Continue for 15 minutes.

5) Filter the extraction mixture.

6)Transfer appropriate and equal aliquots of extraction fluid to two (2) 25 mL graduated cylinders and dilute to 25 mL. The aliquote size is based on the estimated Cr^{6+} concentration in the soil.

Estimated Cr^{6+} Concentration	Sample Size
250-5000ppb	10 mL
0.50-10 ppm	5 mL
2.50-50 ppm	1 mL
50-1000 ppm	1 mL
500-10000 ppm	0.1 mL

7)Add one (1) Chromaver 3^{TM} pillow to one of the graduated cylinders. Allow the solution to react for a minimum of 10 minutes.

8)Pour the contents of the graduated cylinder into viewing tubes.

9)Place the viewing tubes into the viewing box and determine the concentration

$$Cr^{6+}\ ppb = \frac{\text{disk reading (mg/mL)} \times 10^6}{\text{aliquot vol.(mL)} \times \text{sample size (g)}}$$

Quality Control: Add standard solution to soil and analyze as described above.

DISCUSSION

Region 10 has applied this procedure to actual site soils from several sites. The procedure could not be used at some sites due to interferences, but was successful detecting hexavalent chrome in soils from other sites. The Cr(VI) data are presented in Table 1 and Figures 1 through 4, where the procedure was successful. Several laboratory procedures were used for comparison with the HACH kit results. Method 1310 (Toxicity Characteristic Leaching Procedure-TCLP), method 1311 (EP Toxicity) and method 3060 are the laboratory procedures used to extract samples (2),(3),(4). The concentration of hexavalent chrome in the extract was determined by Method 7196 (5).

Figure 1 depicts the relationship between the laboratory methods and HACH kit results. The best correlation is between Method 3060 and the HACH kit results. Both methods use alkaline extractants. The TCLP and EP Toxicity methods correlate poorly with the HACH kit results. Unlike the HACH kit, these procedures require the adjustment of the pH to slightly acid.

Temperature and extraction time dependance were also evaluated using actual site soils. Figures 2, 3 and 4 present this information for two different site soils. Concentrations acquired by Method 3060 can be achieved using the HACH kit with adequate extraction times and extract temperatures. Adequate extraction time is depicted more clearly in Figure 4 for a particular extract temperature.

Figure 1 Laboratory Correlation with Test Kit

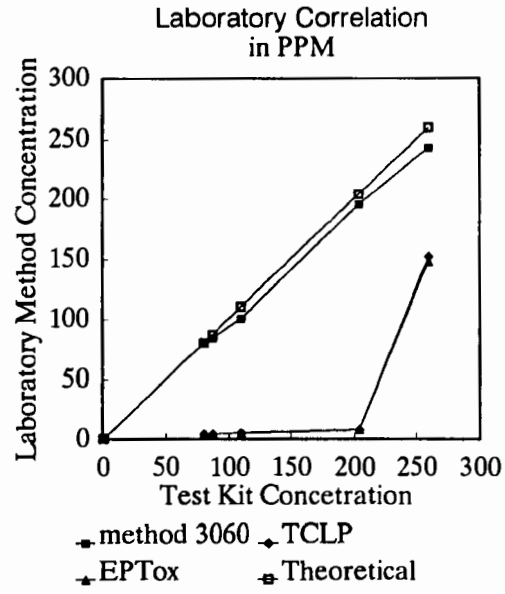

Figure 2 Extraction Time Dependence of Test Kit Results

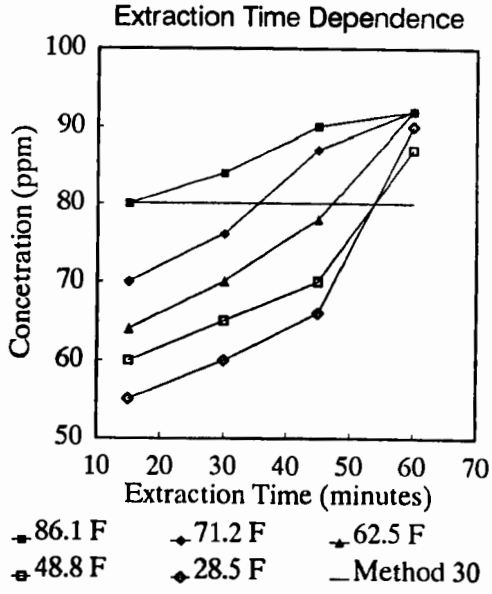

Figure 3 Temperature Dependence of Test Kit Results, Site #1, Sample #1

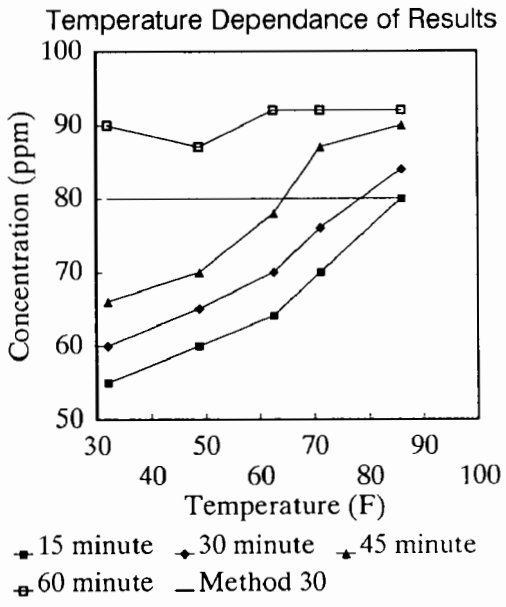

Figure 4 Temperature Dependence of Test Kit Results, Site #1, Sample #2

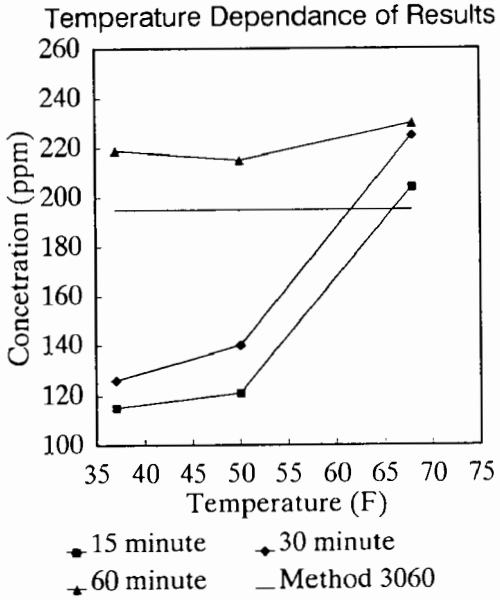

Table 1 Results from use of the test kit

Site,sample #	Temp. (F)	Extraction (min)	Ave. Conc (ppm)	RSD (%)
1,1	86.1	15	80	3.3
1,1	86.1	30	85	2.7
1,1	86.1	45	90	0
1,1	86.1	60	91	1.3
1,1	71.1	15	71	2.7
1,1	71.2	30	76	2
1,1	71.2	45	87	0
1,1	71.2	60	92	3.3
1,1	62.5	15	64	0.9
1,1	62.5	30	70	2.2
1,1	62.5	45	78	0
1,1	62.5	60	91	1.3
1,1	48.8	15	61	6.9
1,1	48.8	30	65	1.8
1,1	48.8	45	70	0
1,1	48.8	60	87	1.3
1,1	32	15	55	3.1
1,1	32	30	60	3.3
1,1	32	45	66	0
1,1	32	60	90	0
1,2	68	15	203	2.8
1,2	68	30	225	2.6
1,2	68	60	230	0
1,2	50	15	121	1
1,2	50	30	140	0
1,2	50	60	215	3.3
1,2	37	15	115	5
1,2	37	30	127	4.6
1,2	37	60	219	0.6
1,3	68	15	87	1.3
1,3	68	30	90	0
1,3	68	60	90	0
1,3	50	15	55	4.2
1,3	50	30	62	0
1,3	50	60	90	3.1
1,3	37	15	50	0
1,3	37	30	57	2
1,3	37	60	90	0
2,1	68	15	260	0
2,1	68	30	287	2
2,1	68	60	285	2.5
2,1	37	15	175	3.3
2,1	37	30	227	2.5
2,1	37	60	275	2.6
1,4	68	15	110	0
1,4	68	30	118	2.9
1,4	68	60	120	0
1,4	50	15	65	1.8
1,4	50	30	78	2.6
1,4	50	60	114	1.5
1,4	37	15	58	0
1,4	37	30	66	0
1,4	37	60	117	4.9
3,1	71.2	15	0.65	1.8
3,1	71.2	30	0.65	1.8
1,5	71.2	15	0.27	4.2

CONCLUSIONS

The HACH kit is a valid field screening procedure for hazardous waste site investigation and remediation. However, attention must be given to the possibility of interferences and adequate extraction time for the particular temperature conditions.

While the HACH procedure correlates well with Method 3060 results, it over estimates TCLP and EP Toxicity results. No false positives were detected with the limited number of analysis and limited number of wastes used in this study.

False negative results can be detected by spiking the extract with Cr(VI) after an analysis indicates no Cr(VI) present. This verification procedure could be run on each soil matrix to reveal interferences.

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NOTE: No official support or endorsement by the Environmental Protection Agency, federal employees, or any other agency of the Federal Government of the product, the procedure, or its manufacturer, is intended or should be inferred by this paper or presentation.

TRANSPORTABLE TUNABLE DYE LASER FOR FIELD ANALYSIS OF AROMATIC HYDROCARBONS IN GROUNDWATER

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INTRODUCTION

We have developed a transportable and fully wavelength tunable laser system for remote fiber optic fluorescence analysis of aromatic hydrocarbons. System components include a pulsed Nd:YAG pump laser, a two stage dye laser, fiber optic probe, monochromator/photomultiplier tube /digital oscilloscope detection system, and 386 portable control computer. The system can easily be moved in a van to remote locations for field operation with power supplied by a 5 kW generator. The data we present here accurately represent the system's current capabilities since the data were taken with the field version of the unit; the only difference from actual field operation is that system power was not derived from the generator.

Our approach improves on other field laser fluorescence schemes because it employs a completely wavelength tunable laser and because we emphasize time resolved detection.

SYSTEM DESCRIPTION

The system components are rigidly attached to a wheeled 2'Wx4'Lx3'H shock-mounted unistrut cart. The Nd:YAG pump laser, harmonic generator, and 0.32 m emission monochromator are located on the base of the cart. The dye laser, frequency doubling crystal, and associated optics are mounted on a 2' x 4' optical breadboard bolted to the top of the cart; the digital oscilloscope is supported over the breadboard. Connected to the system by an umbilical, the YAG laser power supply (approximately a cube two feet on a side) sits on another movable cart. Data acquisition boards, power supplies, stepper motor controllers, etc. are located in an expansion box under the optical breadboard.

The pulsed light emerging horizontally from the harmonic generator is directed up through a one-inch hole in the optical breadboard. As the beam emerges from the hole, a Pellin-Broca prism directs the light parallel to the breadboard surface as it separates the desired dye laser pump wavelength (532 or 355 nm) from the 1064 fundamental. After this separation the pump light is split into separate beams for the oscillator and amplifier cells of the Littman grazing incidence dye laser. The monochromatic and wavelength-selectable visible light from the amplifier cell is frequency-doubled into the ultraviolet with a KDP crystal. The following filter rejects residual visible light from the KDP crystal and passes about 40% of the UV light onto a lens for focussing onto the 600 micron delivery fiber. Figure 1 illustrates the pulse energies at various points in the optical train for 355 nm pumping of Coumarin 500 dye.

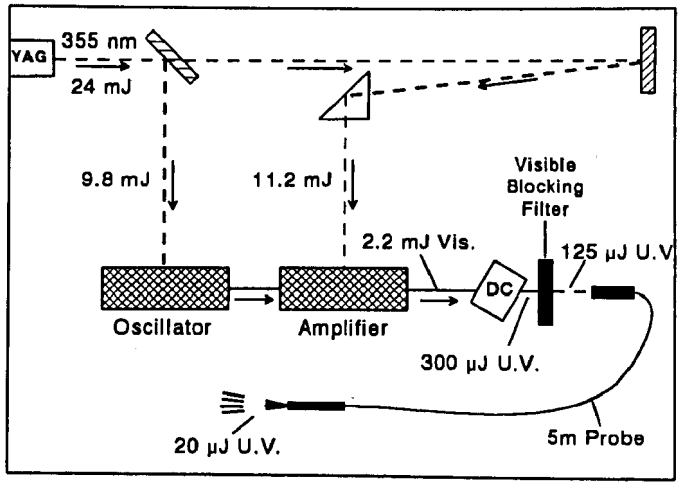

Figure 1. Pulse energy conversion

RESULTS AND DISCUSSION

Although typical of current day-to-day performance, the UV pulse energies available at the probe distal end can be markedly improved with minor modifications. For example, increasing the 355 nm pump energy to 50 mJ and changing the oscillator/amplifier split to ca. 10 mJ/40 mJ will bring the amplifier output to ca. 8 mJ. The efficiency with which the UV is freed from visible light after the doubling crystal can probably be boosted by a factor of two. Some improvement in doubling and launch efficiencies is likely also. Ultimately we expect to achieve 150-250 uJ pulse energies at the distal end of a 5 m probe.

The BTX components require excitation wavelengths shorter than those available from frequency doubling the output of a dye laser pumped at 532 nm; they require pumping at 355 nm. However, nearly any other aromatic hydrocarbon can be probed at sufficiently long excitation wavelength to permit 532 nm pumping of highly efficient dyes such as Rhodamine 6G. Owing to such factors as greater available pump energy at 532 nm (up to 150 mJ with our DCR-11 Nd:YAG laser), conversion efficiencies up to 35% with R6G, and lower fiber attenuation, we can confidently predict that pulse energies of 2 mJ or more can be delivered at 280 nm, for example. In the lab we have routinely produced 3 mJ ultraviolet (prior to launch into the fiber) with only 60 mJ of 532 nm pump energy.

The anthracene calibration curve in Figure 2 illustrates the high sensitivity (better than 10 parts-per-trillion detection limit) and wide dynamic range available for a PAH that absorbs reasonably strongly at a wavelength achievable with 532 nm pumping and not strongly attenuated by the fiber.

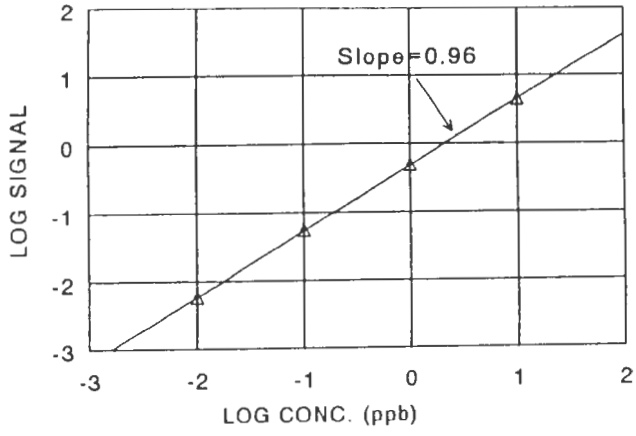

Figure 2. Anthracene calibration curve

For reasons already described (need to pump the dye laser at 355 nm, higher light attenuation by the fiber) and molecular factors (lower molar absorptivity, generally lower fluorescence quantum yield), the detection limits for the BTX components are higher than for anthracene. For example, the limit of detection for p-xylene is currently about 1 ppb (Figure 3). Benzene and toluene are even weaker emitters and their detection limits are correspondingly higher (5 ppb for toluene, 20 ppb for benzene). Nevertheless, the linear calibration plots found over a wide concentration range for all three BTX components are encouraging. Future work should yield detection limits below the MCL's.

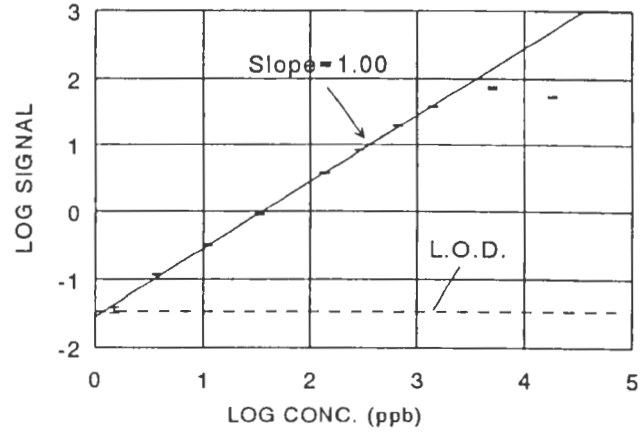

Figure 3. p-Xylene calibration curve

As mentioned in the introduction we plan to exploit the pulsed nature of our laser source as an aid to quantitate multi-component samples. Figure 4 demonstrates the accuracy with which we can measure fluorescence lifetimes.

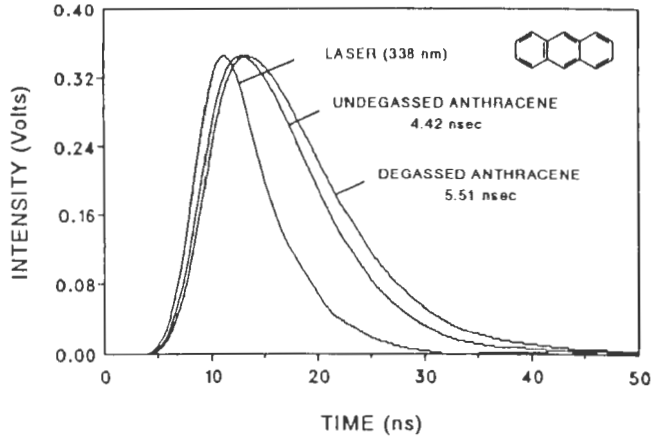

Figure 4. Anthracene lifetime test

We chose anthracene in cyclohexane as our test case because accurate literature values are available. Fluorescence decay profiles in both air-saturated and degassed cyclohexane are shown in Figure 4 along with the laser time-profile. Owing lifetime being short compared to the laser pulse duration, deconvolution is necessary. Moreover, a separate correction must be applied for the differential transit time of light through the fiber at different wave-lengths. Software to accomplish this in nearly automated fashion yielded the indicated lifetimes, which are in excellent agreement with the literature values.

Another way to prove that we are satisfactorily correcting for the fiber transit time effect is to compare lifetimes taken for the identical sample with and without the fiber optic probe. Results are shown for toluene in water in Figure 5. The same lifetime is derived after deconvolution in each case. Note that the time gap between the maximum laser intensity and the maximum fluorescence intensity is less for the probe example; the fluorescence, at longer wavelength than the scattered laser light, takes less time relative to the scattered laser light to travel via the fiber to the PMT. It is noteworthy that the fluorescence lifetimes of the individual BTX components in water are significantly different, whereas in aliphatic solvents they are all about the same. Figure 6 summarizes the values we find for degassed and air-saturated solutions. The roughly factor of two variation between benzene and toluene and a similar factor for toluene relative to p-xylene may prove helpful for separating their contributions to the total fluorescence signal.

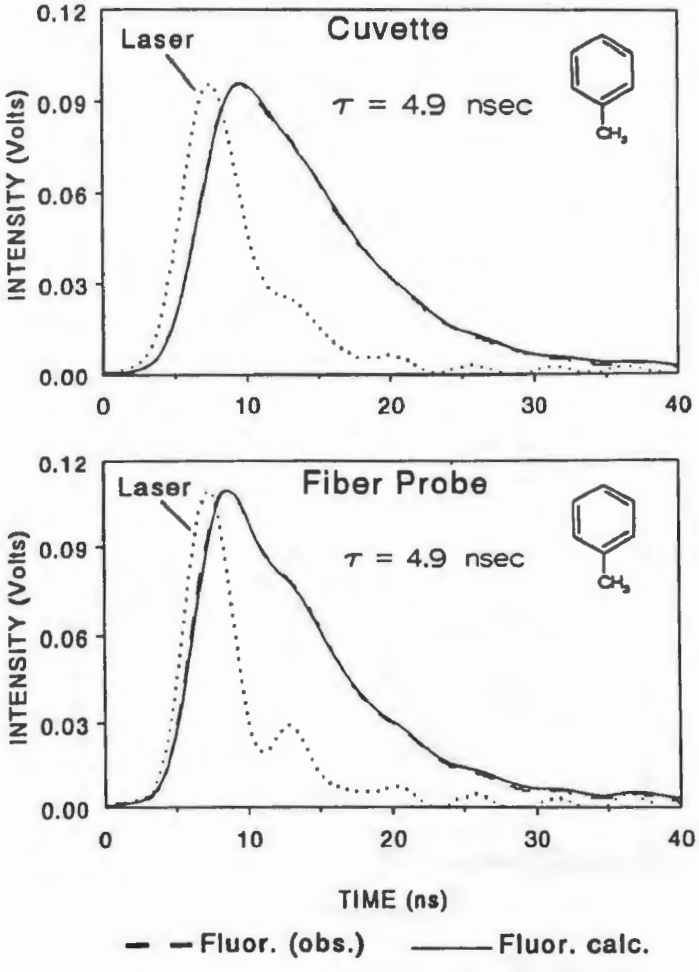

Figure 5. Toluene lifetime

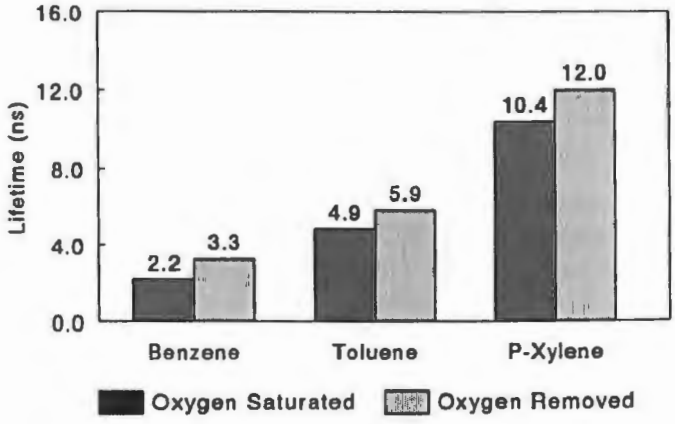

Figure 6. BTX lifetimes

Two popular multi-dimensional fluorescence techniques for chemical analysis are excitation-emission matrices (EEM's) and phase resolved fluorescence. A third possibility is illustrated in Figure 7 (next page); the analyte is JP-4 jet fuel in water. We refer to these plots as wavelength-time matrices, by analogy to EEM's. To generate a wavelength-time matrix, either the excitation or emission wavelength is stepwise varied and a fluorescence time profile collected at each setting. For figure 7 the emission wavelength that has been varied in 3 nm increments for excitation at 262 nm, such that the signal is primarily due to the BTX components.

The wavelength-time matrix at the top of the figure is for water equilibrated with JP-4. This sample therefore contains a high concentration of BTX. The bottom of Figure 7 shows the corresponding wavelength-time matrix for pure water. The narrow feature represents Raman scattering of the water solvent. In the middle picture the water Raman and BTX fluorescence make comparable contributions to the overall intensity. Over the concentration range that the water Raman band can be distinguished from the fluorescence, it can be used as an internal standard.

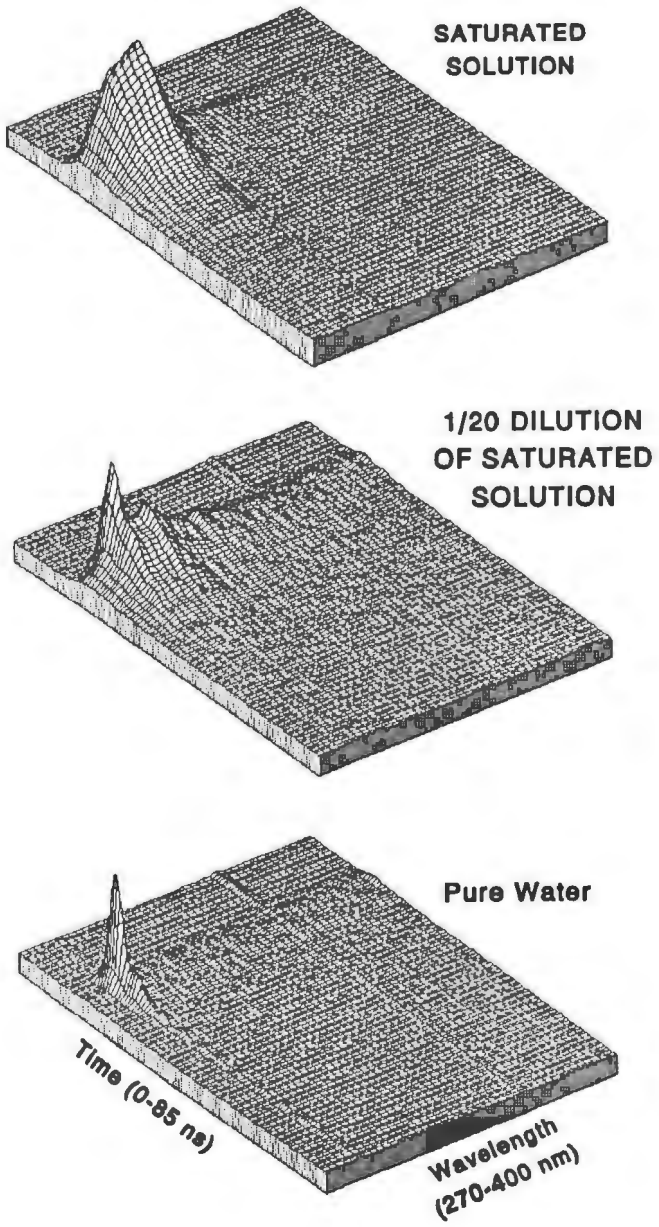

Figure 7. JP-4 wavelength-time matrices

FUTURE WORK

Because the BTX component fluorescence lifetimes are not long compared to the laser pulse duration, their fluorescence profiles are only slightly altered in time relative to that of the laser. Consequently, the Raman signal (rigorously coincident in time with the excitation) is heavily overlapped temporally with the fluorescence, making them hard to separate.

