PROCEEDINGS

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FIELD SCREENING - "QUICK & DIRTY" IS RAPIDLY EARNING THE REPUTATION OF "EFFICIENT & COST EFFECTIVE"

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ABSTRACT

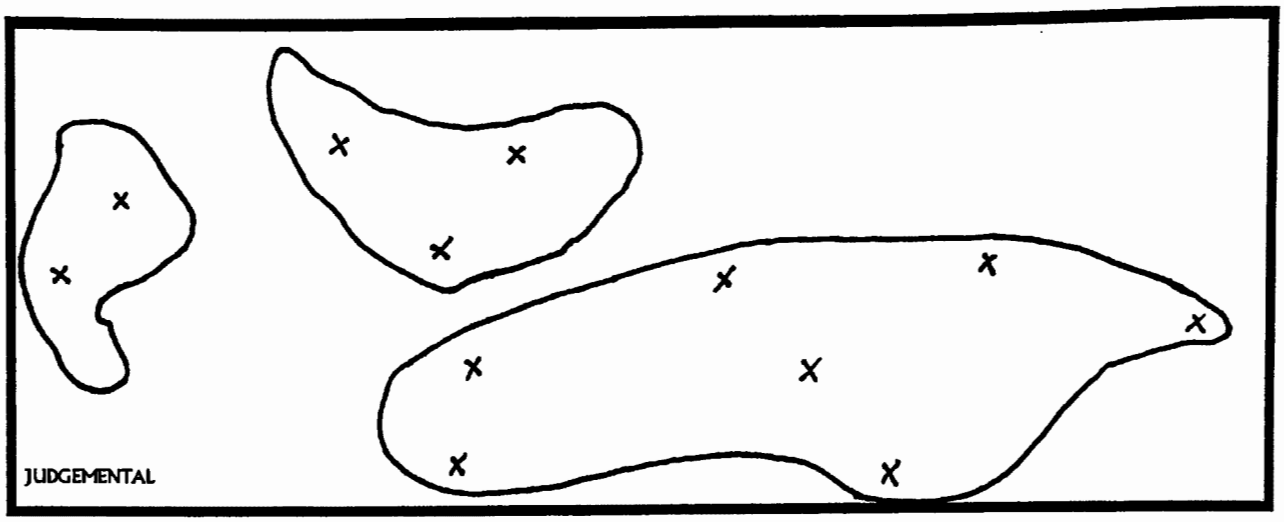
As the numbers of environmental remediations and projects continue to increase, so do the costs associated with them. With this "trend" in the environmental field, many environmental scientists, both in the public and private sector, are realizing the financial and time-efficient benefits of field screening. Existing and emerging field screening technologies that are specifically geared toward "real-time" data and information can provide a means of reducing time and resources typically inherent in most environmental projects. Acceptability and practice of utilizing field screening techniques, as this presentation/paper will demonstrate, is the emerging trend which will be setting the pace for environmental investigations and remediations both today and in the future.

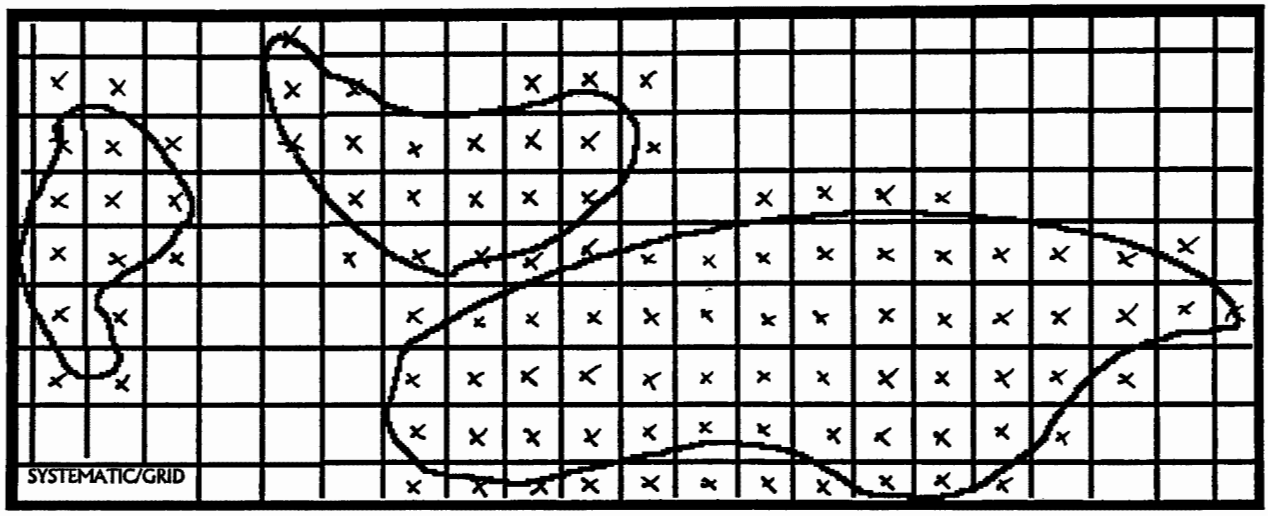
INTRODUCTION

Representative sample collection is a primary function of any successful environmental project, be it site assesment or audit. The ability to achieve this in an inexpensive and time-efficient manner makes this a preferred method for site analysis. Field screening techniques assist in facilitating this quick and cost-effective analysis. As the market of field screening and on-site analysis products increases, so increases the ability to conduct a sound, thorough assesment of evironmentally contaminated sites. This is especially significant where the need of Phase II site-assesments