We will therefore in the future reduce the laser pulse duration to under 1 ns to gain the advantages shown in Figure 8. The indicated fluorescence decay profiles at two different laser pulse durations are for lifetimes close to the actual values for benzene, toluene, p-xylene, and naphthalene. The shorter the laser pulse relative to the fluorescence lifetime, the easier it is to select a time gate for detection such that the laser intensity is nearly zero but the fluorescence intensity is still near its maximum. We believe that the resulting better rejection of background scatter will significantly improve our detection limits for benzene. This technique will also aid rejection of physical scattering as, for example, from soil particles in a monitoring well environment.

ACKNOWLEDGMENT

This work has been supported by the Air Force Engineering Services Center.

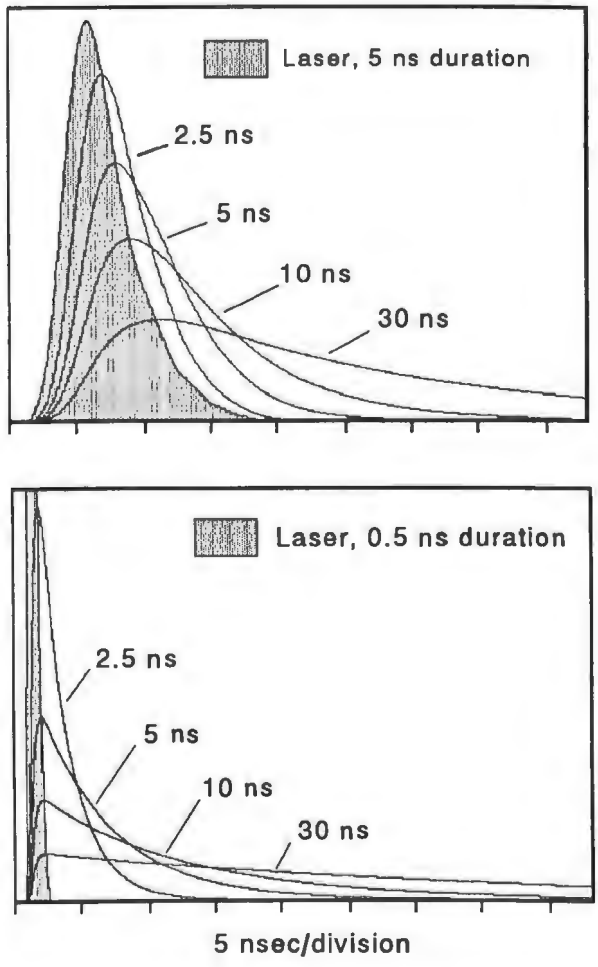

Figure 8. Fluorescence decays

Real Time Detection of Biological Aerosols

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Interest in the environmental impact of biological aerosols has increased due to the implications of aerosolized bio-materials in indoor building pollution; the release of genetically-engineered organisms into the environment; and the release of potentially pathogenic organisms downwind from sewage treatment plants. Efforts to date for the real time detection of biological aerosols have proven unsuccessful due to the lack of the technology to discriminate between potentially hazardous materials and background materials.

The integration of rapid immunoassay technology with a real-time air sampling capability is presently under investigation. A two-stage air sampler with impingement capability has been developed and integrated with an immunologically-based biosensor to effect a real-time aerosol detection capability. The sampler concentrates and impinges 100 liters of air into 100 ul of fluid. The impinged sample is then mixed with the immunoreagents, and the resulting immune complex is trapped onto a nitrocellulose filter while unreacted materials are washed away. Urease, an enzyme which effects a pH change in the substrate buffer, is used as the enzymatic tag. The slope of the resultant pH change is then determined through the use of the Light-Addressable Potentiometric Sensor.

Mass spectrometry offers an alternative means of detection of aerosols. A small, field portable mass spectrometer, based on Quadrapole Ion Storage (QUISTOR) technology, is also being developed and integrated with an air-sampling capability. The concentrated sample will then be pyrolyzed, with the resulting pyrolysates being analyzed by MS or MS/MS. The resulting spectrum will be compared against an onboard library. An artificial intelligence capability will allow unknown materials to be analyzed and retained for future reference.

Efforts to date have centered on materials which are of military interest. Detection levels as low as 1 ng have been achieved in a one minute assay time for the immunoassay system. Non-military uses of this technology can be developed, depending on the applications of the customer and the development of appropriate antibody reagents or mass spectral libraries.

INTRODUCTION

The contributions of biological aerosols to both indoor and outdoor pollution problems have often been neglected. This has been largely due to the difficulty one has in the detection and characterization of the aerosol. Past attempts at detection have relied upon measuring changes in bulk properties, such as heme content or the presence of specific reactions. These attempts failed because they did not possess the sensitivity and/or specificity to distinguish between hazardous and non-hazardous materials. Recent advances in both biosensor and mass spectroscopic technologies are leading to the development

of small, lightweight, and rugged instruments which can be introduced into field applications for detection of biological materials.

THE BIOCHEMICAL DETECTOR

The field assay of biological materials is difficult due to the need for detection of often minute quantities of specific material in the presence of a large background. Immunological-based sensors are being developed which have the capability to differentiate between analytes and background. Antibodies are bound to either optical or electrochemical transducers, and the binding event is measured due to the generation of an optical or an electrochemical event. Typically, fluorescent dyes or chromogenic enzyme substrates are used for the transduction of an optical signal while enzyme-substrate combinations which yield electrochemically active species are used with the electrochemical sensor. Both types of sensors were initially evaluated in this project. The electrochemical one was chosen for further development.

This sensor is referred to as the "Light-Addressable Potentiometric Sensor" (LAPS), and is marketed by Molecular Devices Corporation, Menlo Park, CA, as the Threshold@ system. It is simple in design, consisting of a silicon wafer, on which a layer of silicon oxide/silicon nitride has been grown. This silicon oxide/silicon nitride serves as an electrical insulator and makes the surface impervious to ion migrations from solutions in contact with the surface, imparting a neutral pH sensitivity to the sensor. The transducer is used to monitor the activity of enzyme-labelled antibodies which are used in the reaction. Presently urease, which catalyzes the hydrolysis of urea to carbon dioxide and ammonia, is used.

The immunological reaction takes place on a nitrocellulose filter which is later placed on the sensor surface. A controlling electrode and a reference electrode back-bias the insulator/silicon junction, creating a depletion layer at the junction (absence of charge carriers). A light emitting diode (LED), driven at 10 kHz, illuminates a small area of the silicon chip, creating charge carriers in the depletion layer at that point, which results in an alternating current between the controlling electrode and the bulk silicon. The magnitude of this current is dependent on the surface potential of the silicon oxide/silicon nitride. This surface potential responds in a Nernstian manner to changes in the surface pH. Several LED's can be used on the chip so that multiple sites can be addressed in succession. When coupled with the appropriate immunological reagents, a sensor can be obtained which has a detection capability for several materials in a small area.

The Bio-Chemical Detector, currently under development by the Army, utilizes this sensor technology in conjunction with an aerosol sampler. The sampler impinges aerosols into a liquid medium. This liquid is then transferred to a reaction manifold where the reagents are added. The resulting immune complexes are then filtered through an active membrane which captures the complex. Unreacted reagents are then washed away, and the filter is transferred to the reading module where the pH change is obtained.

This detection system has as a design goal the detection of six different classes of biological materials- bacteria, rickettsia, viruses, and small, medium, and large molecular-weight toxin materials. Other goals include a total sample acquisition time of two minutes with capability of repetitive analysis over a 24 hour period. Initial results have been encouraging with detection limits of nanograms per milliliter of toxin materials being realized with the sensor. Detection limits of 10^5-10^6 organisms per ml have been realized with two of the microbial materials. These detection limits are realized in the 3-4 minute time frame. The next phases of development include better integration of modules and improvements to the immunoassay format.

Although this system is being developed for materials which are of military interest, the use of this system can be extended to other materials through the development of appropriate antibody reagents. It is conceivable that this type of detection system could be utilized where real-time detection of hazardous biological materials is required.

THE CBMS SYSTEM

There is much interest in the development of small, portable mass spectrometer units for field analysis of hazardous materials. Although these units are significantly smaller than their laboratory counterparts, compromises are made with respect to capability and resolution. In addition, the system must be capable of identifying trace quantities of hazardous materials often in the presence of other interfering compounds. This can often be accomplished through the use of a GC/MS system; however, the complexity and logistical burden of this type of system may make it too cumbersome for routine use in the military environment.

The CBMS is an attempt to develop a small, portable mass spectrometer which has the capability to detect trace quantities of materials in the midst of significant amounts of interferents. It utilizes Quadrapole Ion Storage technology (QUISTOR) to accomplish this goal. This technology has allowed for the development of a small, sensitive mass spectrometer which has an MS/MS capability and can be fitted with a variety of probes to enable sampling of ground contaminants or the detection of biological aerosols. The ground sampling probe is commercially available and will not be described in detail here. The biological aerosol sampling capability was the result of an in-house effort at CRDEC. The aerosol material is impacted into a quartz tube with subsequent pyrolysis by IR radiation. The resultant vapor is then introduced into the instrument and analyzed. In the case of bacteria where similar primary spectra are obtained, the unit is then switched into an MS/MS mode where daughter ion spectra are obtained. This has allowed bacterial identification to the Genus level; species level should be possible with the development of the appropriate spectral libraries. In addition, an artificial intelligence capability is being built into this unit so that it will be capable of analyzing spectra of unknown materials and trying to "best guess" what they are.

SUMMARY

Both these systems offer viable approaches to the real time detection of biological aerosols. They also demonstrate two of the principles which can be used to achieve this: one being the specificity of antibody molecules, while the other being the chemical signature; a material would give in the mass spectrometer. The bio-specificity approach requires a lot of up front work in the development of the biological reagents (although the hardware development is not trivial) while the other requires a significant amount of work in the development of appropriate spectral libraries. Both systems are in the early stages of development and show great promise.

LASER FLUORESCENCE EEM INSTRUMENT FOR In-Situ GROUNDWATER SCREENING

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ABSTRACT

We have constructed and laboratory tested a field transportable fluorescence instrument for aqueous pollutant screening. This instrument acquires 3-dimensional laser-excited excitation-emission matrices (EEMs) of environmental solutions. Computer analysis of these EEMs by the least squares method allows determination of the chemical composition of the solutions. Our instrument generates more than 30 laser beams of different wavelengths throughout the ultraviolet region of the spectrum using a laser-pumped Raman shifter, and these beams act as a source for fluorescence excitation. Laser light and fluorescence emission is transported between the environmental sample and the instrument by optical fibers. Our instrumental response is linear with concentration over 3-4 orders of magnitude and detection limits are in the ppb range for many pesticides and pollutants. Three and four component mixtures of groundwater pollutants have been directly analyzed at sub-ppm concentrations in methanol solutions with less than 20 % error using least-squares EEM analysis.

INTRODUCTION

Our group has previously constructed and field tested a Nd:YAG (neodymium: yttrium aluminum garnet) laser-based instrument for in-situ monitoring of groundwater pollution by fluorescence analysis (1-4). This first generation instrument employed optical fibers to carry laser light and fluorescence between the instrument and the groundwater sample. Optical filters were placed before the photomultiplier tube detector to select the emission spectral detection range. Concentrations of fluorescent pollutants that absorbed 266 nm radiation could be determined in the parts per million (ppm) to parts per trillion (ppt) concentration range. However, this instrument was not sensitive to compounds having a low absorptivity at 266 nm and had limited capability to distinguish different fluorescent compounds from each other.

Our second generation instrument, described in this paper, has a much improved ability to analyze the chemical composition of groundwater. This instrument generates an array of laser beams by pumping a Raman shifter with a Nd:YAG laser (5). Addition of a Raman shifter to our initial instrument was relatively simple and inexpensive and allowed the generation of laser beams of different colors throughout the ultraviolet and visible regions of the spectrum (5). This second generation system also employs a small spectrograph and an intensified diode array detector to allow full spectral analysis of laser-induced fluorescence and scattered light. The high-intensity of laser excitation allows rapid emission spectral acquisition, thus, an excitation-emission matrix can be acquired rapidly by sequentially launching each laser beam into the excitation optical fiber and recording the emission spectrum.

Spectral acquisition, processing and analysis is performed using compiled Pascal programs on a 80386 personal computer. This computer arrangement allows rapid formatting and analysis of the large EEM data matrices produced by this instrument (e.g. 25 excitation wavelengths X 700 emission wavelengths = 17,500 data points/EEM).

EXPERIMENTAL

Figure 1 shows a block diagram of our second generation instrument. The third or fourth harmonic of a pulsed Nd:YAG laser (Quanta-Ray model DCR-11) is focussed into a Raman shifter where much of the beam is converted into laser beams of different colors. The YAG laser was operated at 10 Hz, and pulse energies of 35 mJ/pulse at 355 nm and 14 mJ/pulse at 266 nm were employed. Twenty different laser beams between 240 and 330 nm were suitable for the fluorescence excitation of the compounds used in this study. Each Raman-shifted laser beam was selected sequentially by the dispersion unit and launched into one end of a seven-meter optical fiber. The laser light is transported by the excitation fiber to the solutions where it is absorbed by the analyte. An optical fiber similar to the excitation fiber collects and transports analyte fluorescence and scattered light back to the detection system.

Spectra are acquired by dispersing collected light with a 0.27 m spectrograph onto a cooled diode array detector. The emission spectral bandpass of this arrangement is 4 nm. Individual fluorescence spectra are collected, processed, formatted into excitation-emission matrices, and analyzed by least-squares using Turbo Pascal programs. Least-squares analysis involves minimizing the differences between the EEM spectrum and a linear combination of the EEM spectra of each of the individual analytes (6). All programs for data analysis were developed in-house and run on a personal computer. EEM plots shown in this paper were obtained using Surfer software (Golden Software Inc.).

RESULTS

Figure 2 shows the excitation-emission matrices of four groundwater pollutants: the cresol isomers p-cresol and m-cresol, and the carbamate pesticides carbaryl and carbofuran. Figure 3a shows the fluorescence EEM of a solution containing a mixture of all four compounds, and Figure 3b shows the EEM of a mixture containing the compounds m-cresol, carbofuran, and carbaryl. All spectra were obtained with our laser-based instrument using methanol solutions of 1 ppm or less in concentration. The total spectral integration time to acquire these EEMs was less than 5 minutes. Exposure times for individual spectra ranged from 0.5-40 seconds.

The results of the least-squares analysis of the above mixtures are compared with the actual prepared concentration in Table 1. The concentration of all components were determined quantitatively within 20 % for these sub-ppm solutions. We have previously analyzed the composition of a 3-component mixture to within 1.5 % under similar experimental conditions when the components of the mixture exhibit less spectral overlap (7).

Table 2 shows our current detection limits and linear dynamic ranges for the above pesticides and pollutants. These results were obtained from spectra acquired for 5 seconds upon exciting solutions at 266 nm and by measuring the fluorescence intensity at the intensity maximum.

DISCUSSION

The EEMs in Figure 1 show that three of the compounds - m-cresol, p-cresol and carbofuran - have very similar fluorescence EEM spectral profiles. The absorption and emission spectra of these three compounds have intensity maxima within 10 nm of each other. Also, the spectral profiles of these compounds are similar and exhibit little vibronic structure. This type of strong similarity in spectral characteristics makes it relatively difficult to accurately analyze these compounds by EEM analysis.

Our capability to analyze these pollutants as 3- and 4-component mixtures is demonstrated in Table 1. Least-squares EEM analysis provided a reasonably accurate determination of sub-ppm pollutants in simple mixtures without any prior preconcentration, extraction, or chromatographic treatment of the analyte solution. These results

show that we can analyze mixtures of chemical isomers (m- and p-cresol) in addition to mixtures of unrelated pollutants with our instrument.

Table 2 shows that the detection limits of these pollutants are in the ppb concentration range and the linear dynamic extends over 3-4 orders of magnitude. Similar results have been obtained with our instrument for phenol, dibenzofuran and carbazole (7).

More complex mixtures of fluorescent chemicals could be analyzed with our laser EEM instrument by adapting it for use as a liquid chromatography detector. All laser beams from the Raman shifter are produced simultaneously, so each could serve to excite fluorescence at the end of a chromatographic column simultaneously. By using an array of excitation and emission optical fibers and by employing a two-dimensional array (CCD) detector, all spectra of the EEM could be acquired simultaneously. At least fifteen Raman-shifted laser beams in UV region of the spectrum are of sufficient intensity that they could be employed to obtain fluorescence EEM spectra in 1-2 seconds. This instrumental design would provide a dramatic improvement in the ability of our instrument to analyze complex solutions. A recent study by the National Institute of Standards and Technology has found liquid chromatography with fluorescence detection to compare favorably with gas chromatography/mass spectrometry for the analysis of polycyclic aromatic hydrocarbons in environmental samples (8).

Our fluorescence EEM instrument has performed well in laboratory tests. The Nd:YAG laser is a solid state laser and requires little maintenance. The Raman shifter is the only other non-linear optical component in our system, and the operation parameters of this device have been characterized previously (4).

An important aspect of the field compatibility of our instrument is near absence of moving parts. The only moving parts in our instrument are the YAG harmonic generation crystal mounts, the prism rotation stage (to select the color of the laser beam), and the fiber positioning elements (to allow efficient launching of the laser beam into the excitation optical fiber). Relatively large optical fibers are employed in this instrument (0.60 mm core diameter) to simplify the alignment of the laser beam with the excitation optical fiber.

The power requirements of our current instrument are 3000 W, and 9 ft3/hour of dry nitrogen gas is used to purge moisture sensitive optical components. Approximately half of the weight of our instrument (450 lbs) is found in the Nd:YAG laser (220 lbs).

The components of our current fluorescence EEM instrument cost about $50,000, which is well below the total cost of a transportable gas chromatography-mass spectrometer ($300,000). Also, unlike GC-MS, our instrument has the capability to directly analyze non-volatile samples in aqueous solutions.

CONCLUSIONS

The ability of our laser-excited fluorescence EEM instrument to analyze mixtures of cresol isomers and pesticides directly at sub-ppm concentrations in methanol was demonstrated. Detection limits were in the ppb concentration range and the linear dynamic range was 3-4 orders of magnitude. This instrument is a promising device for direct in-situ screening of groundwater pollutants or for interfacing with a liquid chromatograph for EEM spectral analysis of chromatographic eluents.

ACKNOWLEDGEMENT

The authors greatfully acknowledge the assistance of Anthony Bevilacqua, George Jarvis, and Mark Regina in setting up much of the equipment involved in these experiments.

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TABLE 1. Least-Squares EEM Analysis Results for Two Mixtures of Pollutants.

Mixture	Component	Prepared Concentration X 10^{-6} M (ppm)	Least-Squares Calculated Concentration X 10^{-6} M	Percent Error
1	m-cresol	3.21 (0.44)	3.20	0.03
	p-cresol	2.58 (0.35)	2.27	12.0
	carbofuran	2.96 (0.84)	3.53	19.3
	carbaryl	0.795 (0.20)	0.933	17.3
2	m-cresol	3.21 (0.44)	3.75	16.8
	carbofuran	2.96 (0.84)	2.88	2.70
	carbaryl	0.795 (0.20)	0.838	5.41

TABLE 2. Detection Limits and Linear Dynamic Ranges of Pollutants.

Compound	Detection Limit, X 10^{-7} M (ppm)	Linear Dynamic Range, ppm
m-cresol	2.0 (0.030)	0.030 - 10
p-cresol	2.0 (0.030)	0.030 - 10
carbofuran	3.0 (0.085)	0.085 - 5
carbaryl	2.0 (0.050)	0.050 - 2