for real estate transactions is concern. Field screening provides a means of data accumulation that can be achieved without the cost and liability that permanent features, such as monitoring wells, tend to have associated with them.

The typical sequence of activities for site-assesment includes determination that a contamination problem does indeed exist, followed by the establishment of objectives for remediation of those contaminants. It is during the

FIGURE 1
SAMPLE COLLECTION APPROACHES





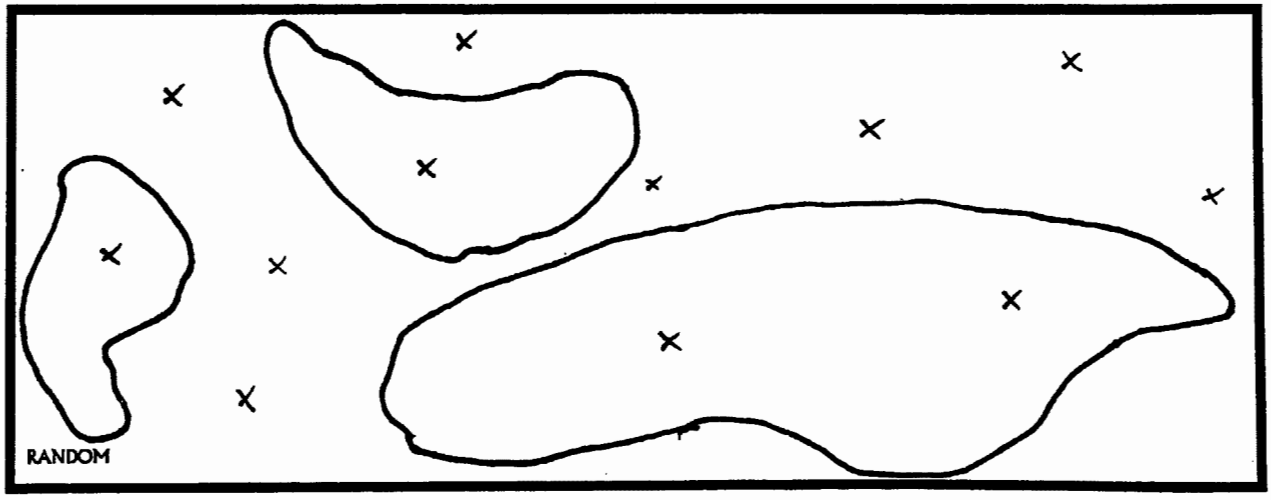
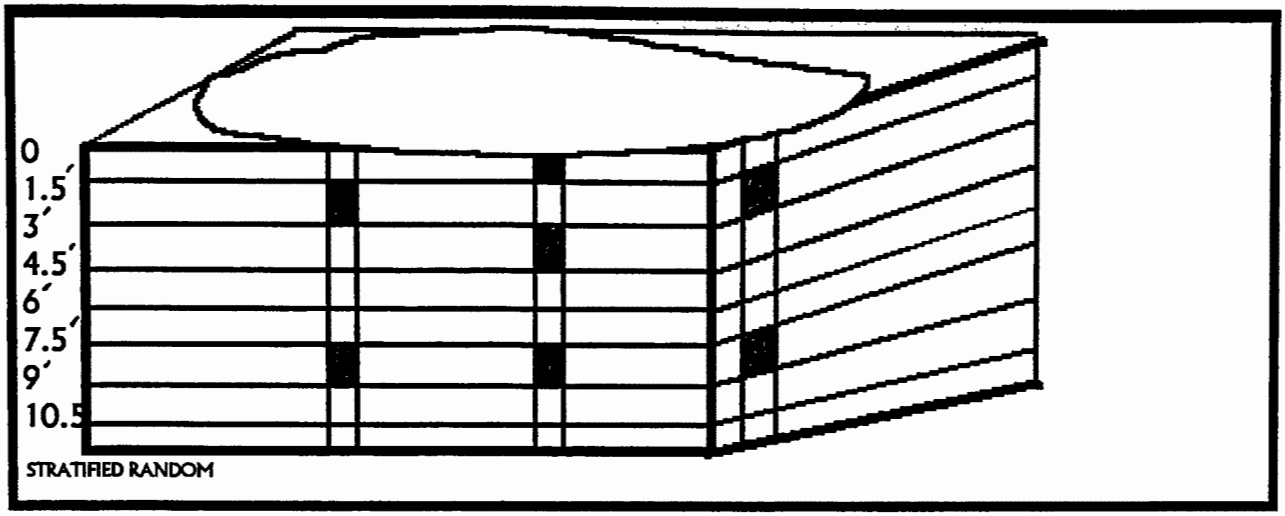
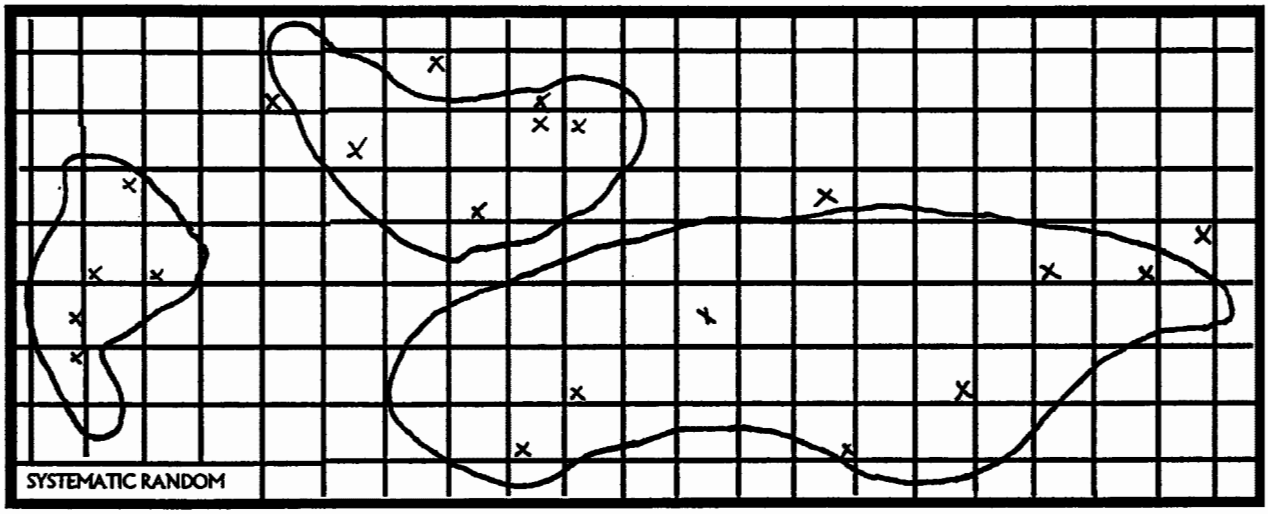