Figure 1: BLOCK DIAGRAM OF SECOND GENERATION INSTRUMENT

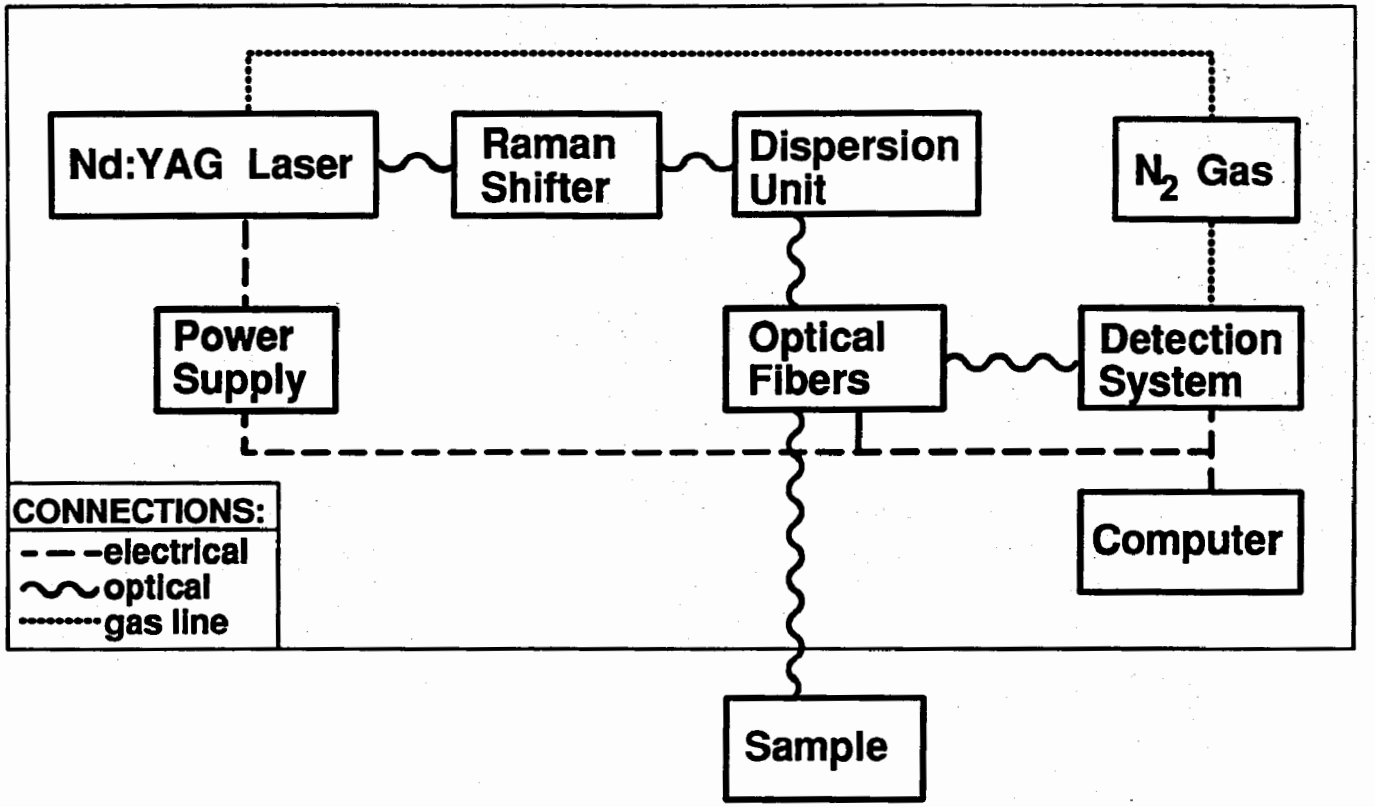


Figure 2: EEM SPECTRA OF POLLUTANTS

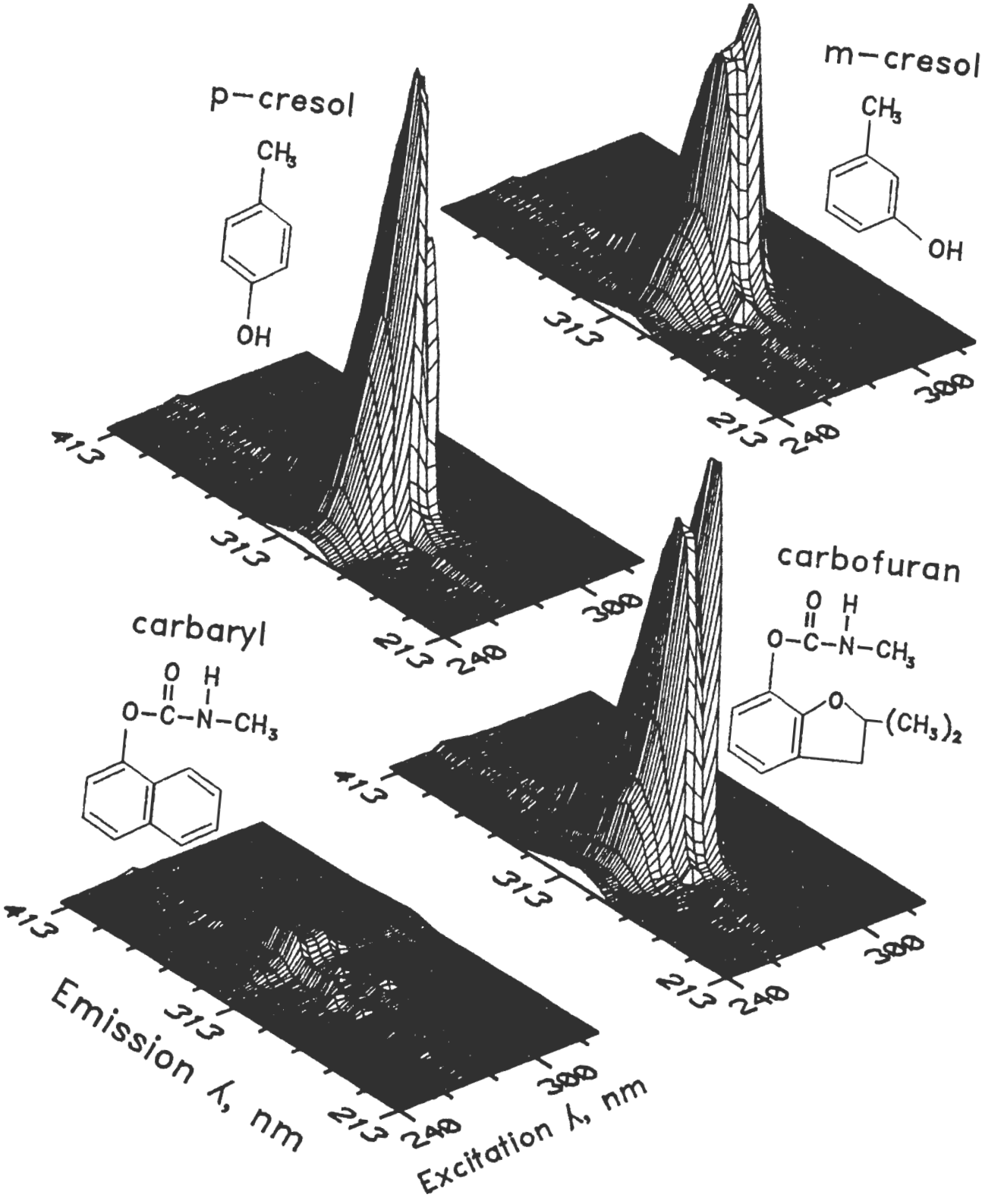
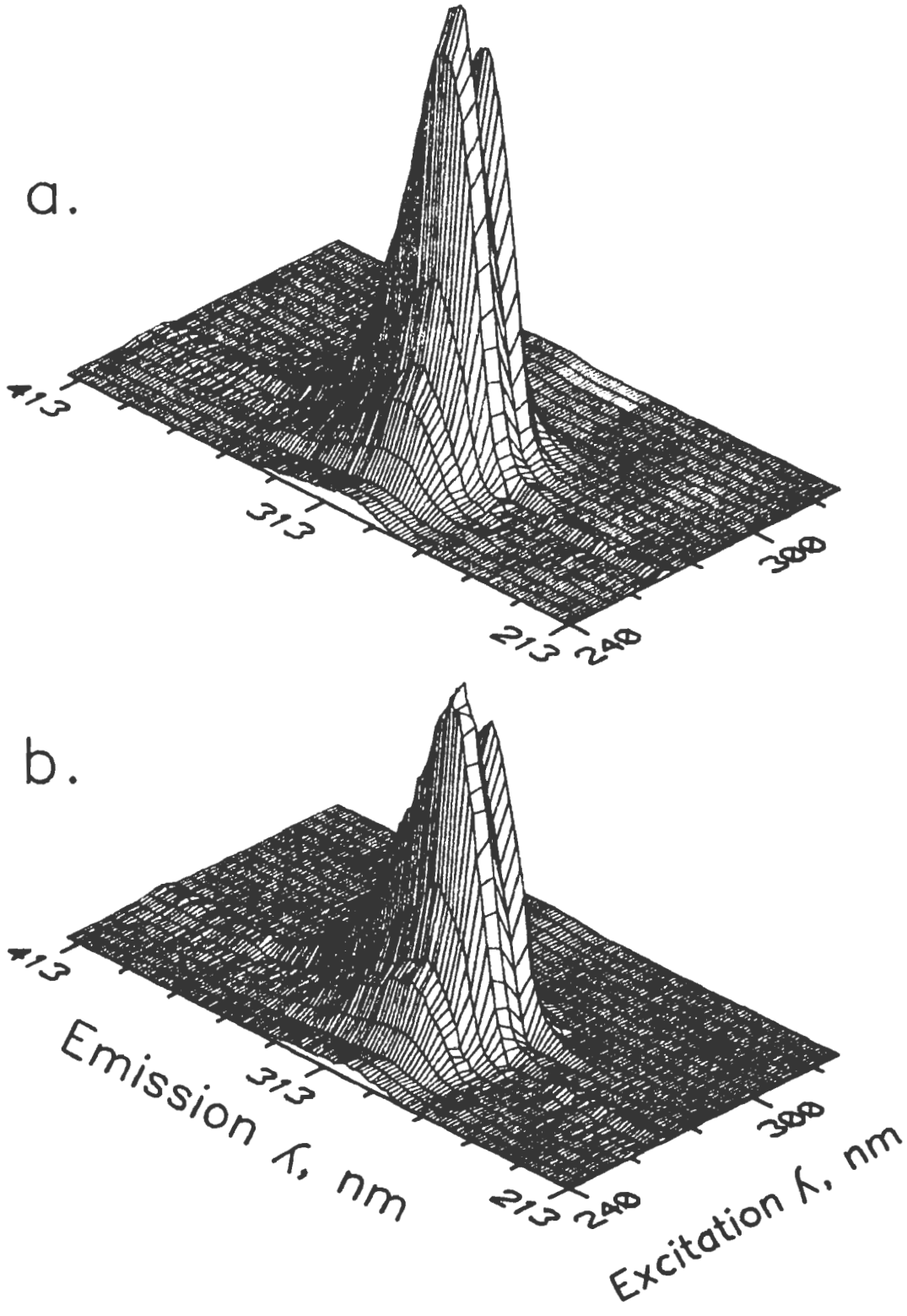


Figure 3: EEM SPECTRA OF MIXTURES



Analysis of Total Polyaromatic Hydrocarbon Using Ultraviolet-Fluorescence Spectrometry

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The first step in the remediation of Manufactured Gas Plant (MGP) sites is an estimate of the extent and degree of contamination. This research has been concemed with the development of a procedure for the field determination of total concentration of polyaromatic hydrocarbons (PAH) in contaminated soils at MGP sites. It is based upon the principle of ultraviolet fluorescence whereby certain chemical substances, PAH among them, emit a portion of incident UV radiation at longer wavelengths. The experimental program which has been undertaken contains three elements: optimization of the PAH extraction technique, miminization of interferences, and quantitation of PAH using UV-flourescence at several excitation wavelengths in order to control nonuniform effects.

Soils were supplied from three MGP sites, and consisted of one or two samples considered to vary in their degree of contamination, as well as uncontaminated samples. Soxhlet extraction (benzene) followed by gas chromatographic measurement of 16 PAH compounds was performed according to EPA method 610. These values were used as baseline information against which comparisons of solvent extraction efficiencies were made. Five solvents were evaluated for their extraction efficiency: benzene, hexane, acetonitrile, 2-propanol, and acetone. Results indicated that both benzene and hexane extracted the maximum amount of PAH, with hexane showing a small advantage for lower-ring and benzene an advantage for higher-ring PAH. The differences, however, were small and hexane was chosen as the solvent of choice based on safety considerations.

Three factors affecting dispersal and extraction of PAH into hexane were evaluated: sample size (actually solvent/sample ratio), mixing time (with and without sonication), and effects of added moisture followed by blending. The primary consideration for maximum extraction efficiency was the dispersal of waste particles in the medium. A further constraint was the fixed size of extraction tubes, 50 ml, which was considered to be a convenient size for manipulations in the field. Under these conditions, a sample size of 2-4 grams (wet weight) in 50 ml of hexane gave maximum PAH removal from the soil.

It was anticipated that the dispersal of particles, and hence extraction efficiency, might be enhanced by sonication, however, this proved not to be the case. Figure 1 shows results for three separate extraction experiments, no sonication, and sonication for 10 to 20 minutes. Total mixing time was the same, 90 minutes. The data reveal that sonication does result in a more rapid initial release of PAH, however, this effect is negated and in fact reversed after the sonication period. As there was no apparent advantage to the use of sonication in improving extraction efficiency or decreasing the total time, its use was discontinued. Figure 1 also shows the minimum mixing time (without sonication) was about 70 minutes. This was further verified in other experiments resulting in the adoption of this mixing time as the standard value.

Somewhat surprisingly, it was found that the addition of distilled water to samples, followed by blending, gave excellent dispersal of particles resulting in acceptable PAH extraction. This is illustrated in Figure 2 which shows total PAH extracted as a function of the water added/sample ratio. Blending also resulted in a greater sample uniformity, thus replicate variability (also shown in Figure 2) is improved. In effect the addition of water acts to yield a more uniform moisture content, regardless of the initial (field) moisture content of the sample.

There are three primary sources of error in measuring total PAH by UV fluorescence: background fluorescence of non-PAH substances, different distribution of PAH compounds from sample to sample, and fluorescence quenching effects (either direct or "concentration"). The approach used to minimize quenching was dilution of the hexane extract (using more hexane) until the interference was eliminated and spike recoveries gave a clear linear response against the fluorometric reading. Figure 3 shows the fluorescence of a hexane extract for several dilutions. As the sample is diluted the response first increases, as the effects of quenching are lessened, and then declines, as the fluorescing substances themselves

are diluted. Quenching effects can be quite subtle; the important factor is to make fluorescence readings at the dilution level which gives a linear recovery curve. For example, Figure 4 shows the results of a spike recovery study for a mixture of PAH added to 1:10,000 dilution of the hexane extract. The x-axis intercept of the regression curve represents the concentration of PAH in the sample. In general it has been found that it is best to make measurements at the highest dilution for which recoveries can be made accurately, usually 10^4 or 10^5.

The accompanying table presents a summary of the results of the research. Gas chromatographic analysis of Soxhlet and hexane extracts are generally comparable indicating acceptable recoveries using the hexane method. As stated previously, fluorescence measurements were made at several excitation and emission wavelengths. It was found that results were relatively insensitive to the emission wavelength, 410 nm giving acceptable responses throughout. The excitation wavelength, however, was very important in determining the response of the instrument and appeared to depend on the distribution of PAH in the sample extract. Unfortunately, no *one* wavelength was satisfactory. As can be seen from results for sample 1C the fluorescence method can be quite accurate when interferences are lacking. Results for samples 1A, 1B, 2A, 3A, and 3B are considered to be acceptable with errors of 12, 3.7, 5.6, 1.5, and 5.3 percent, respectively, relative to the gas chromatographic analysis of the hexane extract.

The accuracy of the fluorescence method at each excitation wavelength was assessed through linear regression of the UV-fluorescence values against the gas chromatographic analysis for total PAH. The results of these regressions were used to compute the relative error of fluorescence at any given level of total PAH concentration. The results are shown in Figure 5. One obvious feature is the radically different character of the error at 250 nm in comparison with other error curves. The error analysis at other wavelengths indicate more well-balanced curves, the error decreasing as the concentration of PAH increases. It appears that measurements made at 280 nm excitation give the most consistent accuracy. Averaging the readings for selected wavelengths, as shown, does not substantially improve accuracy. It is interesting to note that the errors for most of the wavelengths at 100 mg/kg, the target goal for the detection limit, are nearly the same, about twenty-five percent. Given the intended purpose of the method, this is considered acceptable.

Acknowledgements

This research was supported by the Gas Research Institute, David G. Linz, Manager, Land and Water Quality Research.

Summary of UV-Fluorescence Results[a]

			UV-Fluorescence			
Sample #	Soxhlet Extraction	Hexane Extraction	250/410[b]	280/410	315/410	360/410
1C (Clean)	7.32	4.03	6.26±0.15	6.9±0.15	7.51±0.24	7.32±0.29
A1	3539	3398	5436±147	3817±98	4851±192	4413±268
1B	4064	3353	4725±178	2449±98	2650±48	3476±108
2A	2936	2916	6375±226	3273±106	3082±58	2595±117
3A	675	794	966±61	782±14	890±32	1204±52
3B	45.54	39.18	41.25±0	67.5±3	95±5	150±5

[a]All values are mg/kg dry weight for total PAH.
[b]First number is excitation wavelength.
Second number is emission wavelength.

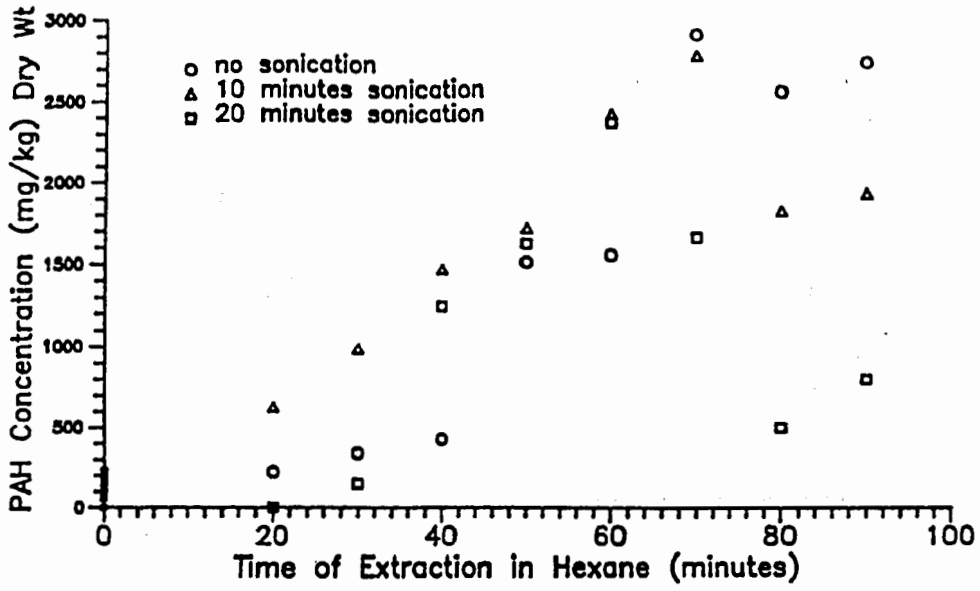

Figure 1: Comparison of Alternative Hexane Extraction Procedures

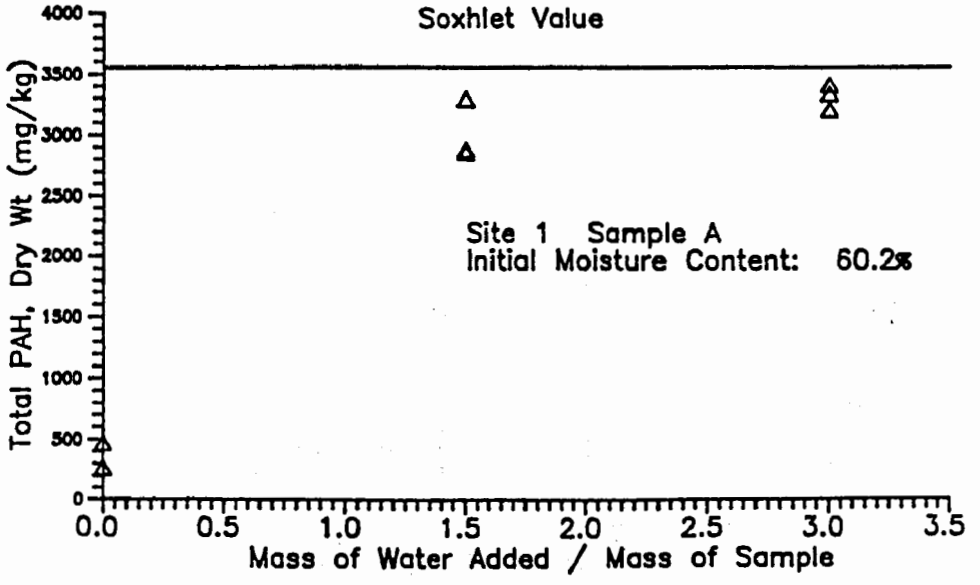

Figure 2: Dependence of PAH Extraction Efficieny on Sample Moisture Content

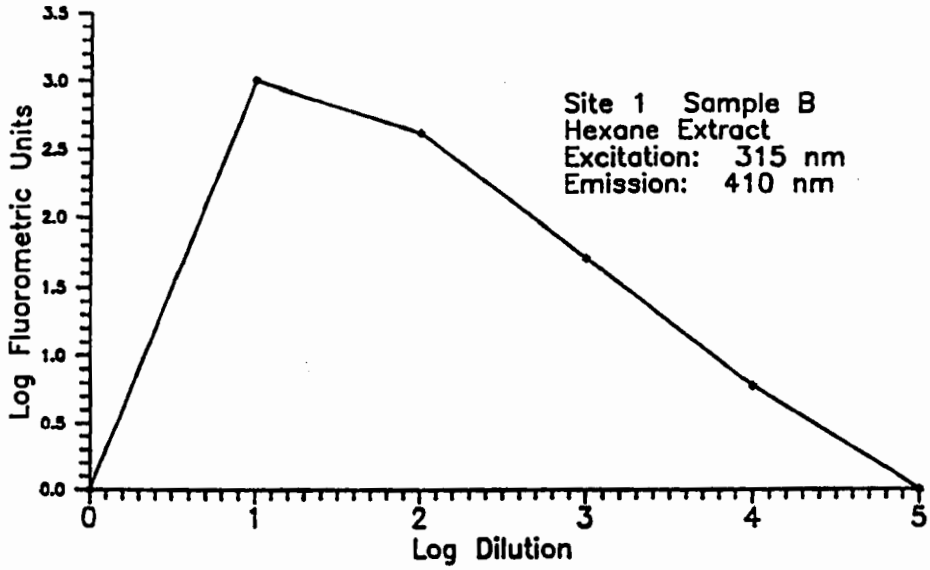

Figure 3: Impact of Sample Dilution on PAH Fluorescence

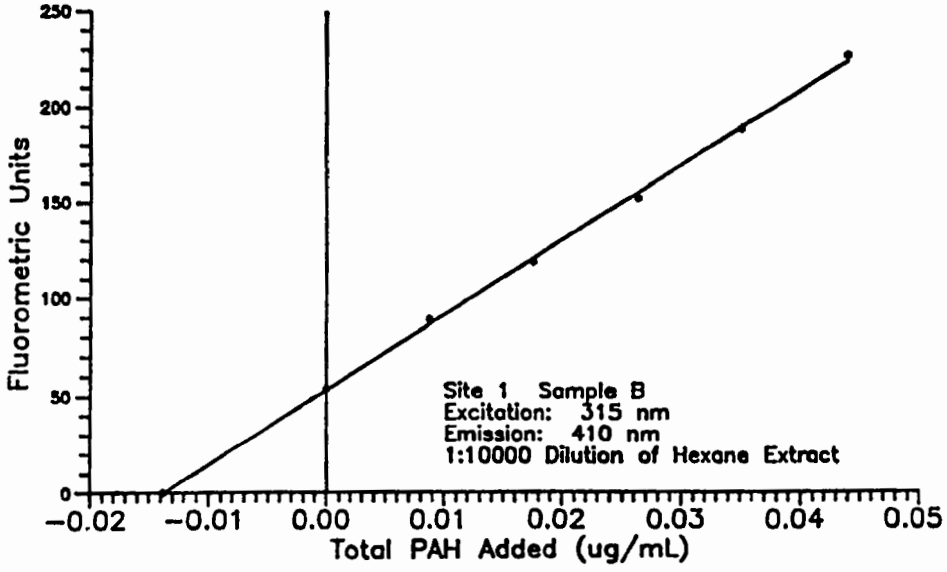

Figure 4: PAH Determination by Method of Standard Additions

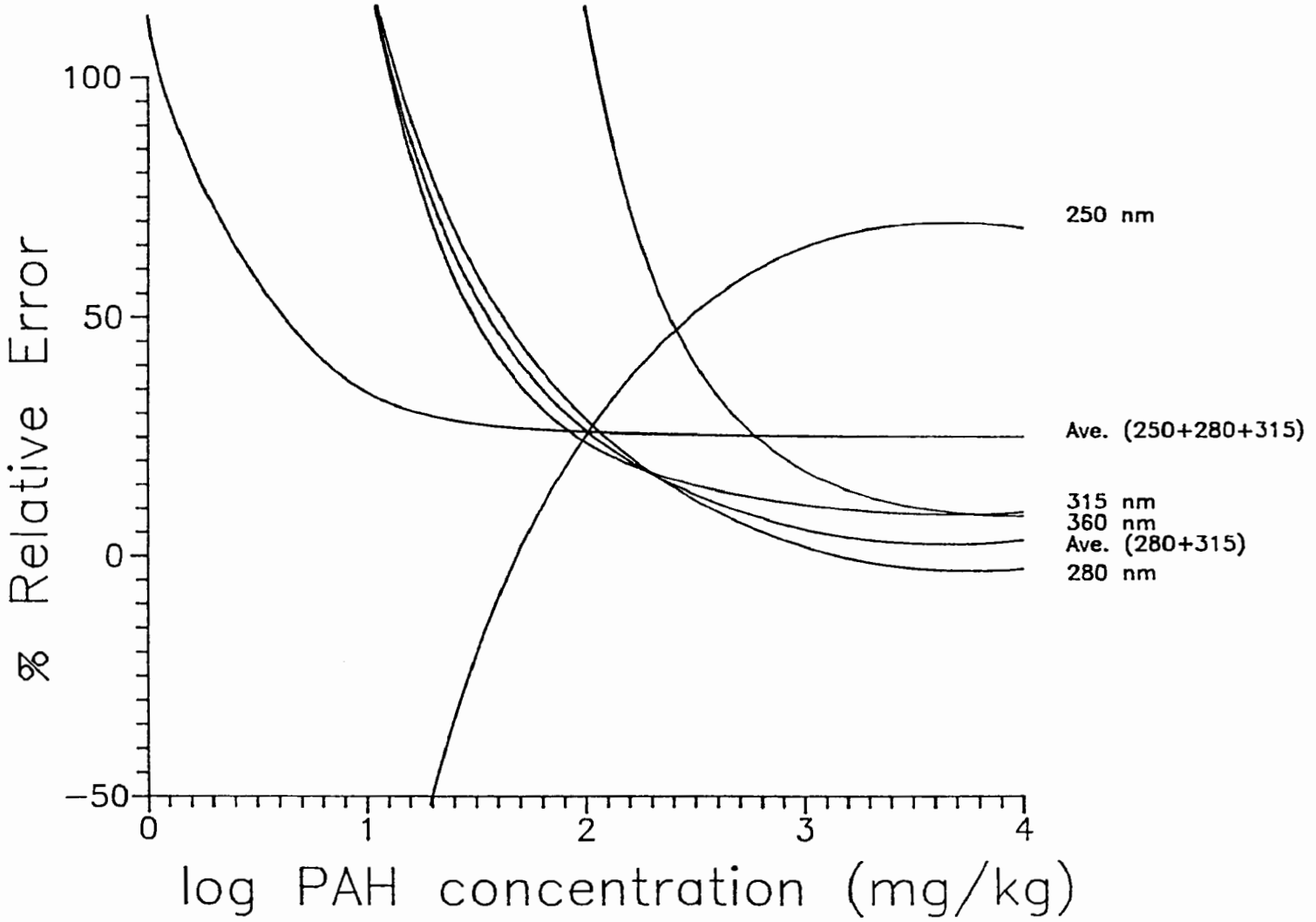

Figure 5. Error Analysis of the UV-Fluorescence Method

ON-SITE ANALYSIS OF CHLORINATED SOLVENTS IN GROUNDWATER BY PURGE AND TRAP GC

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INTRODUCTION

Historically, analysis of volatile organic compounds via purge and trap gas chromatography (GC) has been conducted in laboratory settings where controls were strictly monitored. Recently, however, increased reliability of GC instrumentation combined with the adaptation of quality control procedures make this a suitable analytical technique for successful incorporation into field sampling activities. This screening technique produces an accurate "real time" profile of groundwater contamination which can be subsequently used in deciding the placement of monitoring well screens. This approach not only aids in detecting the most contaminated zone within a given aquifer, but it also serves to reduce field costs associated with traditional "cluster" type well installations. Costs are further reduced as only essential samples are selected for Contract Laboratory Program (CLP) analysis.

This study involved an investigation at a National Priorities List site which produced approximately 200 groundwater samples from screened auger borings. These samples were analyzed on-site for selected chlorinated solvents (1,1-dichloroethane, 1,2-dichloroethene, trichloroethene, and tetrachloroethene) by purge and trap GC. Field screening results were used to determine the distribution of contamination; these results were confirmed by submitting selected samples to a laboratory to be analyzed according to CLP protocols.

The following sections describe how the field screening data were collected and subsequently used in determining the placement of groundwater monitoring well screens. In addition, the quality of these data were evaluated as to their precision and accuracy through rigorous statistical modeling. Finally, a general cost comparison of field screening versus CLP analysis establishes the economic practicality of this technique.

TECHNICAL APPROACH

This field screening procedure was based on USEPA Method 601. A GC equipped with a purge and trap device and an electrolytic conductivity detector (ELCD) was set up in a field trailer in close proximity to the study area. A wide-bore capillary column was used for compound separation, and the total cycle time was approximately 22 minutes. Under these conditions approximately 20 samples could be screened in a 12 hour shift (not including QC samples). Quality control included initial calibration runs, continuing calibration (at the start and end of each day), method blanks, and surrogate spikes (bromofluorobenzene). A description of these quality control measures is provided in the following section. Analyte detection limits as determined by statistical analysis were approximately 1 μg/L.

Temperature Programs and System Operating Conditions:

Purge and Trap:

- Purge: 6 minutes at 35°C (max)
- Purge Flow: 28 - 33 mL/minute
- Desorb Preheat: 175°C
- Desorb: 3 minutes at 180°C
- Bake: 6 minutes at 225°C

Gas Chromatograph/ELCD:

- Column Flow (He): 7-10 mL/minute
- Makeup Gas (He): 30 mL/minute
- Hydrogen: 80 mL/minute
- Initial Temperature: 35°C
- Initial Time: 3 minutes
- Rate: 8°C/minute
- Final Temperature: 135°C
- Approx. GC Run Time: 15.5 minutes

With respect to drilling activities, groundwater samples were collected using 4.25-inch inside diameter hollow stem augers. The lead auger was plugged and modified with the installation of 0.010-inch stainless steel well screen sections (i.e. a screened lead auger). Monitoring wells were subsequently installed in borings where the highest concentrations of chlorinated solvent were identified as established by field purge and trap GC results.

QUALITY ASSURANCE/QUALITY CONTROL

QA/QC was performed to a degree sufficient to evaluate general data quality and system performance while not inhibiting the ability to provide real-time data and high throughput. In general, under normal operating conditions, five analytical runs per day were devoted to QA/QC.

o Initial Calibration: A minimum of one 3-point initial calibration was performed and percent relative standard deviations (%RSD) were calculated for each analyte. An average response factor was used to calculate sample analyte concentrations if %RSD < 30%. Otherwise analyte concentrations were derived from the corresponding calibration curve. The calibration range was 5 to 50 μg/L

o Continuing Calibrations: Continuing calibrations (run at approximately mid-level concentration) were performed at a minimum of every 12 hours and at the beginning and end of each analytical day. Percent deviations (%D) of less than 35% were considered acceptable for verification of the initial calibration curve. Failure of this critera necessitated the reconstruction of the 3-point initial calibration curve.

o Blanks: Method blanks were performed daily before the analysis of any groundwater samples. In addition, system cleaning blanks were run after any groundwater sample containing any single analyte at a concentration exceeding five times the highest calibration level.

o Surrogate Spikes: Bromofluorobenzene was spiked in each analytical run to evaluate sample recoveries and matrix effects. However, no actions were implemented as a result of poor surrogate recoveries.

o Independent Check Standards: To verify the quality of the calibration standards and to evaluate standard preparation procedures, two complete sets of standards were purchased from two independent chemical suppliers. After completing the calibration curve with one set of standards, a blank spike with a known concentration (at or near the mid calibration level) of the second set of standards was analyzed to confirm analytical accuracy.

GROUNDWATER INVESTIGATION

This approach was first incorporated into a remedial investigation conducted at a military industrial complex where previous studies showed groundwater to contain 1,2-dichloroethene, trichloroethene, and tetrachloroethene. The subsurface geology at this site was characterized as glacial outwash consisting of fine to medium sand, and the water table was located approximately 85 feet below the ground surface. The purpose of this remedial investigation was to determine the extent of groundwater contamination migrating from the site. In order to properly delineate the extent of contamination, monitoring well fences were installed perpendicular to the plume axis. Three of these monitoring well fences were required to sufficiently characterize the contaminant plume as to its horizontal and vertical boundaries. In addition to isolating the limits of the plume, field screening data aided in defining the intervals of highest concentration within the aquifer. Where possible within a given monitoring well, screens were installed to intercept the groundwater at depths where the highest solvent concentration was identified. At the lateral extent of the plume, where screening results detected no target analytes at any interval, well screens were installed at depths similar to those where the highest concentration of contaminants were identified in adjacent wells. The plume cross section is shown if Figure 1.

Since the local geology was comprised almost exclusively of fine outwash sands and provided for relatively fast and efficient drilling, the investigation was designed to fully envelop the contaminant plume by collecting a large number of samples for field screening. By doing so, a profile defining both the minimun concentrations around the edge of the plume edge and the maximum concentration along its axis was generated. This method of plume isolation results in very few data gaps. This volume of data provides tremendous benefit to interpretation of groundwater contamination as compared to the traditional approach to well installation which is generally directed by historical data and produces a limited number of data points.

The groundwater exploration program consisted of 29 screened auger borings from which 190 groundwater samples were collected at five to ten foot intervals and analyzed by field purge and trap GC. Sample depths ranged from the water table to 204 feet below the ground surface, and all screened auger borings were completed with the installation of monitoring wells with 5-foot 0.010-inch slot PVC screens. Field GC analyses of the screened auger samples determined the geometry of the groundwater plume. These results indicated the solvent plume exceeded 3,000 feet in width and 7,000 feet in length. Subsequent CLP laboratory analysis of groundwater samples for target compound list (TCL) volatile organic compounds (VOCs) confirmed the field GC results as determined through statistical analysis (to be discussed in the following section).

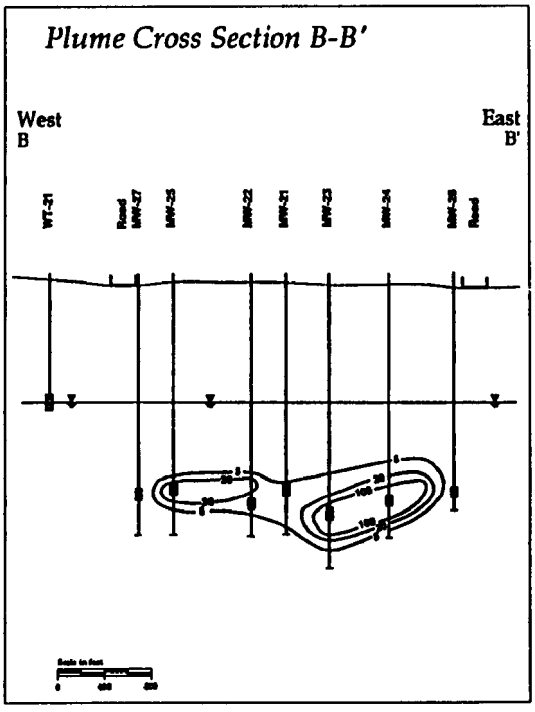

Figure 1

Contaminant Plume Cross Section

CLP VOC analysis indicated the samples contained 1,2-dichloroethene concentrations from less than 1 μg/L to 54 μg/L. The predominant site contaminants, trichloroethene and tetrachloroethene, were also identified at concentrations as high as 670 μg/L and 430 μg/L, respectively. Overall, the field GC program determined that the plume boundaries were sharp, and the plume consisted of two parallel high concentration (> 100 μg/L) lobes.

COMPARISON OF FIELD AND LABORATORY RESULTS

Field GC screening data are used in real-time to facilitate field decisions. Additionally, these data, in conjunction with CLP results, provide information for site characterization. In order to assure that field results are of sufficient quality for use in interpretation of groundwater contamination, the field GC screening procedure was calibrated against laboratory CLP methods. A statistical evaluation was therefore performed to determine the usability of field data.

A set of 35 replicate samples was collected and submitted for both CLP and field GC analyses. The statistical evaluation was based on five replicates of seven samples (five groundwater samples from three screened auger borings and two blind spikes) analyzed both by field GC and by three independent laboratories. Each independent laboratory result was considered to be a "true" value, and the field GC results were compared to each laboratory result individually to test the accuracy of the field results. Target compound concentrations in these samples ranged from non-detect to 125 μg/L in all samples analyzed.

The field GC results, laboratory results, and spike concentrations represent paired data points. To determine if field GC results adequately represent the true concentration in the sample, a statistical test (paired t-Test) was performed under the hypothesis that field GC results equal laboratory results or spike concentrations. Testing this hypothesis is equivalent to testing whether the differences between field results and laboratory results are significantly different from zero. The paired t-Test results indicate that field GC results are not significantly different than either laboratory results or actual spike concentrations. At the 95% confidence level the original hypothesisis not rejected. In other words, there was no statistically significant evidence to indicate that there is a difference between field and laboratory measurements.

In addition to the tests for zero differences between field GC and laboratory results and spike concentrations, a polynomial regression analysis was performed to evaluate the correlation between field and laboratory data. This procedure involved defining field GC results as the dependent variable and laboratory results and spike concentrations as the independent variable. The regression model used was

$$y = c + ax + bx^2$$

where: y = field GC results,
x = laboratory results / spike concentrations,
a,b,c = constant coefficients.

The results of this analysis indicate a strong correlation between field GC results and laboratory results/spike concentration with an adjusted multiple r^2 of 0.965. As can be seen in Figure 2, a graph of the data supports this assertion. The middle curved line in the graph is the least squares quadratic best fit to the data. This best fit line appears to level off at around 100 μg/L; this effect results from the narrow dynamic range of the ELCD as compared to CLP GC/MS techniques (i.e. the linear range of the ELCD was exceeded). The upper and lower curved lines are the approximate 99% confidence bounds about the best fit line.

The leveling off characteristic of the best fit line indicates that concentrations above this range may be underestimated. However, the calibration was designed to accurately quantitate analyte concentrations over a relatively low range of 1 to 50 μg/L thereby producing an accurate description of the edge (lowest concentrations) of the contaminant plume. Although beneficial, accurate quantitation of analytes at high concentrations was not essential to the success of this field program. When anticipated, this problem was remedied by diluting highly contaminated samples by an appropriate factor, thereby achieving the linear range of the calibration.

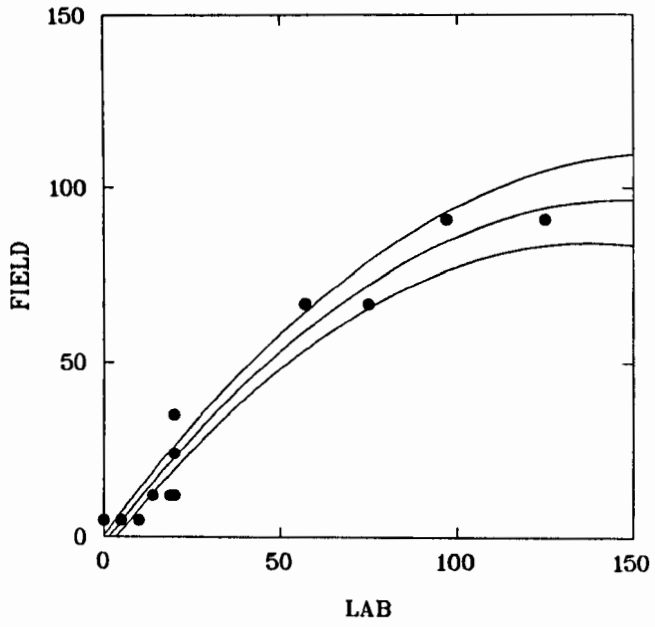

Figure 2

Quadratic Regression Fit of Field v. Lab Data (all units μg/L)

The paired t-Test and the polynomial regression analyses demonstrate a strong correlation between field and laboratory results. Therefore, this screening procedure, combined with the confirmation of selected samples using CLP protocols, provides data of sufficient quality for use in plume delineation.

COMPARISON OF FIELD AND LAB COSTS

In addition to the obvious field operations advantages field screening presents by producing accurate "real-time" data, substantial savings are realized by conducting field analyses and shortening the duration of the investigation. By performing analyses of groundwater samples in the field, analytical costs are minimized. The expense of purge and trap volatile analysis performed by a CLP laboratory ranges from $200 to $400 per sample. In contrast, field screening analysis can be performed at between $50 to $150 per sample. The final per sample cost of field screening analysis is largely dependent on the volume of samples requiring analysis. Since the cost of mobilization and demobilization of a field laboratory is constant regardless of the volume of samples, larger field programs tend to have the lowest per sample field screening analytical costs. If all 200 samples generated from this field program were analyzed by a CLP laboratory the total analytical costs (assuming $300/sample) would run $60,000. Field analysis at $75/sample cost $15,000, and the additional confirmatory laboratory analyses performed in conjunction with the field program (29 samples), brings total analytical cost to $23,700. This represents a savings of $36,300 over the traditional approach.

Although substantial, the overall program savings are not restricted to reduced analytical costs. The traditional approach to site investigation inevitably requires multiple site visits many months apart. These additional visits double and triple program costs relative to a one visit investigation. The costs of mobilization, sampling, shipping ($100 to $300/cooler), and peripheral expenses are also significantly reduced in conjunction with a one visit investigation that field screening provides.

CONCLUSIONS

While the cost savings are an important aspect of field screening analysis, the real-time data acquisition is fundamental to the success of the field program. Typical turn-around time for laboratory data is one month, which relegates the placement of monitoring well screens and surface and subsurface contamination delineation to educated guesses based on historical data. The successes of these field investigations are not known until the field events have ended; multiple iterations may be required to complete remedial investigations. In fact, the success of traditional field investigations may never be fully realized since the presence of many data gaps is inherent to the approach. At this military installation, it is quite possible that the dual lobe character of the contaminant plume would have been overlooked during a multiple phase program dependent on the evaluation of CLP data for well placement information. The use of field analysis allows many critical difficulties to be overcome. Wells were placed at depths of the highest contaminant concentration based on real time information which provided an accurate determination of the contaminant plume. Additional wells can be installed if field screening data indicate the need to fill in data gaps; the real-time information allows these installations to occur while drilling crews are still on-site, thus eliminating additional mobilization charges.

It should be stressed that using field GC screening as an analytical tool is not designed to as a substitute for CLP analysis. One of the principle reasons the technique is so useful and time efficient in the field is much of the QA/QC associated with its CLP analog has either been scaled back or eliminated. Field GC screening should be regarded as merely a single factor in a holistic approach to conducting site and remedial investigations rather than a stand alone analytical method.

The cost effectiveness, time savings, and quality of field analysis combine to and demonstrate the utility of purge and trap GC analyses in the field. Analytical and overall program costs are significantly reduced while the sample database is increased, providing information critical for completing remedial investigations in a timely fashion.

U.S. EPA EVALUATION OF TWO PENTACHLOROPHENOL IMMUNOASSAY SYSTEMS

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INTRODUCTION

The Superfund Amendments and Reauthorization Act of 1986 (SARA) charged the U.S. Environmental Protection Agency (EPA) with effecting more timely and cost-effective remedies at the nation's Superfund sites. The development of improved field screening methods that yield immediate or short-turnaround environmental data can result in major cost savings per monitoring site. The EPA Superfund Innovative Technology Evaluation (SITE) Program was established in response to legislation within SARA. The EPA mandate to research, evaluate, test, develop, and demonstrate alternative or innovative treatment technologies is accomplished within the SITE program. One aspect of the SITE program focuses on monitoring and measurement technologies for contaminants occurring at hazardous waste sites.

This report presents the results of a demonstration of individual field and laboratory-based immunoassays for the detection and measurement of pentachlorophenol (PCP) at hazardous waste sites. PCP has beneficial uses in agriculture and as a wood preservative; however, there are risks associated with its use. Numerous sites on the EPA National Priorities List contain hazardous levels of PCP. Rapid and inexpensive monitoring and measurement technology is useful for monitoring the extent of contamination and the effectiveness of remediation. Immunoassays are gaining recognition as one cost-effective alternative to chromatographic and spectroscopic analytical procedures in large-scale environmental monitoring studies. Immunoassays can be used in the field, have the capacity for an increased sample throughput, and can be used to screen and rank samples for analysis by more traditional analytical methods. Although specific immunoassays have been developed for hazardous compounds of Agency interest, many of these systems have not been properly evaluated for environmental matrices. Agency restraint in utilizing immunoassay technology is partly due to the scarcity of immunoassay methods that have been fully evaluated for environmental applications.

MATERIALS AND METHODS

Westinghouse Bio-Analytic Systems (WBAS), Rockville, Maryland, developed two immunoassay technologies appropriate for screening drinking water, surface water, and ground water samples to detect and measure the presence of PCP. One technology is a 96-well microtiter plate immunoassay designed to accommodate the high sample capacity that might be encountered in a laboratory setting. The plate immunoassay is based upon a rat monoclonal antibody selective for PCP. The method has a stated sensitivity of 30 ppb and a linear dynamic range from 30 to 400 ppb. Although the procedure involves an overnight incubation step, analysis requires less than 0.5 hour per sample.

The second technology is an 8-well immunoassay kit designed to provide rapid, semi-quantitative analysis for PCP in the field, for example, at hazardous waste sites. The kit immunoassay is based upon rabbit polyclonal antisera and requires only about 30 minutes per run. The kit immunoassay has a linear dynamic range of 3 to 40 ppb and a stated detection limit of 3 to 5 ppb for water.

These technologies were submitted to the EPA Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) for evaluation. The study was conducted in two phases. The first phase evaluated the plate immunoassay under laboratory conditions; the second phase focused on the kit immunoassay under field conditions.

EXPERIMENTAL PROCEDURES

In the first phase of the study the plate immunoassay was evaluated using spiked environmental water samples (i.e., drinking water, surface water, and ground water). A methods comparison was conducted between the plate immunoassay and a gas chromatography (GC) detection protocol, as described in EPA Method 604. Extracts were prepared following EPA Method 604 and quantified by both the plate immunoassay and GC. Extracts from a simple solid-phase extraction technique, developed by WBAS, were also analyzed by both the plate immunoassay and GC. For relatively clean water samples, the plate immunoassay can be run without an extraction. Thus, unextracted samples were also analyzed directly by the plate immunoassay. The direct plate immunoassay data were compared to the GC results obtained using the solid-phase and EPA Method 604 extracts.

The second phase of the study consisted of evaluating the kit immunoassay in a field demonstration under the SITE program. The field demonstration occurred at the MacGillis and Gibbs Superfund Site in New Brighton, Minnesota. The kit immunoassay demonstration was conducted in tandem with another SITE demonstration of a technology to biodegrade PCP (BioTrol Aqueous Treatment Systems, Chaska, Minnesota). Though the majority of the SITE study was directed towards the demonstration of the kit immunoassay, part of the study also evaluated the plate immunoassay, because it can be performed under the same field- or mobile-laboratory conditions as the semiquantitative field analysis kit.

Samples consisted of (1) raw ground water known to contain PCP, (2) ground water treated with nutrients prior to the application of a bioremediation technology, and (3) effluent from the bioremediation process. The kit immunoassay was performed by personnel from Science Applications International Corporation at the field demonstration site, and by personnel from the EMSL-LV and WBAS in their respective laboratories. Splits of these samples were also analyzed with the plate immunoassay at the EMSL-LV and WBAS.

RESULTS

The evaluation results for the first phase showed no practical difference among: (1) the plate immunoassay and GC detection of Method 604 extracts, (2) the plate immunoassay and GC detection of solid-phase extracts, (3) analysis laboratories for the WBAS solid-phase and EPA Method 604 extraction protocols followed by immunoassay detection, and (4) the precision of the direct plate immunoassay obtained by the two laboratories. Figure 1 illustrates the comparability between the immunoassay and GC results. This first-phase evaluation generated a 9 percent false

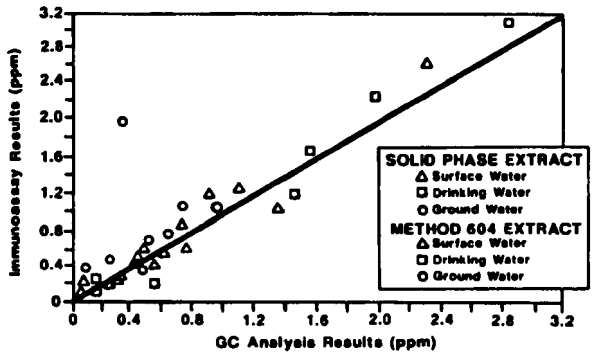

Figure 1. EMSL-LV Plate Immunoassay vs GC Method 604 Results

positive rate (n = 115) and a 0 percent false negative rate (n = 192). The performance of the direct plate immunoassay was not clearly demonstrated by the results of this study. However, with additional testing, it is expected that this particular mode of operation can provide acceptable results in the field as well as in a laboratory to provide a quantitative, high-sample throughput analytical methodology. The minimum detectable level of PCP in the plate immunoassay, approximately 30 parts per billion (ppb) for clean environmental water samples, is appropriate for regulatory use.

The phase-two method comparison was conducted between the two immunoassay methods and EPA Method 8270 (a gas chromatography/mass spectrometry (GC/MS) procedure). For the kit immunoassay, 87.5 percent of the results for the samples taken prior to the bioremediation process were within a factor of two of the GC/MS results. When these same samples were analyzed by the plate immunoassay, 94.4 percent were within the factor-of-two window. Figure 2 shows the results for on-site kit immunoassay and EMSL-LV plate immunoassay compared to the GC/MS results. Both immunoassay analyses of the low-level (effluent) samples gave a comparable range of results, but they were biased high by up to a factor of 2.5 in comparison to GC/MS analysis results.

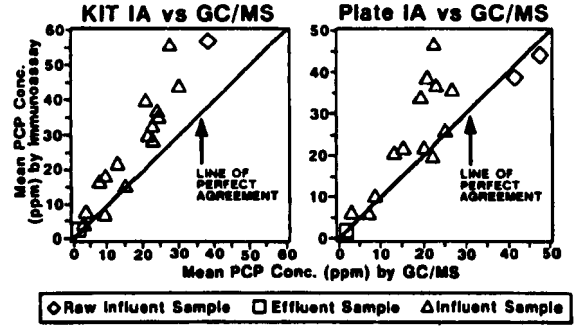

Figure 2. On-site Kit and EMSL-LV Plate Immunoassay vs GC/MS Results

Ranges in ppm for the low-level samples were 0.008 to 0.91 (GC/MS), 0.20 to 2.27 (kit immunoassay), and 0.31 to 1.82 (plate immunoassay). This bias, in view of the rank order of relative responses, does not significantly impact the utility of the technology as a screening tool. Thus, both immunoassays were comparable to the GC/MS results. The kit immunoassay false positive rate was 19 percent (n = 98) and the plate immunoassay false positive rate was 0 percent (n = 21). However, the majority of the kit false positive results were between 3 and 7 ppb, which is near the lower detection limit of the method. If a protocol specifying a minimum value of 7 ppb were used in this study, there would have been a substantially lower false positive rate (5 percent) for the kit immunoassay. No false negatives were observed in this study with either immunoassay technique. This is a critical criterion in determining if the immunoassays can be used as effective sample screening tools for expensive analytical methods.

A variety of QA/QC samples were included in the experimental design for the demonstration to provide comparison performance data for samples of known concentration and matrix. The immunoassay plate results for QA audit samples (nominal 25 ppm PCP concentration) are shown in Figure 3.

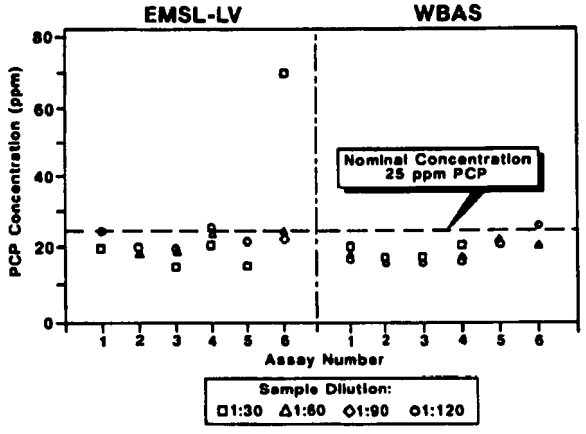

Figure 3. Plate Immunoassay QA Sample Chart for EMSL-LV and WBAS Laboratories

CONCLUSIONS AND RECOMMENDATIONS

Although the immunoassay methods evaluated are not as precise as traditional methods, they have several outstanding features. Principal among these are the rapid turnaround times for total analysis and the low cost per sample. The immunoassay methods are also field portable and require minimal training to perform. The immunoassays have detection limits and linear dynamic ranges comparable to those of traditional methods. A reduced level of accuracy is a limitation usually encountered when a system is configured for simple field-portable use. Though an immunoassay can be developed for a specific target analyte, it may be subject to certain interference effects from non-target compounds as well as from matrix effects unless a more involved extraction is used. However, most cross-reacting compounds are structurally related to the compounds of interest and, because of their intrinsic toxicity, they are frequently analytes of interest for regulatory monitoring as well. It is noteworthy that this study found no evidence of false negative results, an important feature of a screening method. The majority of false positives occurred at values near the lower limit of detection for each method. This rate might be significantly reduced by simple changes in the acceptance criteria for the method.

The information provided by immunoassay analysis, while not solely sufficient for initial site characterization, is frequently useful for detailed characterization of previously identified compounds of interest. Immunoassays are developed to be sensitive to only a particular target compound or a class of related compounds. The overall performance shown in these studies demonstrates that immunoassays can provide appropriate information for rapid on-site field decision making (see Table 1). In addition, the high sample capacity of the

TABLE 1. Method Comparison for PCP Analysis in Water

Performance Parameters	WBAS Kit Immuno-assay	WBAS Plate Immuno-assay	EPA Method 8270 GC/MS	EPA Method 604 GC
Detection Limit (ppb)	3-5	30-40	30-50	1-15
Linear Dynamic Range (ppb)	3-40	30-400	30-200	1-200
Precision	10-15%	5-10%	concentration dependent	10%
Accuracy	±25-40%	±15-25%	±10-20%	±15%
Extraction Required	No	No	Yes	Yes
Rapid On-Site Analysis	Yes	Yes	No	No
Total Analysis Time	1.5 hours/ 10 samples	5 hours/ 40 samples	5 hours/ sample	4.5 hours/ sample
Cost/Sample	$7.50	$2.50	$300-$750	$100-$300

plate immunoassay provides a low-cost screening alternative to higher cost laboratory analysis, the results of which are frequently unavailable for several weeks after sampling.

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NOTICE

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RAPID SCREENING TECHNIQUE FOR POLYCHLORINATED BIPHENYLS (PCBs) USING ROOM TEMPERATURE PHOSPHORESCENCE

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ABSTRACT

The analysis of Polychlorinated biphenyls (PCBs) generally requires selectivity and sensitivity. Even after cleanup, PCBs are usually at ultra-trace levels in field samples, mixed in with other halocarbons, hydrocarbons, lipids, etc. The levels of PCBs typically found in water, soil, tissue, food, biota and other matrices of interest are in the parts per billion (ppb) range. Most current measurement techniques for PCBs require chromatographic separations and are not practical for routine analysis.

There is a strong need to have rapid and simple techniques to screen for PCBs under field conditions. The use of field screening analysis allows rapid decisions in remedial actions and reduces the need for sample preparations and time consuming laboratory analyses. Field screening techniques also reduce the cost of clean-up operations.

This paper describes a screening technique room temperature phosphorescence (RTP), and provides an overview of both this analytical procedure and the instrumentation to detect trace levels of chemical pollutants and related biomarkers in complex environmental samples.

INTRODUCTION

Polychlorinated biphenyls are a class of chlorinated aromatic compounds which have found widespread applications because of their general stability and inertness as well as their excellent dielectric properties. The PCBs have been used in electrical capacitors, transformers, vacuum pumps, adhesives, plasticizers, pesticides, etc. The discovery of PCBs in environmental samples has spurred renewed concerns due to their acute and chronic toxicity, and other long-term health effects. The analysis of PCBs generally requires selectivity and sensitivity. The levels of PCBs typically found in water, soil, tissue, food, biota, and other matrices of interest are in the parts per billion (ppb) range. It is therefore important to develop simple, sensitive and rapid screening procedures for PCBs.