FIGURE 2
SAMPLE COLLECTION APPROACHES - COMBINATIONS





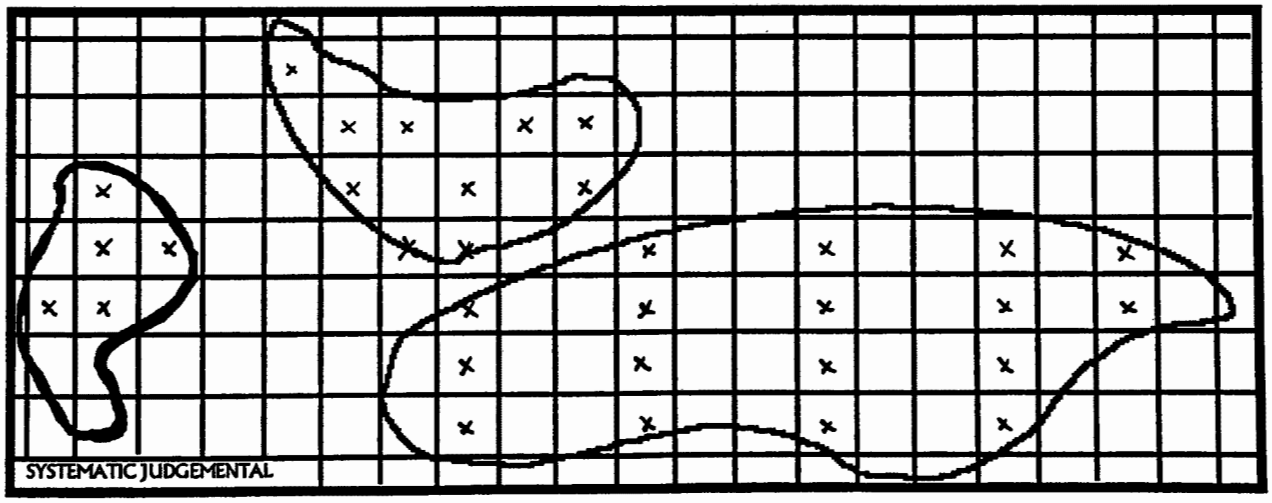
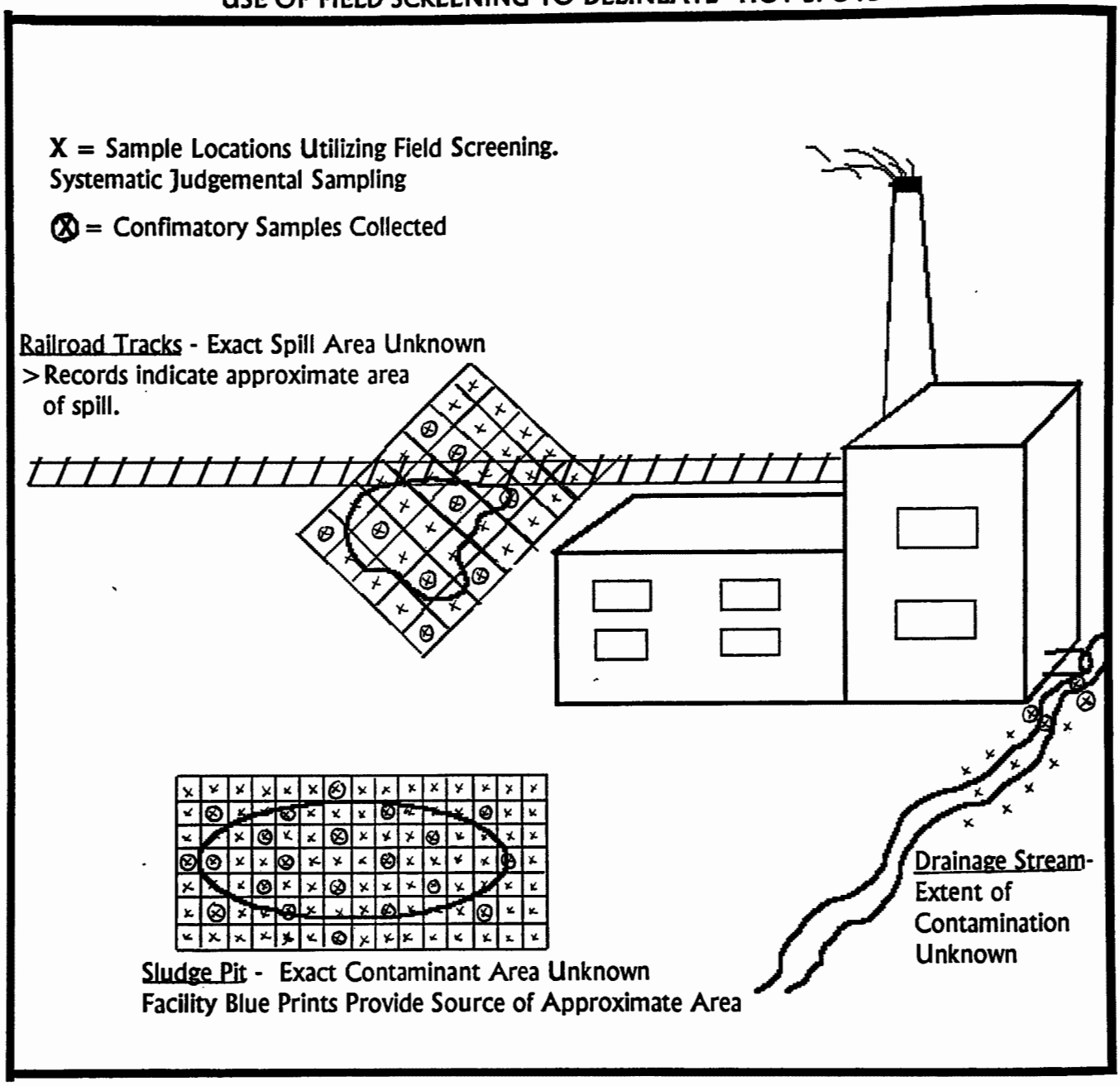


FIGURE 3

HYPOTHETICAL SITE
USE OF FIELD SCREENING TO DELINEATE "HOT SPOTS"



The amount of background information available regarding possible areas of contamination will assist in deciding which type of sampling approach will accurately assess the site. In this hypothetical situation, a moderate amount of information is known regarding location of contaminated areas. Systematic judgemental sampling was utilized and field screening was proven advantageous as the areas of contamination were more acutely defined.