Most of the analytical techniques used for PCBs are not easily adapted to field measurements and generally employ chromatographic separations coupled to a specific detection scheme (e.g., flame ionization detection-FID; electron capture detection-ECD; photoionization detection-PID; thermal conductivity-TC; mass spectroscopy-MS; Fourier transform infrared-FTIR, etc.). A review of analytical techniques for PCBs has been described by Erickson (1). Packed column gas chromatography (GC), thin-layer chromatography (TLC), or high-performance liquid chromatography (HPLC) can be used to provide data on "total PCB" contents in samples. Packed column GC/ECD is the common method for quantification of PCBs as Aroclors in the American National Standards Institute (ANSI) procedures. The PCBs are quantified against an Aroclor standard using the largest peak, or a secondary peak. The GC/ECD technique was used to determine PCBs in sediments and soils (2). If congener-specific determination is required, high-resolution gas

chromatography (HRGC), which uses fused silica capillary columns, would be the technique of choice (3). High-resolution gas chromatography has been used for the analysis of PCBs in transformer fluids or waste oils. Various MS techniques (electron impact MS, chemical ionization MS, coupled MS/MS, etc.) have been used to analyze complex PCB samples. Methods involving perchlorination of the biphenyl ring of the PCB congeners have been used in the determination of PCBs. One of the limitations of the perchlorination approach is due to the fact that biphenyl can also be perchlorinated, thus leading to erroneously high blank levels.

Room Temperature Phosphorimetry (RTP):

The screening technique involved in this study involve Room Temperature Phosphorimetry (4). Conventional phosphorimetry requires the use of low-temperature matrices to reduce the collisional quenching mechanisms and radiationless deactivation processes. Due to the requirement of cryogenic equipment and refrigerant, conventional phosphorimetry has limited usefulness for routine applications in field measurements.

Unlike conventional low-temperature phosphorimetry, RTP is based on detecting the phosphorescence emitted from organic compounds adsorbed on solid substrates at ambient temperatures. The general approach is to obtain a solution containing the materials to be analyzed using rapid extraction procedures (1-3 min). A few microliters of the sample solution are then spotted on a filter paper. The spot is dried for about three minutes with a heating lamp then transferred to the sample compartment of the spectrometer. Measurements can be performed with any commercial spectrofluorimeter equipped with a phosphoroscope.

The sensitivity and selectivity of RTP can be enhanced by mixing the sample or pretreating the filter paper with a heavy-atom salt solution. Salts such as thallium acetate, in lead acetate are efficient in enhancing phosphorescence quantum yields for most PCBs.

Figure 1 illustrates the characterization of Aroclor 1254, a PCB mixture commonly found in environmental samples, using the RTP technique. This figure shows the RTP spectra of Aroclor 1254 using thallium acetate as the heavy-atom perturber. The efficacy and cost-effectiveness of the RTP technique for screening complex environmental samples have been demonstrated in previous studies (4). Figure 2 shows the improved selectivity of the RTP technique by using the second-derivative method. The precision of the RTP measurements is of the order of 15%.

The RTP technique approach offers several advantages: (a) rapid analysis, (b) simple set-up, (c) field applicable, (d) low per-analysis cost. These features of merit make RTP suitable for screening where a rapid estimation for specific PCBs is needed. The use of field screening analysis allows rapid decisions in a cleanup operation and reduces the need for either return visits to a site by a cleanup crew, or extensive and costly laboratory analyses of samples that contain no detectable levels of PCBs. Field screening techniques also reduce the cost of remedial actions by preventing unnecessary excavation of uncontaminated soil.

ACKNOWLEDGEMENT

This research is jointly sponsored by the U.S. Environmental Protection Agency (Interagency Agreement EPA No. DW899339001, DOE No. 1824-B124-A1) and the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Although research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute Agency endorsement of the product.

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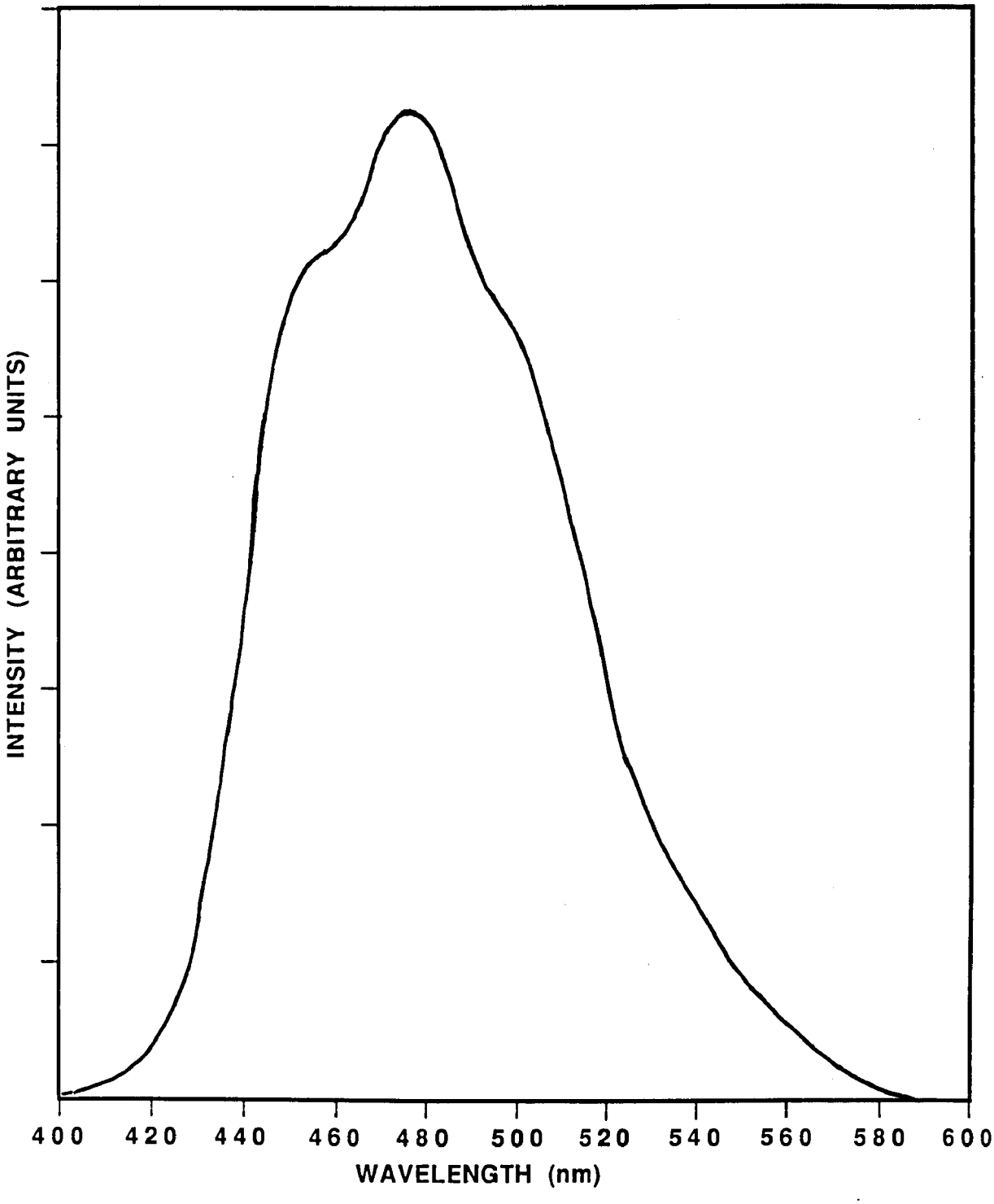

Figure 1

Example of RTP Spectrum of Aroclor 1254

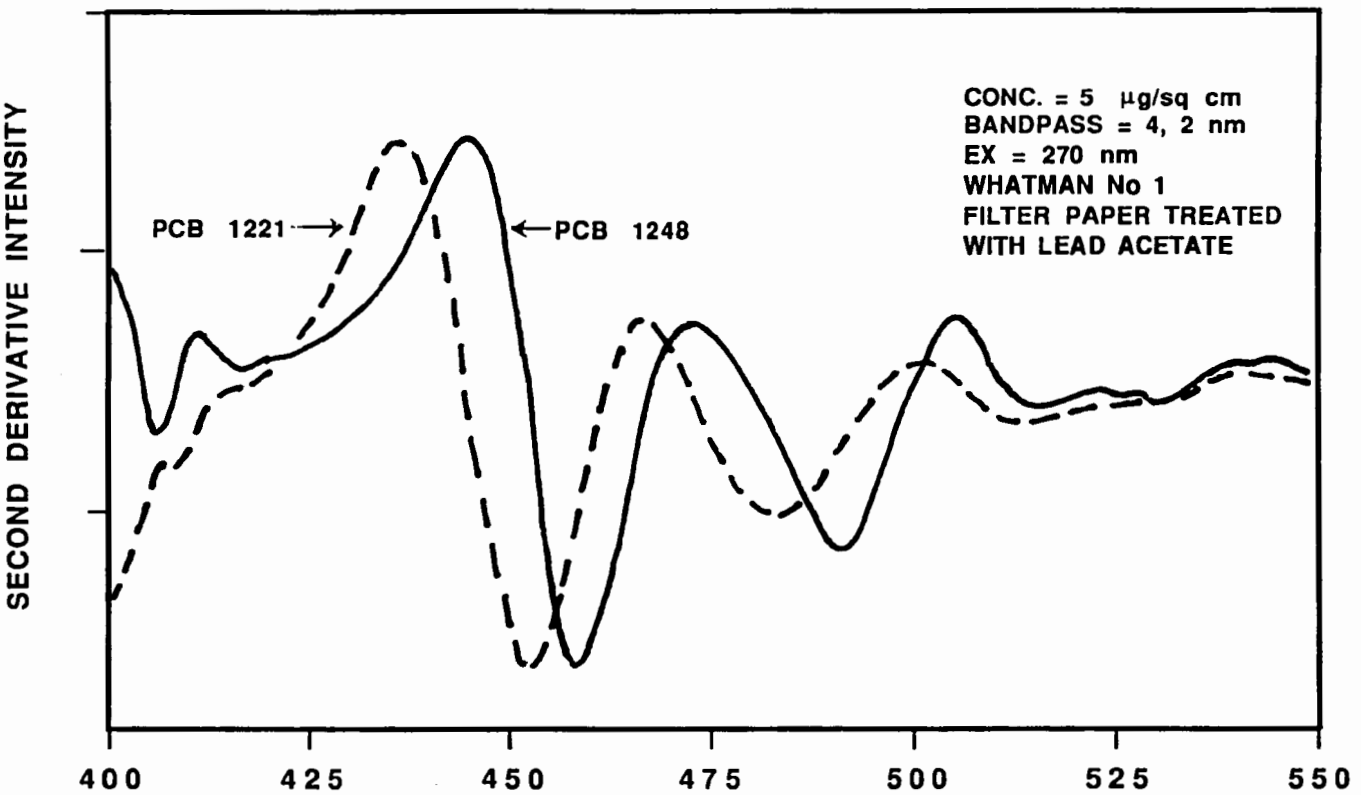

Figure 2

SECOND DERIVATIVE RTP EMISSION
OF POLYCHLORINATED BIPHENYLS

RAPID DETERMINATION OF DRUGS AND SEMIVOLATILE ORGANICS BY DIRECT THERMAL DESORPTION ION TRAP MASS SPECTROMETRY*

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ABSTRACT

Direct thermal desorption of analytes into an ion trap mass spectrometer (ITMS) is being investigated as a technique for the rapid screening of a wide variety of samples for target semivolatile organic compounds. This includes the direct detection of drugs in physiological fluids, semivolatile organic pollutants in water and waste samples, and air pollutants collected on sorbent cartridges. In order to minimize the analysis time, chromatographic separation is not performed on the sample prior to introduction into the ITMS. Instead, selective chemical ionization and tandem mass spectrometry (MS/MS) are used achieve the specificity required for the target analytes. Detection limits are typically 10-50 ppb using a 1 uL aliquot of a liquid sample without preconcentration. Sample turn-around time is 2 to 5 minutes and 3 to 5 target analytes can be quantitatively determined simultaneously.

INTRODUCTION

Recent advances in ion trap technology have led to the development of very sensitive and highly versatile mass spectrometers. These instruments exhibit mechanical simplicity, relatively small size, electron or chemical ionization options, and MS/MS capability on the most sophisticated systems. Because of their small size, ruggedness, and ease of operation, ion traps are especially attractive for potential use in field screening applications. Much work is currently being performed by several groups on the development of screening methods for volatile organics in environmental matrices. This paper describes the use of ion trap mass spectrometry for the direct analysis of target semivolatile organics in a variety of samples including organic pollutants in water and drugs and metabolites in physiological fluids.

EXPERIMENTAL

All experiments were performed with a Finnigan MAT ITMS ion trap mass spectrometer. This instrument was equipped with an electropolished vacuum manifold and dual 300 L/sec turbomolecular pumps to minimize problems with background contamination. Additionally, the manifold and ion trap cell were heated continuously to a temperature of 200°C using infrared lamps to further minimize contamination problems. The ITMS was configured with all of the necessary electronics for ion ejection, MS/MS, and axial modulation experiments. Scan functions for the detection of target compounds were written by the authors using the editor program provided by the manufacturer.

Samples were introduced into the ITMS by means of a thermal desorption device which was coupled with an open/split interface as shown in Figure 1. The thermal desorber was constructed in our laboratory and was designed to be compatible with sorbent tubes which are 3 inches long and 0.25 inches in diameter. The cap of the thermal desorber has a septum which enables the direct injection of liquid samples onto a sorbent tube without removing it from the desorber body.

The analysis of target semivolatile compounds is typically performed by injecting 1 uL of liquid sample into the thermal desorber onto the head of a 1 cm long packing of Tenax. The Tenax trap is heated for 10 seconds with 450 watts of power while simultaneously being purged with a flow of helium at 40 to 60 mL/min. Compounds which are vaporized from the sample are carried by the helium into an open/split interface which is constructed from a 6 inch length of 500 micron megabore capillary tubing and a 15 inch length of 150 micron uncoated fused silica capillary tubing. The 150 micron capillary acts as a restrictor between the ITMS vacuum chamber and atmospheric

pressure. The split ratio is approximately 95:1 with the bulk of the sample diverted to the split vent. In order to minimize the condensation of compounds in the transfer lines, they are maintained at a constant temperature of 200°C. No chromatographic separation is performed on the sample prior to introduction into the ion trap.

For target compound analysis, the ITMS is typically operated in chemical ionization MS/MS mode. Isobutane is normally used as the chemical ionization reagent gas due to its ability to discriminate against common hydrocarbon interferences. Quantification is performed by collecting a series of MS/MS spectra for the target analyte over a period of approximately 3 minutes starting at the time the sample is heated and desorbed from the Tenax. Reconstructed plots of ions which are characteristic of the MS/MS fragments for the target analyte are integrated and compared with an external calibration curve.

RESULTS AND DISCUSSION

An important application of this technology is for the rapid detection of target semivolatile organic pollutants in ground water samples. For example, as shown in Figure 2, acrylamide can be quantitatively determined at low part-per-billion levels in 1 uL of ground water with a sample turn around time of less than 4 minutes. Calibration curves are linear over at least 3 orders of magnitude and reproducibility is typically 10-20% at the 95% confidence intervals as shown in Figure 3. This method has also been shown to be capable of the detection of pesticides such as dieldrin as shown in Figure 4.

In addition to the detection of semivolatile organic pollutants in ground water samples, the same methodology may be used for the detection of target drugs in physiological fluids including urine and saliva. As shown in Figure 5, cocaine can be directly determined in urine at less than 100 ppb using 1 uL of a sample without preconcentration or chromatographic separations. Sample turnaround time is approximately 3 minutes and linearity is good over 2 to 3 orders of magnitude as shown in Figure 6. Using this technique a wide range of drugs of abuse have been examined including cocaine, phenobarbital, amphetamine, methamphetamine, THC, and codeine, among others. Further, extensive work has demonstrated that nicotine and several of its major metabolites can be quantitatively determined in the urine of smokers and potentially in the urine of non-smokers as well. This should prove especially useful as a technique for helping to assess the level of human exposure to environmental tobacco smoke.

In addition to the application of this technology to the determination of target semivolatile organic compounds in liquid samples, it is also useful as a technique for the determination of trace levels of semivolatile organics in air samples. For this particular application, an air sample is collected off-line using a small air sampling pump and a suitable resin cartridge. Samples can be collected for a preset period of time for TWA values or grab samples may be collected for an instantaneous measurement. The sorbent tubes are then simply loaded into the thermal desorber and heated for 10 seconds to vaporize the adsorbed analytes. The experimental parameters are otherwise identical to what has previously been described. Using this method, part-per-trillion level detection limits have been demonstrated for several different organophosphonate compounds in air. In addition, extensive work has demonstrated that the level of nicotine in environmental tobacco smoke can be quickly determined using this method.

Although the examples which have been described have only involved the detection of a single target analyte, it is currently possible to determine up to 4 different compounds in a single injection by use of alternating or multiplexed scan functions. This is a means of using the host computer to rapidly switch the conditions within the ion trap so that a spectrum of a different analyte can be obtained. Current software requires approximately 0.5 second to switch from one compound to another, however, thus limiting the total number of compounds that can realistically be determined during the time scale of a direct thermal desorption experiment. Improvements in the ion trap software should help to alleviate this problem.

CONCLUSION

Direct thermal desorption into an ion trap mass spectrometer is a sensitive tool for the rapid detection of target semivolatile organic pollutants in air and ground water and drugs and metabolites in physiological fluids. Detection limits are generally 10-50 ppb in a 1 uL liquid sample without preconcentration and linearity is typically 2 to 3 orders of magnitude. Sample turn around time is 3 to 4 minutes and up to 4 different compounds can be simultaneously determined in a single injection.

ACKNOWLEDGEMENT

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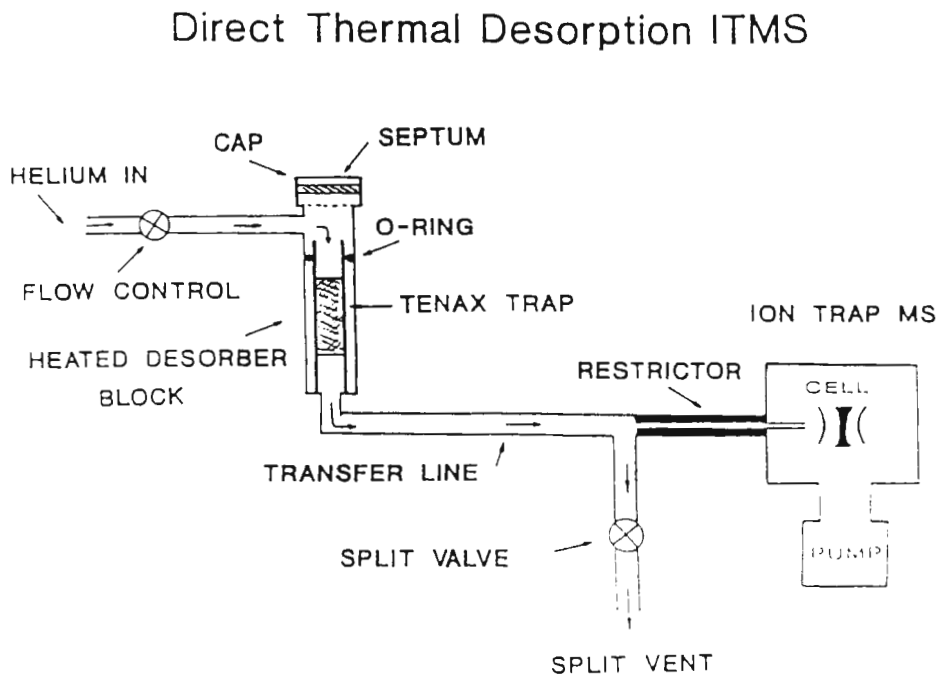

Figure 1 Apparatus for the direct thermal desorption of semivolatiles into the ITMS.

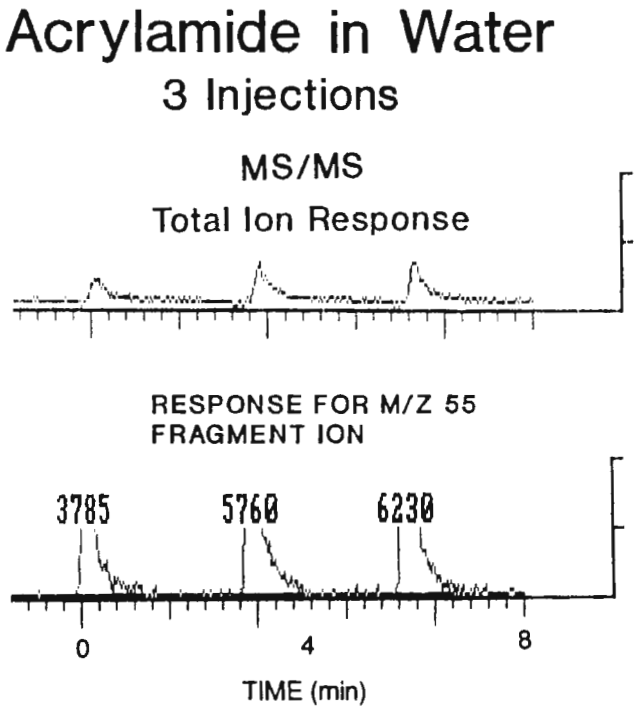

Figure 2· Repeated 1 uL injections of acrylamide in water into thermal desorber.

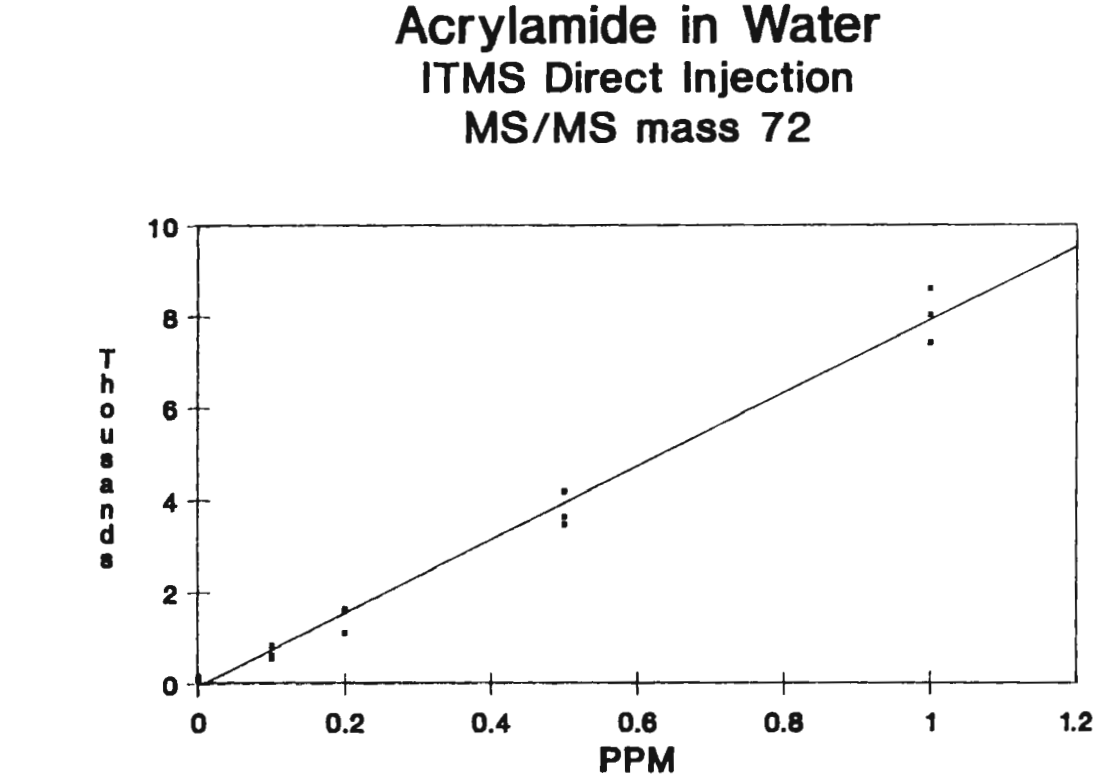

Figure 3 ITMS response curve for acrylamide in water.

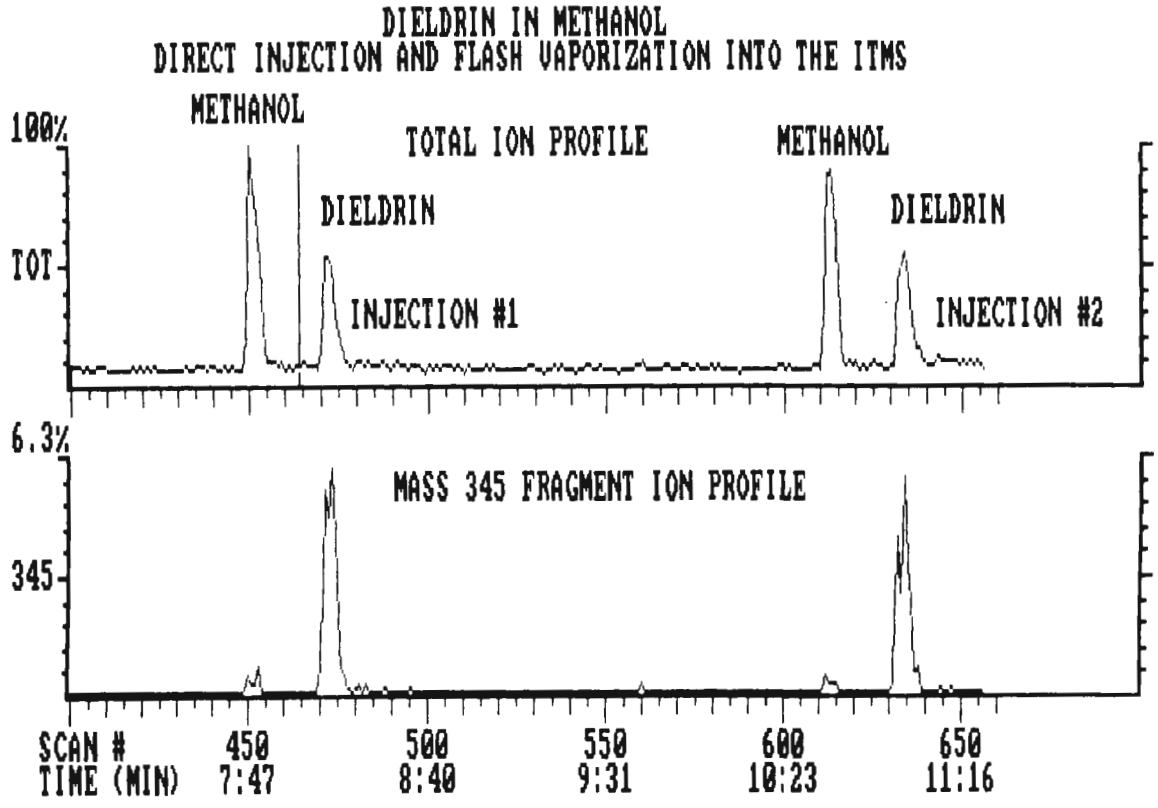

Figure 4 Repeated thermal desorptions of dieldrin into the ITMS.

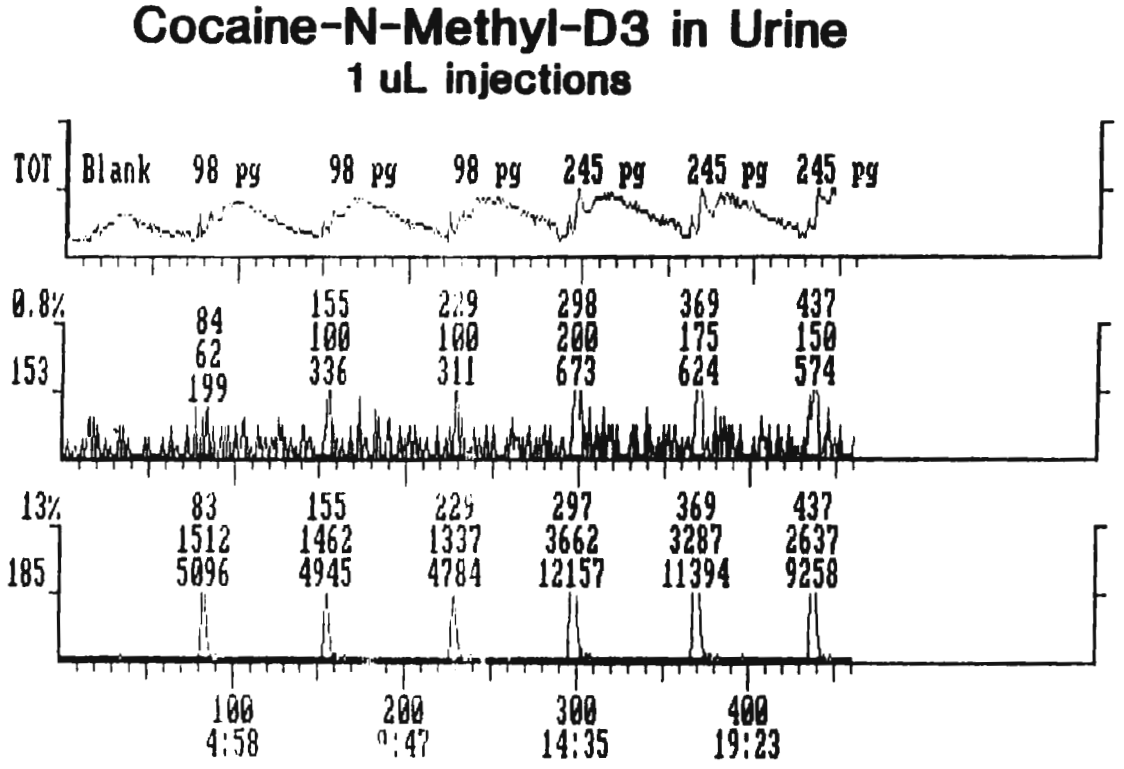

Figure 5 Repeated injections of cocaine in urine into the ITMS.

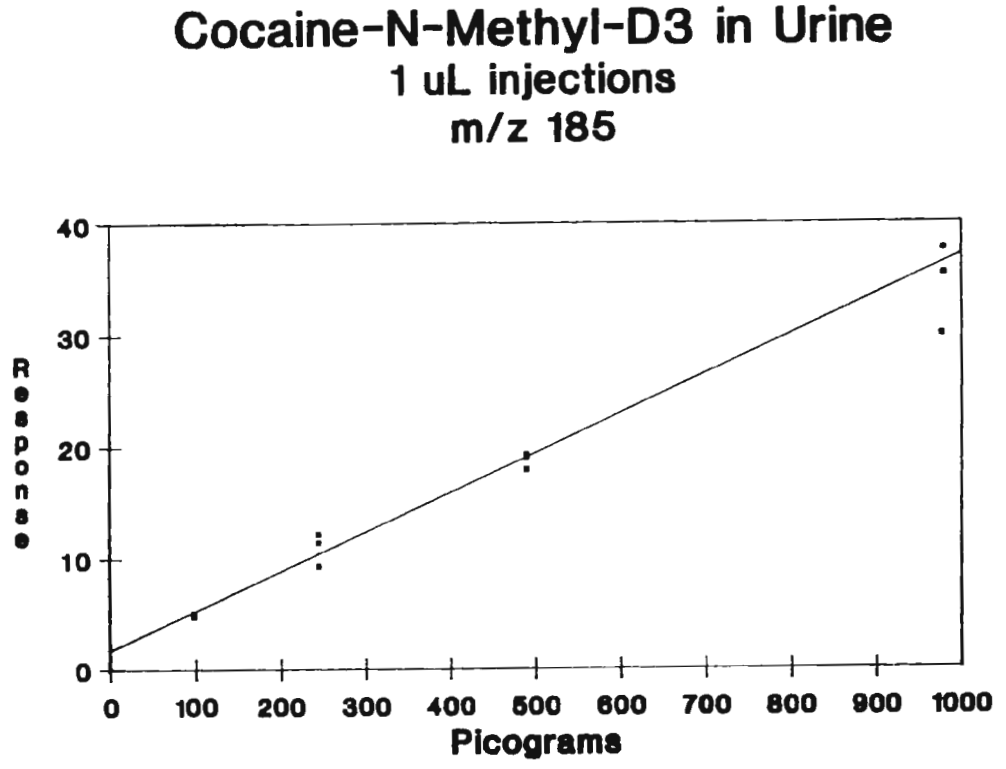

Figure 6 ITMS response curve for cocaine in urine.

A NEW APPROACH FOR ON-SITE MONITORING OF ORGANIC VAPORS AT LOW PPB LEVELS

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ABSTRACT

A new, very compact, gas chromatograph has been developed that uses scrubbed ambient air for its carrier gas. The instrument uses an internal pump to collect a vapor sample, concentrate it onto a small Tenax sorbent tube, and thermally desorb it (via backflush) into the isothermal (65°C) chromatographic column for subsequent analysis. Pump, valve, and concentrator sequencing is controlled automatically by an on-board microcomputer that also records the detector responses and determines baseline corrected chromatographic peak heights, positions, and concentrations. The instrument is small, (ca. 1/3 cu. ft.) lightweight, (12 lbs) and consumes little power (e.g., 10 Watts). The selective measurement of a variety of organic vapors at concentrations from a few ppb (by volume) to 100 ppm has been demonstrated.

INTRODUCTION

Environmental monitoring is a growing challenge, driven by ever increasing demands for higher sensitivity, higher selectivity, greater portability, and lower cost. In the last decade, portable gas chromatographs have become very popular for this application owing to their high sensitivity and the broad acceptance enjoyed by the chromatographic method within the analytical community. Many of the current instruments, while effective, offer less than optimal solutions to workers required to perform on-site environmental measurements. The disadvantages exhibited by some existing portable chromatographs include such things as the need for external supplies of carrier gas, poor or non-existent control of column temperature, high cost, extensive reliance on operator adjustments and operator interpretation of chromatograms.

The main objective of this project was to develop a very small, low cost, portable gas chromatograph that was *fully* automatic, requiring merely that the user turn on the power, provide a sample, and read the results from a digital display. A further aim was to afford the user great flexibility both in the power supply requirements and in the reporting of data directly to personal computers, printers, and modems. Finally, it was required that the instrument exhibit sensitivities and selectivities significantly higher than that demanded by most environmental monitoring applications. These objectives were successfully met by the portable instrument described here.

MATERIALS AND METHODS

System Overview

A schematic of the vapor monitor instrument is shown in figure 1. Air samples can be drawn into the instrument using a small on-board air sampling pump. The samples pass through a tenax GC concentrator tube where many organic vapors are effectively trapped. Introduction of the concentrated sample into the GC column is accomplished by heating the concentrator and backflushing the vapors into the column. Sample injection, operation of the GC column, and data analysis are controlled by the microcomputer following a schedule illustrated in figure 2. Once the chromatogram is completed, the microcomputer determines retention time, baseline corrected height, and vapor concentration for all peaks, using the calibration tables stored in memory for up to three user-defined retention time windows. On power-up there is a warm-up cycle during which the oven temperature stabilizes at 65°C. During the warm-up period the system microcomputer performs diagnostic checks on the oven, detector, carrier gas pump, and internal circuitry. Local interaction with the instrument is via the front panel keypad and display which prompts the user with menus through the operation of the instrument. It can also be controlled remotely via connection to the 1200 baud RS232C serial communication port of a PC or a modem connected to a telephone line. The instrument is contained in a rugged 1/8 inch thick aluminum case and can be powered either from an external 12 volt battery or directly from 120 volt AC power.

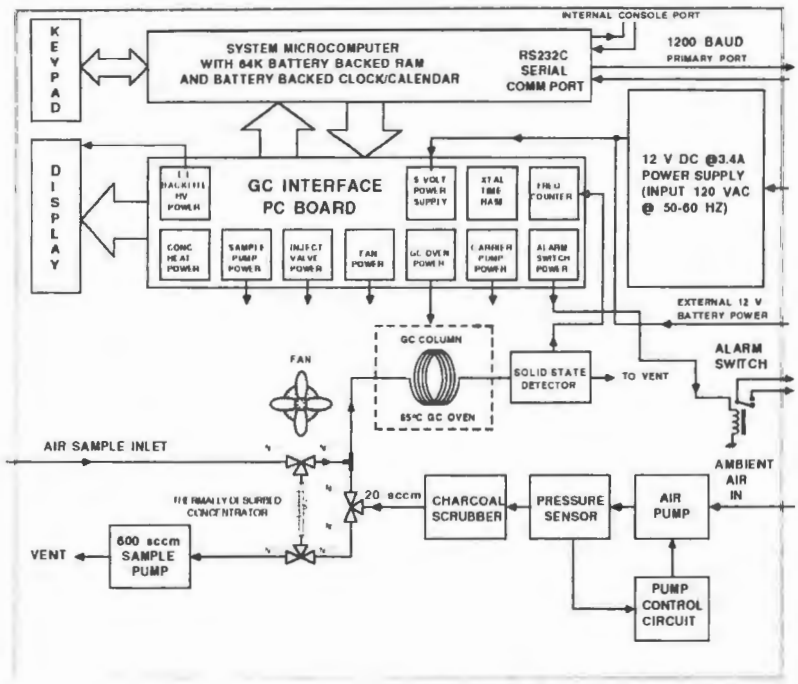


Figure 1. Portable gas chromatograph system diagram

Chromatographic Column

The instrument uses an isothermal (65°C) 1/8" diameter, 35 inch, chromatographic column packed with 10% TCEP (tricyanoethoxypropane) on 80/100 mesh Supelcoport. The column provides satisfactory resolution for monitoring all but very complex vapor mixtures. The column is wound on a 2.5 inch diameter aluminum block that contains a heater. The column and heater are housed in a styrofoam block to assure a constant temperature environment. Once hot, the column oven assembly consumes less than 6 watts of power to maintain the 65 °C temperature to within ± 0.5°C.

Carrier Gas

The carrier gas is generated from ambient air using a small compressor pump and an activated carbon scrubber to remove impurities. The pressure in the scrubber tank is held constant by means of a silicon chip pressure sensor connected in a feedback control loop to the carrier gas pump. The carrier gas pump pulses on and off to add air to the scrubber tank as required. The duty cycle of this pump is low, typically less than 10%. Power consumption of the carrier gas generator is typically less than 100 mW when generating a 12 sccm flow rate through the 35 inch column. Flow rate is maintained constant to better than ±0.5 sccm of the setpoint regardless of ambient temperature or pressure variations. Scrubber life is dependendent on ambient conditions but typically is 500 to 1000 hours. Scrubber replacement takes less than 5 minutes.

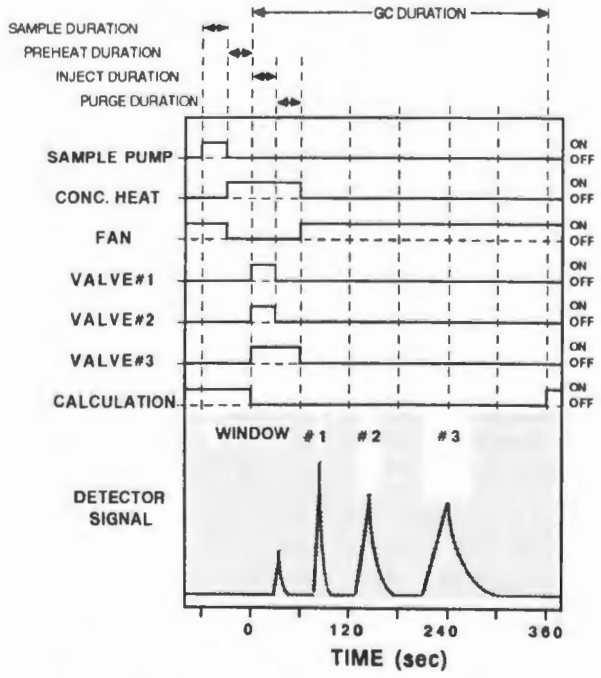


Figure 2. Typical run schedule for chromatograph

Sample Enrichment

The high sensitivity of this instrument results from the use of a concentrator to enrich the sample vapor concentration prior to injection into the column. Sample enrichment is achieved by compressing the organic vapors present in a large volume of air into a much smaller volume for injection into the GC column. This is done by sampling the ambient air at a high collection rate (e.g., 600 sccm) and passing the sample through ca. 50 mg of tenax GC in an adsorbent tube that traps most organic vapors except for the very low boiling compounds (and water vapor). The adsorbent tube is then heated to 140°C to vaporize the trapped organics which are then injected into the GC column using a much lower rate of flow (e.g., 12 sccm). After injection, the concentrator is cooled by a fan to permit efficient sample collection on the next trial. The comparatively low 140 °C desorption temperature was selected to extend the operating lifetime of the adsorbent to 1000 hours or more. Sample collection can be performed concurrently with the chromatographic run to minimize the analysis time. The sample collection and injection times are user programmable to optimize the performance of the gas chromatograph. The enrichment factor of the sample concentration procedure is thus normally adjusted by varying the sampling time. The practical limits for sample concentration are a function of such parameters as the adsorbent used, the bed depth, the vapors to be concentrated, and desorption temperature. At a typical sampling time of 30 seconds the effective concentration factor will be approximately 50X. The instrument was designed to collect vapor samples either automatically from ambient air present at a 1/8 inch Swagelok fitting on the front panel or from a sampling line to permit access to more localized areas or in restricted locations. It is also possible to add a septum to the gas inlet fitting so that vapor samples can be introducted directly onto the sample concentrator by syringe injection.

System Purging

The instrument offers the capability of purging the internal sample injection system with clean air. When the user selects a purge duration from the system menu, the concentrator and associated valving are flushed with clean air immediately after the sample is injected onto the column. This process removes residual vapors from the concentrator sorbent and assures that low volatility contaminants are not injected into the column.

Solid State Sensor

The proprietary solid-state detector used in the instrument is a very robust device whose operating lifetime is measured in years. Vapors eluting from the GC column adsorb onto the chemically sensitive coating of the detector. This vapor/coating interaction results in a signal whose frequency is related to the vapor concentration. The detector exhibits some preferential sensitivity to aromatic hydrocarbons but it also responds well to aliphatic hydrocarbons, alcohols, esters, and halocarbons. By changing the detector coating composition the detector can be tailored to respond in a selective fashion to many other organic vapors such as organophosphorus pesticides.

System Calibration

The instrument is normally calibrated using five concentrations of each vapor (e.g., benzene, toluene and xylene). These data define the shape of the calibration "curve", which is then stored in memory for data analysis. The instrument can be readily re-calibrated to compensate for changes in sensitivity over time. A single point span calibration is sufficient. If the experimentally measured concentration of a vapor standard differs from the known concentration, a system Response Factor, R, can be adjusted so that the measured concentration equals the known value. Changing the R factor adjusts the entire calibration curve.

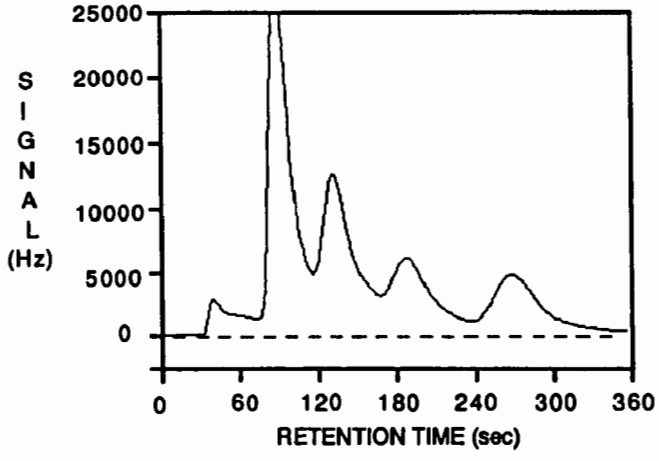


Figure 3. Typical chromatogram for benzene (1), toluene (2) ethyl benzene (3), and o-xylene (4)

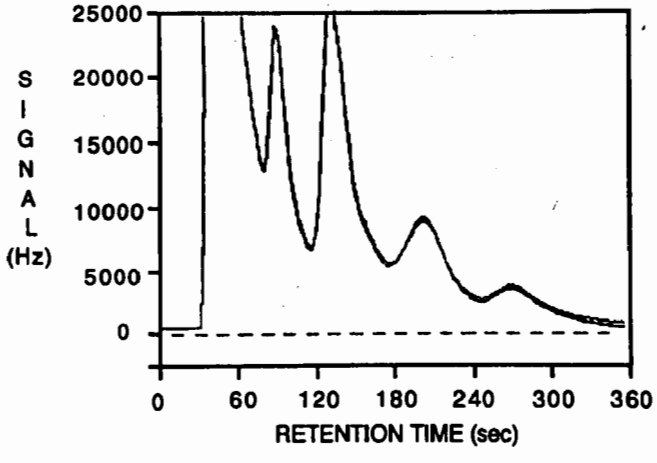


Figure 4. Chromatogram for four consecutive runs of unleaded gasoline vapors in air showing BTEX

Data Analysis and Reporting

Once the chromatogram is complete, the on-board microcomputer determines retention times and baseline corrected heights of the peaks occurring in up to three user selected retention time windows. Window location and width are specified independently for the analytes of interest. After the chromatogram data have been acquired, the data are smoothed and analyzed to check for peaks. When a peak is detected in a window then baseline correction is performed prior to determination of the peak height. This is done by drawing a straight line from the valley points that are detected before and after the peak location. Thus, tangent skimming is achieved. It then automatically determines the concentrations of the selected vapors using the calibration tables stored in memory. Each calibration "curve" consists of up to five, piecewise linear segments that help correct for non-linearities in the overall system response. Results of the latest measurement are displayed on the Liquid Crystal Display (LCD) on the instrument panel. Up to 8 hours of the most recent data are stored in non-volatile memory. The user can report results of the latest run or report all stored data in a variety of formats selected from the menu. The instrument can be interfaced directly to a PC terminal to display the data visually, or to a printer to provide a hard copy. The user can choose to display or print the latest chromatogram in real time, print out a listing of all peaks in the chromatogram, or print a listing of all data stored in memory without header information to make it compatible with many popular spreadsheet programs available for personal computers. The user also has the option of reporting data remotely via a telephone modem.

RESULTS AND DISCUSSION

A sample chromatogram for benzene, toluene, ethylbenzene and o-xylene in air is presented in figure 3. Figure 4 illustrates the chromatographic repeatability of the instrument. Here four consecutive chromatograms of unleaded gasoline vapors in room air are superimposed. The repeatability of the peak height and peak position exhibited by the instrument is noteworthy. Further evidence of the excellent repeatability was obtained from numerous automatic samples taken by the instrument. For example, when exposed to repeated samples of a benzene gas standard at 0.93 ppm the results shown in figure 5 were obtained.

Run No.	Signal (Hertz)	Measured Conc. (ppm)
1	26,010	0.930
2	26,041	0.931
3	25,995	0.930
4	26,010	0.930
5	26,064	0.932
6	26,022	0.931
7	26,084	0.933

Figure 5. Reproducibility of Portable GC Peak Response To Benzene at 0.93 ppm

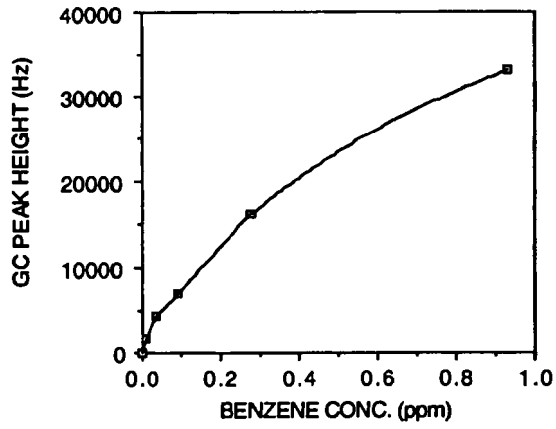


Figure 6. Benzene calibration curve

The calibration curve for benzene is shown in figure 6. It should be noted that on this curve the benzene sample having a concentration of 0.011 ppm produced a peak height of approximately 2000 Hertz. The typical detector noise observed on this instrument was approximately ±2 Hz. Thus, the 11 ppb benzene sample produced a signal to noise ratio of approximately 1000 to 1 thereby suggesting that highly accurate quantitative work at these concentration levels is possible. Other compounds besides BTEX can also be monitored with this simple instrument. Figures 7 & 8 show chromatograms for trichloroethylene and tetrachloroethylene, respectively, using the same column conditions as used in the BTEX analysis.

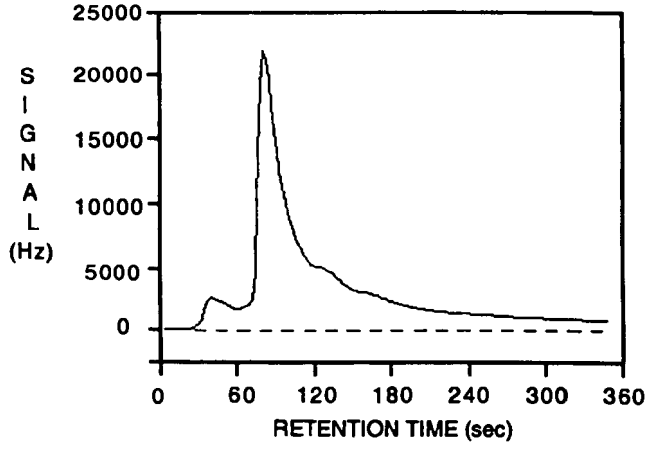


Figure 7. Chromatogram for trichloroethylene

CONCLUSION

This portable gas chromatograph was designed to take advantage of the most recent solid state technology. The use of modern solid state chemical and physical sensors affords a dramatic reduction in the instrument complexity, size, and cost by allowing the use of scrubbed ambient air as a carrier gas. This very important feature greatly simplifies the logistics of operating and maintaining a portable gas chromatograph. The extensive use of digital microcomputer technology makes it extremely easy to connect into multi-instrument networks or data processing computers. The instrument has been demonstrated to be highly effective for monitoring hazardous organic vapors in the low parts per billion range in "real-world" matrices. It can be programmed to respond to a wide range of organic vapors and can be used for single sample analysis as well as continuous, unattended monitoring.

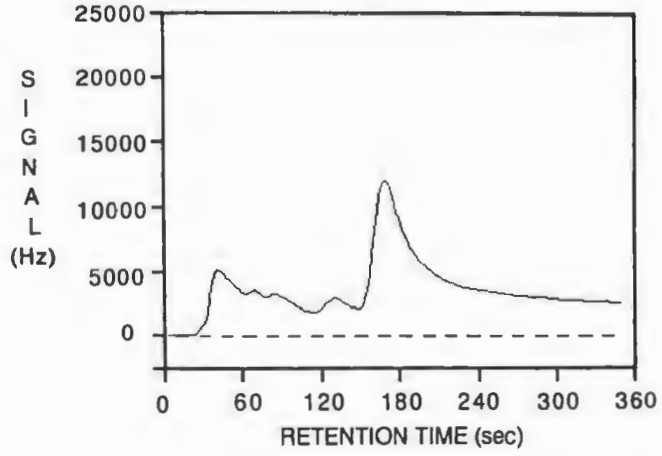
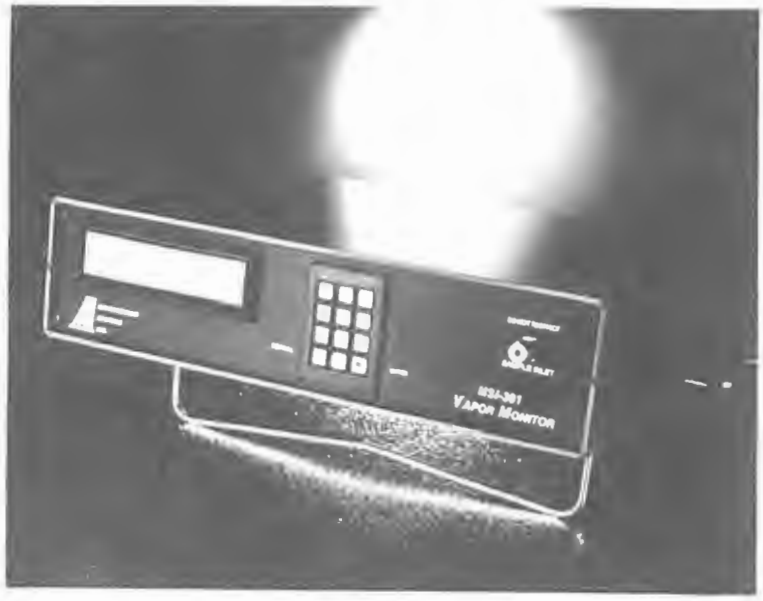


Figure 8. Chromatogram for tetrachloroethylene



A RAPID SCREENING PROCEDURE FOR DETERMINING TRITIUM IN SOIL

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Tritium, as tritiated water, is occasionally found in soil samples collected for investigations being conducted to identify the sources of soil and ground water contamination at the Lawrence Livermore National Laboratory (the major constituents of concern are volatile organic compounds and gasoline). It is important to quickly identify samples that contain tritium, and to estimate tritium activities or concentrations before submitting samples to contract analytical laboratories for conventional chemical analyses as most laboratories are not equipped to handle radioisotopes.