TABLE 1

SITE INVESTIGATION TIME TRACKING OUTLINE

(estimated per project)

	TASK:	TIME: (approx)
1.	Background information search; Tasking	65
2.	Site Access; Reference Material	60
3.	Site Reconnaissance	20
4.	Sample Projections; Coordinate with Laboratory Sample Coordinator	16
5.	Bottle Prep; Equipment /Vehicle Prep.	40
6.	Work Plan/Safety Plan Preparation	40
7.	Field Work; Field Tasks	150
8.	Equipment Re-stock/Cleaning/Decon General Equipment Maintenance	40
	TOTAL TIME:	431 HOURS

**NOTE: These times do not include values related to laboratory turn-around times and/or analysis times.

establishment of the project objectives that consideration for field screening comes into discussion. The statistical design of sampling should support the established project objectives. This is especially relevant for the data quality objective (DQO) process. It is these statistics that verify the samples as being representative of the matrix being considered. Common sense, when evaluating the statistical considerations, will identify the value and pertinence of field screening. The ability to field screen, as opposed to collecting multiple samples for laboratory analysis, will significantly reduce project expenditures. Whereas the actual extent of contamination on-site might need to be determined, field screening provides a resource for eliminating the need for total laboratory analysis of all the sample points indicated/determined during the statistical evaluation. Confirmatory sampling of the field screened sample points should be conducted so as to reduce the probability of false-negatives. This confirmatory sampling assists in supporting the specific DQO process established for the project.

The sampling approach that is determined to be adequate for contaminant delineation is typically one of three main processes. *Judgemental*, *systematic*, and *random* are the three primary sample collection approaches (figure 1 demonstrates each of these approaches). There are, of course, combinations of these three approaches (figure 2) which will be specific to the particular project and established DQO's. Field screening can assist project coordinators in reducing the need for random sampling by delineating the "hot-spots" of a particular site (see figure 3 for a hypothetical site). Utilization of field screening will result in a scaled-down systematic sampling approach or judgemental sampling. All of this "scaling-down" takes place within a hastened time frame due to the real-time data generated from the field screening activities.

On average, an entire sampling episode can take upwards of 360(est.) staff hours (1)(table 1). This primarily includes site access, reconnaissance, equipment preparation, sample collection, sample packaging and shipping, and equipment decon.. The inevitable wait for laboratory analysis and subsequent return of data is not a part of this estimate. Depending on the type of analysis required, laboratory analysis and data return/review can take several more weeks. CLP turn-around, for example, for sample analysis can take an estimated 50 to 60 days before the data is returned for evaluation. Utilizing field screening techniques can provide data responses within minutes and/or hours after sample collection. Clearly, it is advantageous to utilize field

screening as much as possible. Depending on the particular site situation, field screening may also provide a quick answer as to whether possible immediate control measures are needed to avert further contamination and possible health hazards to the public.

The costs associated with field screening are markedly less than those incurred through laboratory analysis. Generically, the cost of a particular piece of equipment to be used for field screening will be apparent in the initial purchase of the particular piece of equipment. A portable volatile analyzer, such as a Micro-Tip, will have an initial purchase price and subsequent servicing fees, but can be utilized for many projects and many years. Laboratory analyses can incur costs per parameter and on a one-time basis. As each laboratory facility will have its own schedule for fees, it is therefore difficult to accurately assess the costs for parameter analysis. Table 2 is an example of cost comparisons between various field screening techniques/equipment and laboratory analysis. It is important to remember that the one-time up-front cost of purchasing the equipment is something that can be recovered over many years, and that particular laboratory analysis fee is per sampling episode and per project.

What follows is a brief snyopsis, by matrix, of some of the available field screening kits/equipment and the relative costs. The costs are estimated and it is not the intention of this paper to endorse one particular product over another. Rather, this presentation is designed to provide the reader with a basis for realizing some of the products that are available for field screening.

WATER (INCLUDING GROUNDWATER)

Field Atomic Absorption (in field laboratory) - Metals
Detection Limits; 0.1 ug/l (most metals)
Analysis Time; 2 min./sample (after sample prep)
Cost; $20 - 30,000 initial cost (est.)
Comment; Easy set-up in stationary or mobile field lab. Can be run off a portable generator. A specific cathode lamp is required for each element being analyzed.

WATER CONTINUED,...

Immunoassay - Organic Analysis
Detection Limits; 50ppb to 5,000ppm (varies)
Analysis Time; 4 to 5 hrs./multiple plate (several samples)
Cost; @$55/sample or @$22,000 for the system
Comment; This is still a developing method, but gaining respectability. Advantages include rapid, accurate results, minimal sample prep., non-hazardous reagents, limited sample volume needed. Limitations include crossreactivity and possible concentration equivalents. (2)

Immunoassay - PCB Analysis
Detection Limits; $\geq$ 5ppm to ppb (varies depending on kit)
Analysis Time; @30-45 minutes (will vary)
Cost; @$100-200/sample
Comment; Easy to analyze, rapid, accurate results. Multiple samples per kit. (3)

Xray Fluorescence (XRF) - Metals
Detection Limits; 100 - 600 ug/l (varies)
Analysis Time; @5-10 minutes/sample (10-30 min. prep. time)
Cost; $80,000 unit - @$50-80/sample
Comment; Limited sample volume needed (@40ml), rapid screening, simultaneous detection (multiple elements/sample).

Headspace Analysis - Organics
GC/MS system, OVA (FID), HNU (PID)
Detection Limits; Varies depending on the instrumentation utilized, but usually can detect in the ug/l range.
Analysis Time; Multiple samples per hour.

Note: Other standard anayses include those for pH, disolved oxygen, conductivity, Oxidation reduction potential (Eh), and temperature. These parameters can be part of one whole unit, such as submersible units, or individual tresting instrumentation. All offer a variety of options depending on the product. Analysis time is usually minutes. Cost will vary depending on the product and its capabilities.

SOIL

Most of the field testing kits and products that are available for water analyses are also availble for soil analysis. Costs, analysis time, and benefits will be directily similar to those listed for the water analyses.

Penetrometer Testing
Analysis; Soil electrical conductivity measurements
Piezometric measurements
Soil temperature
Penetrometer testing for groundwater, soil gas, soil, and ability to install small diameter piezometers.
Costs; Will vary depending on the usage and time for set-up.
Comments; Estimated that several hundered goetechnical soundings have been performed in one day. (4)

Soil Gas
Passive samplers, OVA, HNU, etc.
Analysis Time; Will vary depending on the bore-hole time, sample collection, and analysis - typically 90-120 minutes/sample.
Costs; Will vary depending the product used.
Detection Limits; Suited for low-concentration contaminants.
Comments; Samples are a result of hand-operated augers, hand-driven devices, hydraulically driven devices, and mobile drilling rigs. Can provide infromation on areas of contamination within one day. This will depend on the number of cores being collected and the ability to mobilze at various sample points. Site specific conditions (i.e. depth to groudwater, sub-surface geology) will guide the specific methods to be used during the project. Depths of sample will vary depending on the particular equipment used. For example, hand augering will generally achieve depths of 10 to 20 feet, while hydraulically driven devices will achieve depths of 50 feet or more.

Fiber Optic Sensors - Method under development
Analysis; Able to detect contaminants to ug/l in soil, water, and air.
Permits real-time analysis which is especially useful in difficult or hazardous situations, including spill clean-up monitoring.
Costs; It has been indicated that this will have low developmental costs, but high operational costs (equipment costs included)
Comment; Involves use of optical fibers attached to various analytical instrumentation. Can be effect to large distances, but requires a dedicated fiber for each pollutant to be monitored. Fiber bundles are being developed to allow for analysis of several pollutants at once.

SUMMARY

As this presentation has described, there are many benefits to be acquired through the use of field screening techniques. Analysis time and costs will vary depending on the product utilized, but offer the advantage of obtaining real-time data/information regarding the contaminants and their locations at a site. By utilizing field screening techniques, project organizers/managers will be able to obtain knowledge about the contaminants present on-site as well as delineate the major areas ("hot-spots") of contamination. Analytical costs and staff hours can be significantly reduced thus providing an economic savings to the overall project.

This presentation has provided a brief overview of the economic and time-effective benefits of field screenig and offered insight into the variety of methods available to acquire real-time data and information regarding site contaminants. As the number of available products increases, so does the acceptance and utilization of these field screening methods. As this presentation has demonstrated, field screenig - "quick and dirty" is rapidly earning the reputation of "efficient and cost effective".