Traditional methods for determining tritium concentrations in soil require distillation or freeze-drying to collect soil water, but both methods are time consuming and costly. Therefore, we needed to develop a rapid screening method for determining the tritium concentration in soil. Initially, we attempted to determine the soil tritium content by direct liquid scintillation counting of small aliquots of the soil samples. However, direct counting limited the size of the sample, raising the detection limit of the analysis. Also, many soil samples contained materials that were extracted by the liquid scintillation cocktail solvent, causing drastic reduction of counting efficiency and further decreasing analytical sensitivity.

Upon further work, we found we could obtain reliable, reproducible results by direct extraction with water. This method is simple, eliminates interfering materials from most soil matrices, and is very cost effective compared to traditional methods. A weighed amount of soil is vigorously agitated in a measured volume of water. After centrifuging, the supernatant is decanted and tritium activity is determined by liquid scintillation counting for 10 minutes. The measured activity is adjusted for the amounts of soil and water used in the extraction. Depending on the amounts of soil and water used, the method can measure tritium concentrations down to 1 pCi/g of soil (approximately 10,000 pCi/L at 10% soil moisture). The entire extraction procedure for 12 samples requires less than 30 minutes. Results can then be used to choose samples to be analyzed for tritium, using more rigorous distillation methods.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Field Preparation and Stabilization of Volatile Organic Constitutents of Water Samples by Off-Line Purge and Trap

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INTRODUCTION

Purge-and-trap gas chromatographic analysis has a 20 year history of successfully analyzing volatile organics in water. The technique is quantitative, sensitive, and able to be automated. Purge-and-trap is used in all major EPA monitoring programs; RCRA, CERCLA, NPDES industrial wastewater, and drinking water.

A conventional system is illustrated in Figure 1. It is an integrated system, i.e. the purge vessel and sorbent trap are connected directly to the gas chromatograph in a laboratory environment. Water samples must be collected in the field, chemically stabilized, atmospherically sealed, and shipped to a laboratory while chilled. When received at the lab, they must be stored at 4° C. until analyzed, and at least for CERCLA, these samples must be analyzed within 10 days of receipt.

Open-loop purging system with on-line trap and thermal desorption facility

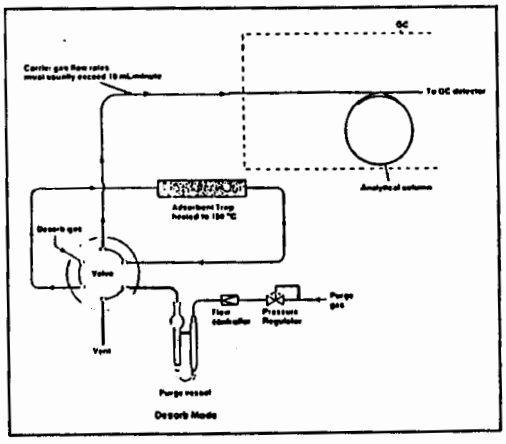

Figure 1

While this existing analytical system works well, this paper will demonstrate that it is not necessary for the purging to be done in proximity to the chromatographic analysis.

Purge-and-trap systems which incorporate an integral (on-line) thermal desorption device (shown in Figure 1) have been found to suffer from several limitations. These limitations can adversely affect the practical performance of such on-line systems. Among the limitations are:

- RISK OF CARRYOVER BETWEEN SAMPLES. This can occur when a particularly high concentration sample is analyzed.
- RESTRICTED COMPATIBILITY WITH HIGH RESOLUTION CAPILLARY GC + MS DETECTION.
- RESTRICTED STORAGE TIME FOR WATER SAMPLES.
- INCREASED CHANCE OF SAMPLE CONTAMINATION. This can happen because of stabilizers added to the sample to prevent haloform formation, or from atmospheric contamination of the aqueous sample from improper sample seals.

One solution to overcoming these potential problems is to separate the purge-and-trap volatile chemical collection and concentration from the desorption-chromatographic analysis. In other words, perform the chromatography **off-line** from the sample concentration.

The performance of one such off-line, fully automatic thermal desorption system (Figure 2) has been evaluated for this work. System details and results from these investigations are presented below.

Open-loop purging apparatus with removable trap suitable for off-line, two-stage thermal desorption

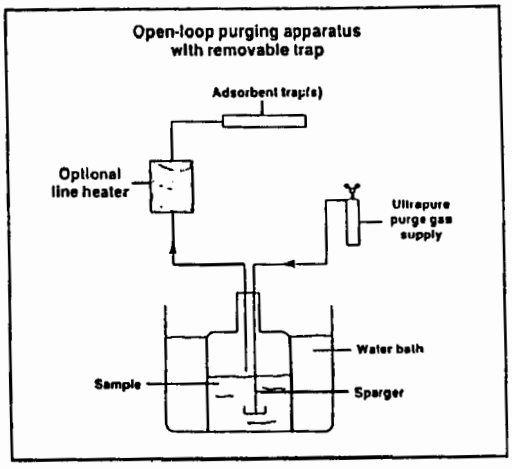

Figure 2

ADVANTAGES OF SEPARATING PURGE-AND-TRAP FROM CHROMATOGRAPHIC ANALYSIS

Using portable traps in combination with an automatic off-line purge unit enables water to be sampled using conventional EPA purging methodology at field sampling stations. Once sampling is completed, the tubes may be capped and transferred for thermal desorption GC analysis at a central laboratory facility. This approach immediately overcomes two of the major drawbacks of conventional on-line methodology:

- NO RISK OF CARRYOVER BETWEEN SAMPLES.
- GREATLY EXTENDED MAXIMUM SAMPLE STORAGE TIMES.
- DISTRIBUTED FIELD SAMPLING COMBINED WITH CENTRALIZED LABORATORY ANALYSES.

An automatic thermal desorption instrument allows multiple sample tubes to be analyzed without operator attendance. With the Perkin-Elmer Model ATD-400 up to 50 sorbent traps can be can be analyzed in one carousel loading. These traps, in the form of sampling tubes, are compatible with the method detection limits specified by EPA 500 and 600 series methods, as well as those purge-and-trap methods in the RCRA SW-846 analytical method manual.

For long term storage, the sorbent tubes can be capped with brass Swagelok (TM) caps and one-piece PTFE ferrules. Such tubes, spiked with benzene, toluene and m-xylene, are available as certified standards (Ref.1), and have been shown to be stable for up to two years of storage time.

In addition, data reported by the Netherlands Organization for Applied Scientific Research shows that chlorinated hydrocarbons on Tenax (TM) are stable for over 2 years. Multiple analyses for trichloroethylene and tetrachloroethylene (Figure 3) carried out over a two year period had a reproducibility with less than 10% RSD at storage temperatures ranging from 4°C to 40 °C (Ref. 4).

STABILITY OF VOLATILE CHLOROALKANES ON TENAX

Storage Temperature °C	Component	Initial Mean Charge ng	RSD%	# Rep	24 Month Mean Recovery ng	% Rec.
4°	Trichloroethylene	840	2.0%	15	856	102%
	Tetrachloroethylene	806	1.9%	15	781	97%
20°	Trichloroethylene	840	2.0%	15	816	97%
	Tetrachloroethylene	806	1.9%	15	756	94%
40°	Trichloroethylene	840	2.0%	15	842	100%
	Tetrachloroethylene	806	1.9%	15	765	95%

Ref: TNO Division of Technology for Society: Netherlands Organization for Applied Scientific Research, Report No. R90/268.

Figure 3

The ATD-400 also overcomes a third limitation of conventional procedures, i.e. incompatibility with high resolution capillary GC and mass spectrometric detection, by using an optimized two-stage thermal desorption process (Figure 4).

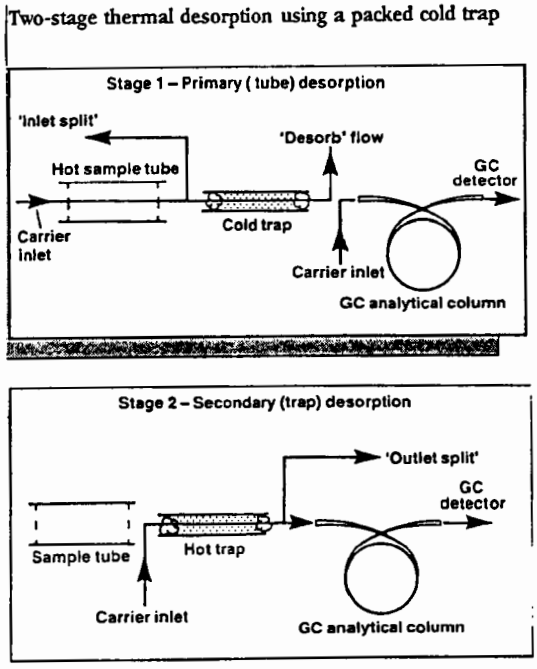

Figure 4

In this system, the primary trap (or tube) is heated and purged with carrier gas for several minutes to ensure complete elution of all retained components. These components are swept by the gas stream into a secondary cold trap held at subambient temperatures and comprising 1/8th-inch quartz tubing packed with approximately 20 mg of a selected adsorbent. Following this primary tube desorption stage, the secondary cold trap is heated rapidly at approximately 2400° C, thus transferring the pollutants into the GC analytical column in a very narrow band of vapor. This extremely rapid heating of the secondary trap produces peak widths of approximately 1 second, resulting in :

- UNCOMPROMISED HIGH RESOLUTION CAPILLARY CHROMATOGRAPHY and
- EXCELLENT COMPATIBILITY WITH MASS SPECTROMETRIC DETECTION (Figure 6).

The quantitative performance of the system for trace levels (nanograms) of components in the presence of relatively large masses (~20 mg) of water was investigated. These results are tabulated in Figure 8. These data demonstrate that the excellent quantitative performance of the ATD-400 was unaffected by a large mass of water present in the sample.

Recovery from sample tubes showing the effect of water

Identity	Calculated Amount in ng Chloroform	Benzene	Toluene	p-Xylene
1. Mass injected 4 ng level	4.44	3.99	3.92	4.24
2. 1st Replicate 4 ng level-dry	4.86	4.61	4.66	4.68
3. 2nd Replicate 4 ng level-dry	5.96	4.59	4.89	6.02
4. 1st Replicate 4 ng level + water	4.50	4.96	3.42	3.33
5. 2nd Replicate 4 ng level + water	4.13	3.68	3.29	3.14
6. Redesorbed Tube 4 ng level	n.d.*	n.d.	n.d.	n.d.
7. Mass injected 20 ng level	22.20	18.95	19.60	21.20
8. 1st Replicate 20 ng level-dry	22.26	19.40	19.80	21.36
9. 2nd Replicate 20 ng level-dry	22.16	20.33	19.06	20.87
10. 1st Replicate 20 ng level + water	24.39	21.85	19.35	19.99
11. 2nd Replicate 20 ng level + water	23.78	22.40	19.67	21.05
12. Redesorbed Tube 20 ng level	n.d.	0.40	n.d.	0.30
13. Car Park Air Sample – 12 litres	0.92	13.14	25.07	28.99
14. Range at 95% Confidence levels (+/- 2 SDs)	2.01	1.13	1.30	3.46

*– none found

Figure 5

A big advantage of the packed type of secondary cold trap is that there is negligible risk of trap blockage by ice formation. The formation of ice blockages is a major drawback of conventional capillary cryofocusing systems. By using a packed cold trap, it is also possible to retain extremely volatile components (i.e. C_3 and even C_2 hydrocarbons) using electrical cooling rather than a liquid cryogen. [N.B. The inability of simple liquid nitrogen cooled cyrofocusing systems to retain even medium volatility components has been reported by Grob and co-workers (Ref. 2). It is also advantageous to any form of automatic chromatographic analysis if liquid coolant is NOT required.]

By using only a low mass of adsorbent (~20 mg) in the secondary trap of the ATD-400 and by enabling high maximum temperatures (up to 400°C) to be selected when required, the system eliminates any possibility of sample carryover on the secondary trap.

Detection limits as low as 5 ppt have been reported using the off-line thermal desorption-GC analysis technique for the determination of VOCs in water (Ref.3).

CONCLUSION By using standard EPA purge-and-trap methodology in combination with enhanced off-line, two-stage automatic thermal desorption-GC analysis, confidence in analytical methodology is retained and the inherent disadvantages of conventional on-line instrumentation are overcome. This approach offers:

- VASTLY EXTENDED SAMPLE STORAGE CAPABILITY
- NO RISK OF CARRYOVER BETWEEN SAMPLES
- EXCELLENT COMPATIBILITY WITH HIGH RESOLUTION GC AND MS DETECTION (Figure 6)

In addition, by using a fully automatic two-stage desorption instrument, this approach lends itself to

- FIELD SAMPLING AND CENTRALIZED ANALYSIS.

Sample tube containing 4 ng each of chloroform, benzene, toluene and p-xylene and 20 ng of water analyzed using a Model ATD 400/ Model 8700 GC/Mass Spectrometer System

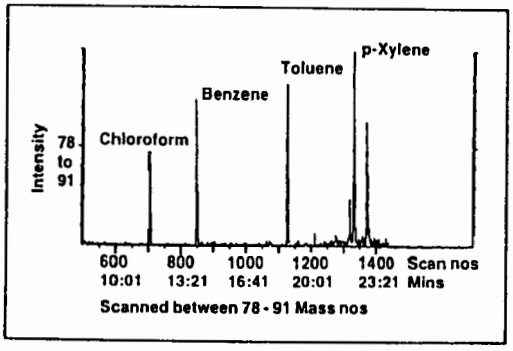

Figure 6

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   Community Bureau of Reference (BCR)
   Rue de la Loi 200
   B-1049 Brussels
   Belgium

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3. *Modified Analytical Technique for Determination of Trace Organics in Water Using Dynamic Headspace and Gas Chromatography-Mass Spectrometry.* Bianchi, Varney, and Phillips, J. of Chrom. 467 (1989), pp 111-128.

4. *Stability of Chlorinated Hydrocarbons on Tenax*, F. Lindqvist and H. Bakkeren, Netherlands Organization for Applied Scientific Research, TNO Division of Technology for Society, Report No. 90/268.

A FIELD-PORTABLE SUPERCRITICAL FLUID EXTRACTOR FOR CHARACTERIZING SEMIVOLATILE ORGANIC COMPOUNDS IN WASTE AND SOIL SAMPLES

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Richland, Washington

INTRODUCTION

Rapid, field-portable methods for measuring the concentration of semivolatile organic compounds are desirable for on-site characterization of contaminated soils and sediments. Supercritical fluid extraction (SFE) provides a viable alternative to current liquid extraction methods, which include Soxhlet and sonication methods. Compared to current liquid extraction methods, SFE is rapid, large quantities of glassware are not needed, large volumes of solvent are not required to be used or concentrated, and fewer sample handling and sample preparation steps are involved. Because of these characteristics, SFE lends itself to in-the-field extraction of solid samples of environmental concern.

In SFE, a supercritical fluid is used as a mobile phase passing through the solid matrix. The semivolatile organic compounds of interest are partitioned into the supercritical fluid, after which they are collected and analyzed. The liquid-like solvating power and rapid mass-transfer properties of a supercritical fluid provide the potential for more rapid extraction rates and more efficient extraction due to better penetration of the matrix than is feasible with liquids.

A prototype field-portable supercritical extractor was developed and tested at four different field locations, including two coal-tar-contaminated sites, a petroleum-tar-contaminated site, and a polychlorinated biphenyl (PCB)-contaminated site. In addition, the results obtained from replicate SFE extractions of a coal-tar contaminated soil were compared to the results obtained from replicate Soxhlet extractions of the same soil; the results obtained from the SFE extraction of several coal-tar-contaminated soils were compared to the results obtained from an on-site microextraction of replicates of the same soils; and the results obtained from the SFE extraction of PCB-contaminated soils were compared to the results obtained from analyses performed by a CLP laboratory using replicate soil samples.

EXPERIMENTAL

Apparatus

A schematic diagram of the field-portable SFE apparatus is shown in Figure 1. Although not apparent from the schematic diagram, the extraction cell heating mantles and restrictor heaters are mounted on top of the apparatus and the collection vessels are mounted vertically on its right side; this configuration maintains the device's compact design and allows easy manipulation of the extraction cells, restrictors, and collection vessels. Overall, the device measures approximately 14 in. wide by 14 in. high by 13 in. deep and weighs approximately 23 kg. It was designed specifically for field applications where portability, extraction speed, ease of operation, minimal requirements for ancillary supplies, and sample analysis flexibility are more significant factors than in laboratory applications. The apparatus was designed for use with carbon dioxide, but other pressurized liquids or ambient pressure liquids could also be used.

A reciprocating high-pressure liquid chromatography pump supplies pressurized carbon dioxide to the extraction cell, where the sample to be extracted is housed. To prevent the pump from vapor-locking, it is necessary to cool the pumphead assembly and the incoming flow of liquid carbon dioxide; lightweight cooling is obtained by single-stage thermoelectric devices. The pressurized carbon dioxide and the extraction cell are heated in a cylindrical heating mantle oven. The carbon dioxide pressure is reduced to atmospheric pressure through a flow restrictor made of fused silica capillary tubing (50 cm x 100-μm I.D.); the restrictor passes through a heated ceramic tube furnace into the collection vessel that contains collection solvent. A close-up of the collection vessel assembly is shown in Figure 2. The restrictor is passed through a septum seal into the glass restrictor support tube of the glass collection flask. Solvent is added to the flask (usually to at least one-half the height of the finger; 10 to 15 mL). A thermoelectric-cooled copper block with a tortuous flow path is connected to the exit of the glass collection flask to serve as a condenser to minimize losses

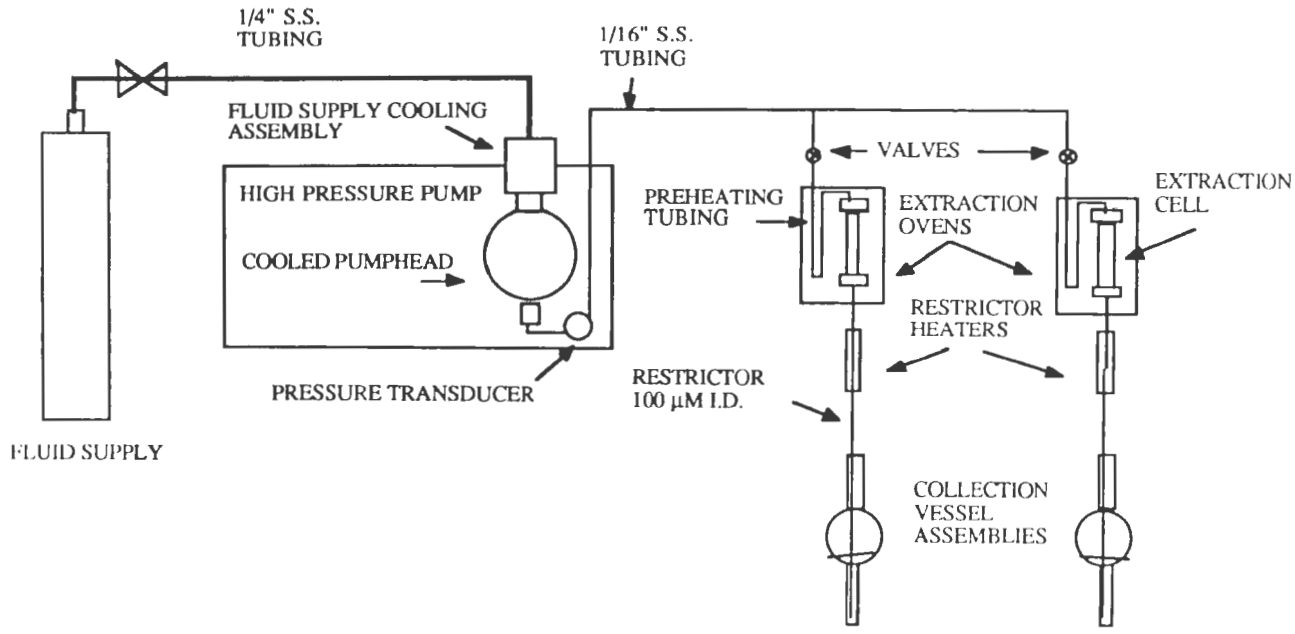

Figure 1. Schematic diagram of the portable, analytical-scale SFE apparatus.

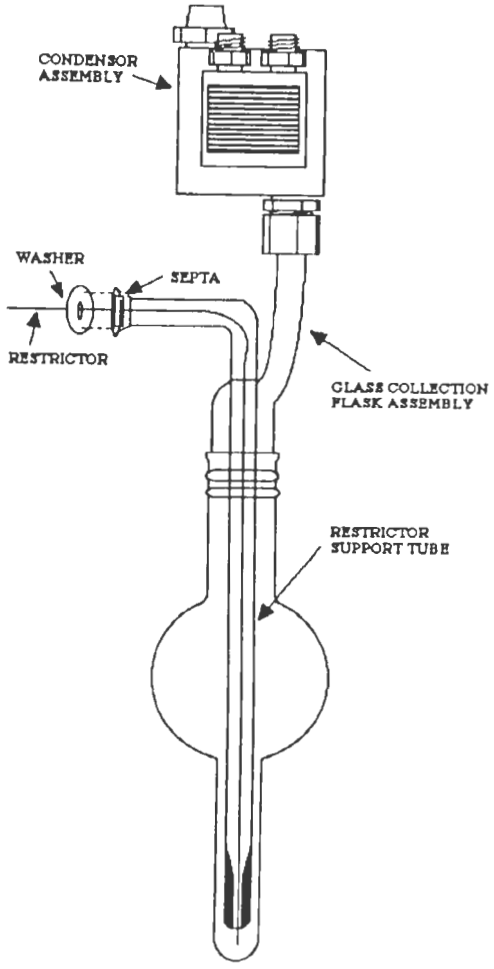

Figure 2. Extract Collection Vessel Design

due to solute volatility or entrainment in the escaping carbon dioxide.

The apparatus is designed to extract a single sample at a time, but it has tandem sample processing capabilities with two extraction cell ovens, two restrictor heaters, and space for two collection vessel assemblies. This allows near-continuous extraction of samples since one sample can be connected or removed from the apparatus while another one is being extracted.

Field Extractions

The equipment necessary for the extraction and analysis of coal-tar-contaminated soil (including the SFE apparatus and a gas chromatograph for extract analysis) were shipped via overnight air express to a utility site in the Midwest. It was set up in about 2 h on the day before samples were taken. The utility provided some soil samples taken from different locations on the site; several of the samples (1 to 2 g) were extracted using the SFE apparatus with carbon dioxide at 100°C and about 290 bar for approximately 20 min. The flow rate was very fast because the soil was sandy. 2-Chloroanthracene (approximately 50 µg) was added to the methylene chloride collection solvent to serve as an internal standard. The extract from one of the more contaminated samples (IL-B-3) was analyzed in the field for polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) using a fused silica capillary column coated with DB-5 (J & W Scientific, Folsom, CA) and a flame ionization detector (FID); calibration was performed with standard PAH mixtures at three different concentration levels. Results are given in parts per million (ppm; µg/g) of the soil sample as taken.

Additional coal-tar-contaminated soil samples were extracted and analyzed at a second field location. Nine coal-tar-

contaminated soil samples obtained from drill cores at the site of a waste dump from an abandoned manufactured-gas site in the Northeast were extracted in the field using carbon dioxide at 100°C and between 300 and 400 bar for 15 min. The extracts were analyzed for PAH using GC, as described above.

Ten petroleum-based oil-tar-contaminated solid samples were collected from various places around a gas plant in the Northeast, the third field location. Some of them required the addition of clean soil, silica gel, or glass beads to facilitate extraction because of their "sticky" consistency. The samples were extracted in the field using carbon dioxide at 100°C and about 350 bar for approximately 20 min. The extracts were analyzed for PAH using GC, as described above.

The applicability of the SFE method for the analysis of PCB-contaminated soils was demonstrated at a contaminated site in the Northwest, where 17 soils were extracted and analyzed in the field. Fourteen of these samples were extracted with carbon dioxide at 100°C and pressures of 350 to 400 bar for 15 to 20 min; three of these samples were extracted at pressures of 250 bar for 20 to 25 min. The extracts were analyzed in the field for Aroclor 1260 PCB compounds using GC, as described above, except calibration was performed using a standard Aroclor 1260 PCB mixture. Eight of the extracts were further analyzed in the laboratory using GC with a chlorine-specific electron capture detector (ECD).

SFE Comparisons

SFE was compared to Soxhlet extraction using a coal-tar-contaminated soil sample from the second field location described above. Five 2-g replicates were extracted using SFE with carbon dioxide at 100°C and approximately 350 bar for 30 min. Each of the five replicate SFE extractions were analyzed by GC in triplicate, and 15 individual PAH compounds (ranging in size from two to five rings) were quantified. Five 2-g replicates of the same soil were Soxhlet-extracted overnight using 250 mL each of methylene chloride. The extracts were then concentrated using a rotary evaporator operated at 40°C. The Soxhlet extracts were then analyzed by GC in the same way as were the SFE extracts. The quantitative results obtained from the two extraction methods were compared using an F-statistic at 95% confidence limits.