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2

COST EFFECTIVE MANAGEMENT OF LARGE DRUM JOBS UTILIZING HAZSCAN ANALYSES AND U. S. EPA's NEW DRUMTRAK SOFTWARE

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ABSTRACT

The U. S. EPA Superfund Program is constantly addressing sites with numerous drums, tanks and other containerized wastes. The magnitude of these sites can range from a few drums to tens of thousands of drums; however, regardless of size, keeping track of the sampling, analyses and disposal data can often require a significant amount of resources and time. Hazscan analyses complemented with the U. S. EPA's new DrumTrak computer software can save time, money and resources when applied to these particular projects.

The analytical cost for tens of thousands of unknown drums can result in millions of dollars, not to mention the time involved with obtaining the results. Alternatives to this might include analyzing the material for a few chosen parameters or fully analyzing only a small percentage of the containers. This also can prove to be costly in both time and overall project costs, as well as developing a possible safety hazard due to incomplete analyses. An alternative to this is a succession of screening tests which identify the waste chemical characteristics in a relatively short period of time.

This series of screening tests are typically called "Hazscan" or Hazcat" analyses. These tests include water reactivity, air reactivity, water solubility, organic solubility, pH, cyanide, sulfide, oxidizer, peroxide, flammability, chloride and a screen for polychlorinated biphenyls (PCB's). Based on the Hazscan testing, the drums can then be composited for further analytical and off-site shipment in truckload volumes.

Hazscan testing can easily be performed either on-site in a mobile laboratory or off-site at a stationary laboratory. Regardless of the location chosen to perform the analyses, a tremendous amount of data will be generated as a result of the sampling and characterization analyses. This information can be placed into a database; however, most database applications are limited to sorting the data and generating reports.

Kiber Environmental Services, Inc. has recently completed assisting the U. S. EPA's Emergency Response Team in developing a computer program designed to aid in the management of data on drum sites. The program allows the user to quickly manipulate and generate reports based on the sampling and analytical data generated from **each** container.

These reports can be used to aid in the planning and development of a disposal management plan, classify the containerized wastes based on the results of the Hazscan testing and provide a tracking system for each container on site from the initial sample point to off site disposal. The Program has an additional advantage in that it allows a pen-based computer to be used to enter the data as samples are being collected in the field.

This approach provides an alternative to the extensive analytical testing and overwhelming amount of data utilized today and can be easily applied to any project containing large quantities of unknown wastes.

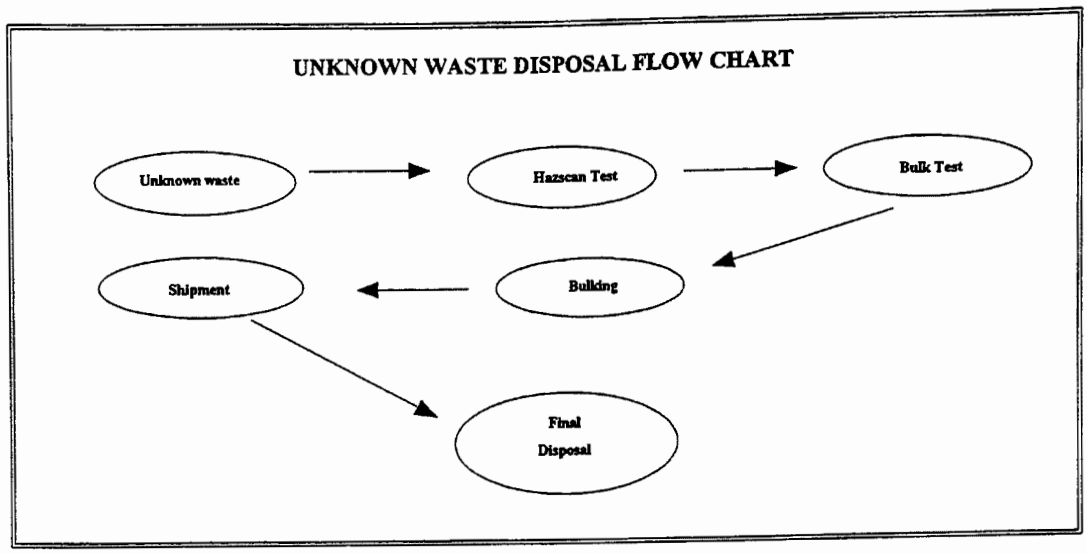
INTRODUCTION

Abandoned drum sites often pose serious challenges to environmental cleanup organizations from both the public and private sector. These sites often have hundreds or even thousands of containers of unknown waste which have the potential to be reactive, shock-sensitive or even explosive. The drums, tanks or other waste containers are typically scattered in an unorganized fashion throughout the site and are for the most part in various stages of deterioration. Clues to what may be in the tanks and drums can be gained from the past history of the location or facility; however, often times, past histories can be limited or deceiving.