The same nine coal-tar-contaminated soil samples that were extracted using SFE at the second field location described above were concurrently extracted in the field by an independent laboratory using a microextraction method. Two-g samples of each soil were extracted in 15-mL culture tubes with 10 mL each of 1:1 methylene chloride: acetone. The soil-solvent mixture was agitated for 30 min, after which the solvent was decanted and concentrated to 0.5 mL. The extracts were analyzed for PAH by GC. The relative percentage differences of the quantitative results between the SFE and microextraction methods were calculated for each compound, these differences were then averaged for each of the samples to determine the agreement between the analytical results from the two field methods.

Subsamples of the 17 PCB-contaminated soil samples described above were extracted and analyzed by an independent CLP laboratory using Soxhlet extraction and analysis by GC using an ECD. The results were compared to the SFE results.

RESULTS

The two-ringed PAH compound, naphthalene, was found to be the PAH of highest concentration in the IL-B-3 soil sample at 750 ppm. It was followed by the three-ringed PAH compound, phenanthrene, at a concentration of 400 ppm. The highest concentration of a heterocyclic PAH compound was determined to be dibenzothiophene (a three-ringed compound containing one sulfur heteroatom) at 20 ppm. The highest concentration of an alkylated PAH was determined to be 2-methylnaphthalene at 320 ppm. Pyrene (a four-ringed pericondensed PAH compound) and chrysene (a four-ringed catacondensed PAH compound) were detected at 170 and 48 ppm, respectively. Benzo[a]pyrene (a five-ringed PAH compound) was detected at 36 ppm. The concentrations of the parent PAH compounds decreased with increasing molecular weight.

Of the nine coal-tar-contaminated soil samples extracted and analyzed at the second field site, only one contained PAH compounds at concentrations greater than 1 ppm. Naphthalene was the PAH compound of greatest concentration in this sample with a concentration of 180 ppm. Phenanthrene was detected at 29 ppm, and pyrene at 5.5 ppm. The highest concentration of a PAH compound detected in five of the other soil samples ranged from 0.1 to 0.9 ppm. No PAH compounds were detected in two of the soil samples above the minimum detectable limit of approximately 0.01 ppm.

The levels of PAH detected in the ten petroleum-tar-contaminated samples ranged from low ppm to low parts per thousand (mg/g). The samples that contained the highest levels of PAH were described as tar, oily tar, or sluff tar samples. The highest overall levels of PAH were detected in the sample described as tar. The next highest overall levels of PAH were detected in the two field pile samples (described to be a mixture of soil and sluff tar) and an oily tar sample from a manhole pit; these samples contained about five times less PAH than did the aforementioned tar sample. Five of the samples were described as tar-contaminated dirt and their PAH levels were about one order of magnitude less than those detected in the oily tar or sluff tar samples. The lowest levels of PAH were detected from a sample from a composting tub in the curing stage.

There was wide variability in the levels of PCBs detected in the soils from the fourth field site.The levels of Aroclor 1260 detected in the 17 PCB-contaminated soil samples ranged from <10 to 19,000 ppm. These results show how the areas of most contamination can be located with little turnaround time during a site characterization using SFE. The ECD results obtained later in the laboratory were all either less than or the same as the FID results obtained in the field; these results were not surprising since many of the soil samples were contaminated with diesel fuel and hydraulic oil, which may have caused the FID results to be inaccurate because of coeluting hydrocarbon compounds.

When the quantitative results from five SFE extractions and five Soxhlet extractions were compared for 15 PAH compounds ranging from two to five rings in size, it was found that statistically significant differences could only be detected for two of the 15 individual PAH compounds. Thirteen of the compounds were detected at the same level for both extraction methods. The two compounds that gave differing results were both high-molecular-weight benzopyrenes; for these compounds slightly lower amounts (approximately 20%) were detected in the SFE extracts than were detected in the Soxhlet extracts. These results indicate good agreement between the SFE and the traditional Soxhlet extraction methods.

The same two coal-tar-contaminated soil samples that contained no detectable limits of PAH compounds when extracted using SFE also contained no detectable limits of PAH when extracted using the microextraction method. For the seven other samples that were extracted by the SFE and microextraction methods, the relative percentage differences between the results of the two extraction methods ranged from 16 to 44%. The data indicated that SFE generally gave higher concentrations of the lower-molecular-weight compounds (two rings in size) than did the microextraction method. Overall results, however, indicated that the two field methods were comparable for these particular soil samples, especially considering the extremely low levels of PAH contamination that were present (mainly in the parts per billion, ng/g, range), and that each sample was only analyzed one time by each method.

The comparison of the results from the field SFE extraction and analysis of PCB-contaminated soils to those obtained by an independent CLP laboratory indicated the two methods gave results of the same order of magnitude.

CONCLUSIONS

SFE was shown to be a rapid, field-portable method for the analysis of PAH and PCBs in soil and other solid environmental samples. The SFE method gave results that were comparable to the results obtained by traditional extraction methods.

SFE should prove useful as an efficient means for rapid characterization during site assessments and at sites undergoing remediation treatments. The method should also be applicable for measuring the concentration of other semivolatile organic compounds of environmental concern.

ACKNOWLEDGMENT

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Detection of mercuric ions in water with a mercury-specific antibody

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INTRODUCTION

Exposure to toxic amounts of mercury can lead to serious health problems, with long-term consequences for the affected population. Thus, simple, sensitive, and convenient procedures are needed for detection of mercury in the environment to prevent these problems from arising.

In this paper, an ELISA is described that detects mercury at concentrations of 0.5 ppb or greater in water. Between 0.5 and 10 ppb mercury, the absorbance is proportional to the log of the mercury concentration. The assay is specific for mercury, in that no other metal tested interferes with the quantitation of mercury. In addition, the assay requires little preliminary processing of the sample and can be done with only one hundred microliters of sample.

MATERIALS AND METHODS

Materials

An EP Extract Metals Quality Control Sample was obtained from the Environmental Protection Agency, Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 45268. The sample contained 0.2 mg/L Hg^{++}, 100 mg/L Ba^{++}, 1 mg/L Cd^{++}, 5 mg/L Cr^{+++}, 5 mg/L Pb^{++}, and 5 mg/L Ag^{+} in distilled water adjusted to pH 5.0 with acetic acid.

Standard Reference Materials 1641 and 3133 were obtained from the National Institute of Standards and Technology, Office of Reference Materials, Gaithersburg, MD, 20899. SRM 1641 consisted of mercury at a concentration of 1.52 ug/ml in 2% nitric acid, and SRM 3133 contained 10 mg/ml mercury (as 16.2 mg/ml mercuric nitrate) in 10% nitric acid.

Detection of mercury in water by enzyme-linked immunosorbent assay

Ninety-six-well microtiter plates (EIA/RIA grade, Costar Corp., Cambridge, MA) were treated with BSA-glutathione, blocked, and used for ELISA. One hundred microliter aliquots of water containing known amounts of mercuric chloride, ranging from 0.2-200 parts per billion, were added to the wells of the microtiter plate for 30 minutes. The plates were washed three times, then ascites fluid containing a mercury-specific monoclonal antibody was added for 30 minutes at room temperature, followed by goat anti-mouse u chain conjugated to horseradish peroxidase (Kirkegaard and Perry Laboratories, Inc., Gaithersburg, MD). After incubation for 30 minutes at room temperature, the plates were washed, and 100 ul of ABTS peroxidase substrate (Kirkegaard and Perry Laboratories, Inc., Gaithersburg, MD) were added to each well. After 15 minutes incubation, the absorbance of each well at 405 nm was measured with a Titertek Multiscan MC multichannel spectrophotometer (Flow Laboratories, Rockville, MD).

Cold-vapor atomic absorption spectrometry

Mercury concentrations of some samples were determined by cold-vapor atomic absorption in the Diagnostic Laboratory, Department of Veterinary Sciences, University of Nebraska-Lincoln with a Mercury Monitor flameless atomic absorption spectrophotometer (Model 1255, Milton Roy Inc., LDC Division, Riviera Beach, FL). Before analysis, the samples were treated with $SnCl_2$ in 10% HCl to reduce mercuric ions to elemental mercury, and the mercury concentration was determined by comparison with a mercury standard (Mercury Reference Standard Solution, Fisher Scientific) treated in the same manner.

For direct comparison of mercury quantitation by atomic absorption and ELISA, the mercury standard was diluted to a nominal concentration of 100 ppb in 0.1 M HEPES, pH 6.8. Two aliquots were then removed. One was diluted in HEPES buffer to the appropriate concentrations for analysis by immunoassay, while the other was diluted in 10% nitric acid ('Baker Analyzed' 70-71%, Trace Mineral Analysis, Baker Chemical Co.) for atomic absorption measurement. Mercury was then measured as described above for each method.

Mercury quantitation in EPA and NIST samples
Each of the samples from the Environmental Protection Agency and the National Institute of Standards and Technology was diluted in water to mercury concentrations of 1-200 ppb, then used in the ELISA as described above. The results were compared with a standard curve constructed from ELISA analysis of water containing known concentrations of mercury. The mercury concentrations of the samples used for construction of the standard curve were also measured by atomic absorption.

Interference with mercury detection by other metals in the ELISA
A 2 mM solution of each metal salt in water was diluted to concentrations of 20 uM, 200 nM, 20 nM, and 2 nM. Fifty microliters of each concentration were added to individual microtiter wells treated with BSA-glutathione. Fifty microliters of SRM 3133 containing mercury at concentrations ranging from 1-200 ppb were added to the appropriate wells. The plates were incubated at room temperature for 30 minutes, after which time the plates were washed and assayed by the ELISA described above.

RESULTS AND DISCUSSION

An immunoassay capable of detecting small amounts of mercury in water was developed with the use of an antibody that reacts with immobilized mercuric ions. Table 1 shows the results of seven replicate analyses for each mercury concentration, along with the means, standard deviations, and coefficients of variation. Absorbance approximately twice that of background was consistently noted for mercuric ion concentrations as low as 0.5 ppb when compared to water with no added mercury, and concentrations of 0.2 ppb were 50% above background. Frequently, concentrations of mercuric ions at 0.1 ppb demonstrated absorbance in this same range (data not shown). A linear relationship between A_{405} and the log of the mercury concentration was obtained in the range of 0.5-10 ppb, as indicated by a correlation coefficient of 0.998 within this interval.

In addition to its linearity, the assay was highly reproducible. Standard deviations were less than 11% of the mean at 0.2 ppb and generally decreased as the concentration of Hg^{++} increased to 10 ppb. In all cases, except for the sample containing no Hg^{++}, the coefficient of variation was 10% or less. These results also indicated that the ELISA was as sensitive for mercuric ion detection as the atomic absorption procedure recommended by the EPA, which is capable of mercury detection down to 0.2 ppb, but requires a 100 ml sample to do so (1).
Since cold-vapor atomic absorption is currently the method of choice for mercury determination, it was important to determine how well ELISA results correlated with atomic absorption analyses. To do so, an atomic absorption mercury reference standard was diluted in 0.1 M HEPES, pH 6.8, to a mercury concentration of 100 ppb. At this point, two aliquots were removed and diluted to the appropriate concentrations for immunoassay or atomic absorption as described in Materials and Methods. Samples containing 0, 2, 4, 6, 10, and 15 ppb mercury were then analyzed by both methods. As shown in Figure 1, the results obtained from the two methods were in close agreement, as indicated by a correlation coefficient of >0.99. In addition, the standard deviation of the immunoassay at most mercury concentrations was the same or less than that obtained by atomic absorption. These results demonstrated that, under the conditions of this assay, quantitation of mercury by ELISA was as precise as cold-vapor atomic absorption.

Since most samples for mercury analysis by cold-vapor atomic absorption are stabilized in strong acid, it was of interest to determine whether the immunoassay could detect mercury in samples treated similarly. Two samples obtained from the National Institutes of Standards and Technology, SRM 3133, which consisted of mercuric acetate in 10% nitric acid, and SRM 1641, which contained metallic mercury in 2% nitric acid, were assayed by the Hg^{++}-specific ELISA. Each sample was diluted in water to mercury concentrations from 1 ppb to 100 ppb before analysis. As shown in Figure 6, mercury could be detected in each sample at concentrations of 1 ppb, although the absorbance at that concentration was approximately half that obtained with water containing the same amount of mercury.

The specificity of the assay for mercury was investigated with the use of an EPA quality control sample containing 0.2 mg/L Hg^{++}, 100 mg/L Ba^{++}, 1 mg/L Cd^{++}, 5 mg/L Cr^{+++}, 5 mg/L Pb^{++}, and 5 mg/L Ag^{+} in distilled water adjusted to pH 5.0 with acetic acid. The sample was diluted to known Hg^{++} concentrations, which were assayed by ELISA and

compared to results obtained with standards consisting of known concentrations of mercuric chloride in water (Figure 3). Reactivity was obtained with both the EPA sample and the water standard at 2 ppb mercury, and the absorbance for both samples was linear up to 20 ppb mercury. Reactivity was due to the presence of mercury and not to recognition of one of the other metals, since a sample containing all of the metals except mercury in the same concentrations as in the EPA sample gave the same absorbance as water containing no mercury.

The results in Figure 3 did not reveal whether higher concentrations of these or other metals would interfere with the assay. Therefore, concentrations of individual metal ions from 1 mM to 10 nM were examined for interference with detection of various concentrations of mercury in SRM 3133. Several metal salts, including ferrous sulfate, lead acetate, selenium dioxide, and silver nitrate, did not interfere with mercury detection, even when they were present at a concentration of 1 mM and mercuric ion was only 2 ppb. Other metal salts, however, including barium chloride, cadmium chloride, chromic chloride, cupric chloride, gold chloride, nickel chloride, and zinc chloride, did interfere, but usually only at the highest concentration (1 mM), although gold chloride also demonstrated interference at 10 uM. Figure 4 represents results obtained with barium chloride, which is typical of all metal chloride salts tested, except gold chloride, which also demonstrated some interference at a concentration of 10 uM.

ELISA assays have been adapted to a variety of analytical procedures in recent years because of the exquisite specificity of monoclonal antibodies. The assay described here involves recognition of immobilized mercuric ions by a specific monoclonal antibody. The use of an ELISA for detection of metal ions circumvents many problems associated with atomic absorption. For instance, samples can be analyzed in parallel, enabling large numbers of samples to be processed at one time. In addition, quantitative analysis can be performed with a simple spectrophotometer or microtiter plate reader. Automation of the photometer thus makes practical the processing of a large number of samples, allowing for the implementation of large-scale monitoring programs. Since the assay yields a visible color change, semi-quantitative procedures can be developed which require no electronic instrumentation for evaluation. Thus, the assay has the potential for field use. Finally, the procedure requires only 0.1 ml of sample, up to 1000-fold less than required by atomic absorption for maximum sensitivity, and it can, therefore, be used to analyze samples available in volumes insufficient for cold-vapor atomic absorption.

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1. Methods 7470 and 7471. (1986) Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods. 2nd Edition. Office of Solid and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

2. Determination of Mercury by the Cold Vapor Technique. (1985) p. 171-173. Standard Methods for the Examination of Water and Wastewater. Sixteenth Edition. American Public Health Association. Washington, D.C.

Table 1. Statistical analysis of ELISA data from mercury detection in water.

	Mercury concentration (ppb)						
Rep.	0.0	0.2	0.5	1.0	2.0	5.0	10.0
1	0.196[a]	0.302	0.401	0.759	1.123	1.592	2.064
2	0.153	0.272	0.469	0.765	1.180	1.750	2.000
3	0.140	0.272	0.413	0.749	1.338	1.665	1.988
4	0.123	0.278	0.496	0.787	1.323	1.817	2.053
5	0.108	0.237	0.445	0.711	1.195	1.751	1.963
6	0.123	0.303	0.398	0.716	1.093	1.610	2.059
7	0.113	0.280	0.520	0.588	1.044	1.717	1.968
mean	0.137	0.278	0.449	0.725	1.185	1.700	2.014
std. dev.	0.030	0.022	0.048	0.066	0.112	0.082	0.044
coeff. var.	22.277	7.994	10.710	9.118	9.419	4.806	2.187

[a]Values represent the absorbance at 405 nm of ELISA analyses done as described in Materials and Methods. The data shown are the same as used to derive the graph in Figure 1. The correlation coefficient (r) between A_{405} and the log of the mercury concentration between 0.2 and 10 ppb is 0.998.

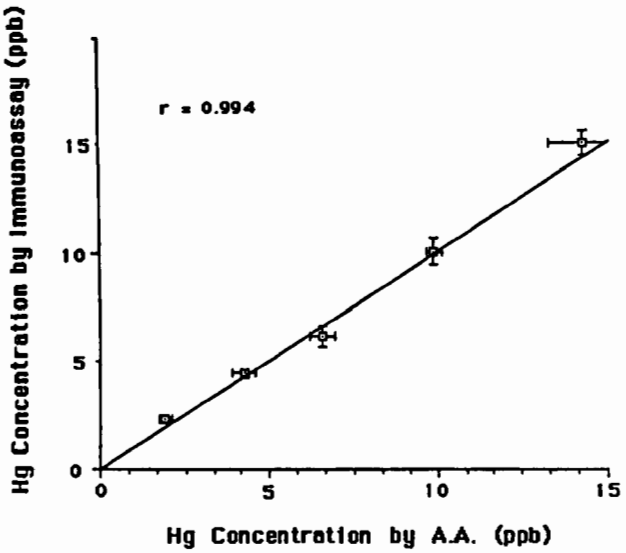

Figure 1. Comparison of mercury detection by ELISA and atomic absorption. An atomic absorption mercury reference standard was diluted to mercury concentrations of 2, 4, 6, 10, and 15 ppb in either 0.1 M HEPES, pH 6.8, for analysis by ELISA or in 10% nitric acid for cold-vapor atomic absorption. Each sample was then analyzed as described in Materials and Methods. The values shown represent the mean and one standard deviation of quadruplicate analyses by immunoassay and triplicate analyses by atomic absorption.

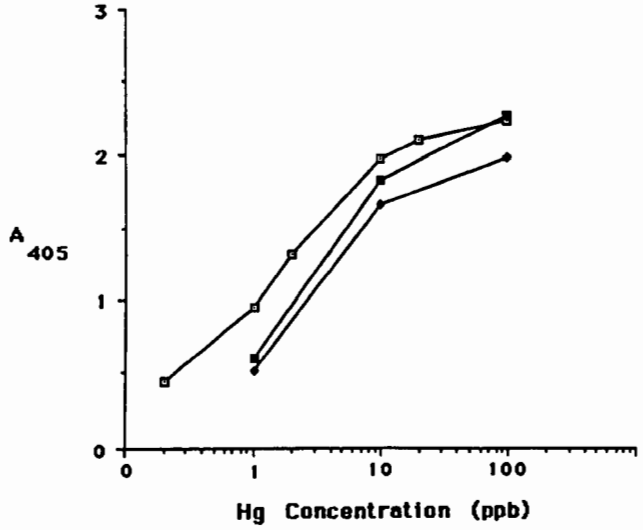

Figure 2. Detection of mercury in National Institute of Standards and Technology Standard Reference Materials. SRM 1641 (■) and SRM 3133 (◆) were diluted in water to mercury concentrations of 1, 10, and 100 ppb, then analyzed by ELISA as described in Materials and Methods. A control consisting of known concentrations of mercury in water was included for comparison (⊞). SRM 1641 consisted of metallic mercury at a concentration of 1.52 ug/ml in 2% nitric acid, and SRM 3133 contained 16.2 mg/ml mercuric nitrate in 10% nitric acid. Each point represents the average absorbance obtained from quadruplicate analyses of each sample.

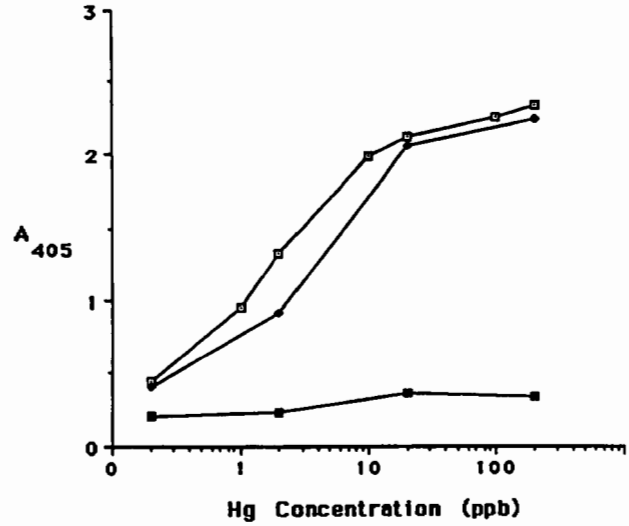

Figure 3. Detection of mercury in the EPA Quality Control sample by ELISA. The QC sample (◆) and $HgCl_2$ (⊡) were diluted in water to mercury concentrations ranging from 0.5-200 ppb, then analyzed by ELISA as described in Materials and Methods. A sample was included that contained the same concentration of all other metals as the QC sample but without mercury (⧈). The absorbance obtained in analysis of both water without added mercury and the EPA sample without mercury was 0.263. Each point represents the average absorbance obtained from quadruplicate analyses of each sample.

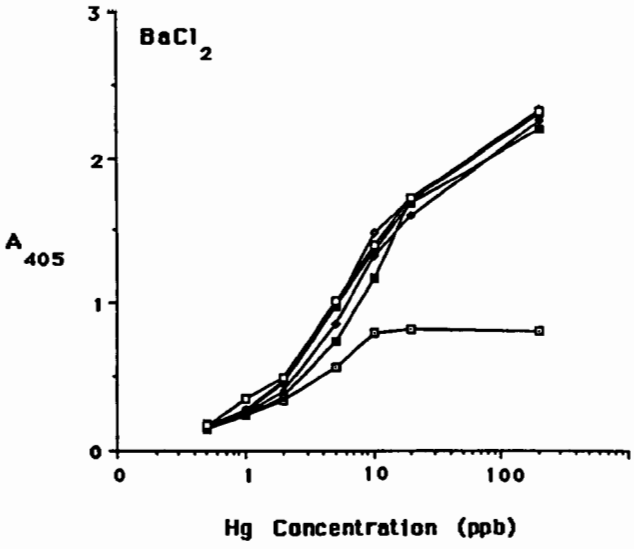

Figure 4. Effect of barium chloride on mercuric ion detection by ELISA. Barium chloride at 0 nM (□), 1 nM (■), 10 nM (◇), 100 nM (⧈), 10 uM (◆), and 1 mM (⊡) concentrations were added to mercuric ion standards to determine their effects on the quantitation of mercury at concentrations ranging from 0.5-200 ppb. For each concentration of metal salt, a control containing the same concentration of metal salt but with no added mercury was included. These values were below 0.2. Each point represents the average absorbance obtained from quadruplicate analyses of each sample.

THE EFFECTS OF PRESERVATIVES ON RECOVERY AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS.

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OBJECTIVE: To evaluate the effects of selected preservatives (stabilizers) on the recovery of volatile organic compounds (VOCs) from contaminated soils. The study provides practical improvement to the current sampling, preservation, and analytical methods for VOC measurement in soil.

APPROACH: Prior to evaluation of preservatives, two concerns should have been addressed.

a) The establishment of an appropriate delay time beyond spiking to achieve equilibrium between spiked VOCs and the soil matrix. Second, allowing for significance losses of spiked VOCs in soil to be able to evaluate the effectiveness of preservatives.

b) To choose an effective method to retard biodegradation of VOCs in soil from time of spiking till completion of analysis.

Upon establishment of the above objectives, we proceeded with evaluation of the following preservatives:

1) The effects of methanol/water mixture (1% and 10%), as the extracting solvent in the purge and trap analysis of VOCs in soil.

2) The effects of two types of anhydrous salts in preservation of VOC contaminated soil at low moisture content.

3) The effects of two types of anhydrous salts in preservation of VOC contaminated soil at high moisture content.

4) The effects of two solid adsorbents in preservation of voc contaminated soil at low moisture content.

EXPERIMENTAL

Soils: Three real soils each with different TOC. The soils were collected from same geological area but different horizons.

VOCs: Chloroform, 1,1,1-Trichloroethane, Trichloroethene, Tetrachloroethane, 1,1,2,2-Tetrachloroethane, Benzene, Ethylbenzene and Toluene at the level of 150 µg/Kg.

Time Delay: The delay time experiments were conducted for 8 days beyond spiking with sampling intervals at 0, 3, and 8 days. Statistical analysis of data revealed after 3 days and from 3 to 8 days storage at 4° C significant losses of VOCs are occurring. The U.S. EPA's contract laboratory program specifies analytical methods which include holding time requirements for all soil and water samples collected through Superfund and RCRA. These programs require analyses of VOCs in soil and water to be completed within 10 days of sample receipt by the laboratory. The result indicated the importance of stabilizers and preservatives for accurate measurement of VOCs in contaminated soil.

Biodegradation: A literature review revealed no preservative have been used to stop biodegradation of VOCs in soils. However, mercuric chloride was used to retard biological activities in soil and water. We used mercuric chloride at a rate of 2.5 mg/ 5.0 g soil.

Aqueous Methanol: Mixture of methanol/water (1% and 10%)were prepared to reduce surface tension of extracting solvent (water) used in purge and trap method of analysis for VOCs. Soils with organic contents higher than 1.5% did show any improvement. Soils with very low organic content, however, resulted in improved recovery.

Anhydrous Salt (Low and High Moist Soil): Anhydrous salts were added to soils at two moisture

levels to pick up water from soil matrices and release the adsorption sites. In addition, the added salts could have produced a saline solution by adding water prior to purge and trap method of analysis. The result indicated no improvement on recovery of VOC's were noticed even at higher moisture content.

Solid Adsorbents: Solid adsorbents (desiccants) were added to different soil types. The statistical analysis of results revealed solid adsorbents are found to be significantly more likely to give higher recoveries of spiked VOCs ($P=0.05$) in 42 out of 60 situation tested. Solid adsorbents always significantly gave better recoveries for soil C (TOC <0.1%). In addition the effects of sample prep using current EPA methods and utilization of solid adsorbents were evaluated.

Detection Limits: The detection limits of an SRI gas chromatograph in series with a Tekmar LSC-2000 sample concentrator and a Dynatech PTA-30S autosampler were evaluated using water and soil control samples.

CONCLUSIONS

Further work is needed to develop more preservatives especially for VOCs and field test current findings of this study.

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