Options for removal of the waste material are non-existent until the waste can be identified as to its chemical contents. Options for identification of the waste material as well as options for disposal are numerous and depending on the choice, some of these options can be quite costly. Sampling only a small number of the drums and making the assumption the remaining material is similar to the ones sampled could result not only in sending material to a facility which is out of specification, but also expose site personnel to a potentially hazardous situation resulting from blending unknown and or incompatible materials. A typical approach to the removal would be to identify and characterize, blend similar materials and dispose of each segregated wastestream. This approach is detailed below.

DETAILED APPROACH

An approach taken for removal of waste at any unknown drum site should be organized and planned properly. Steps should be taken to assure the end result of removal and disposal of the waste is always held as the overall objective of the project. Removal and disposal of the waste is typically more cost effective by shipping the material in bulk quantities. In order to accomplish this, drums which exhibit similar chemical and physical characteristics can be blended together. Once blended, the materials can be shipped off-site. This process is outlined below:



In order to blend the materials the waste should be screened individually for characteristics which may cause the material to be hazardous as well as reactive when mixed with other materials. This screening process can serve as the first step in the identification process of the waste. This process need not be detailed, but should include screening tests to access the chemical and physical characteristics of the wastes. The process should also not be time consuming due to the potential number of samples that will have to be processed (hundreds or even thousands).

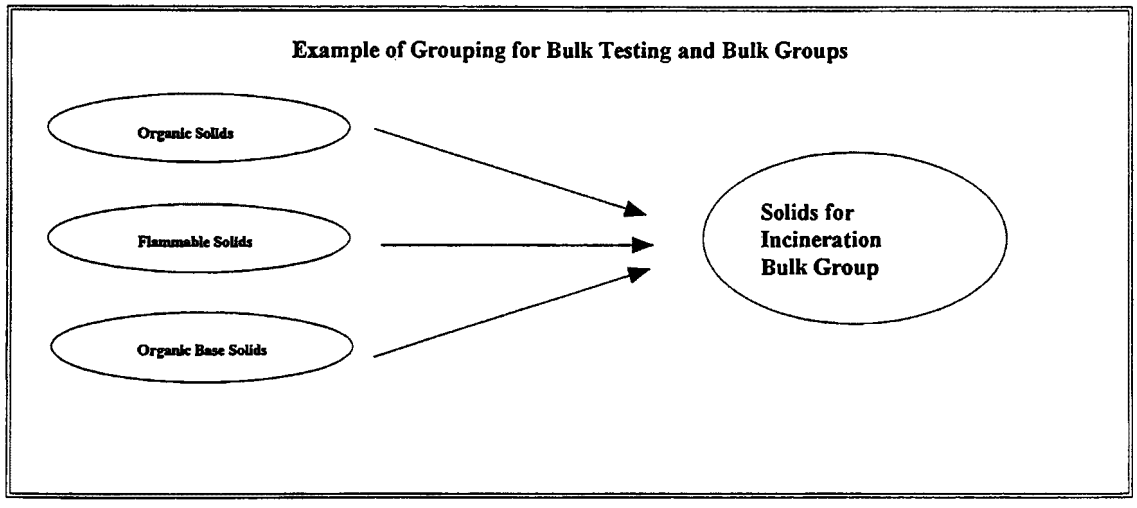
The regime of "Hazscan" or "Hazcat" screening tests which have been successfully utilized on large drum projects both public and private sector includes thirteen separate screening tests which can identify potentially reactive material as well as a majority of the Resource Conservation and Recovery Act (RCRA) characteristics. These tests include air and water reactivity, radioactivity, water and organic solubility, pH, cyanide, sulfide, oxidizer, peroxide, flammability, chloride and PCB's. The tests, with the exception of the flashpoint and PCB screen are all wet chemistry methods that employ a series of color and/or phase changes that indicate a positive test result. The flammability screen is performed utilizing a setaflash closed cup tester and the PCB screen is performed utilizing a gas chromatograph.

Results gained from these tests can aid a chemist in classifying the material into hazard characterizations such as water soluble acid oxidizing liquids, water soluble cyanide liquids and organic soluble flammable solids. Positive test results from each of the screening tests are used to flag to the individual container as to its contents. For example, a sample with a positive test result for water solubility, oxidizer and a pH of 2 would indicate a water soluble, acid oxidizing material. This method of classification would continue until all drums or waste materials were placed into a hazard classification. These classifications can then be utilized

to "group" the drums into chemically compatible bulking groups for additional testing and analyses.

The next step in the removal process is the blending or "bulk" testing. The purpose of bulk testing is to attempt to duplicate the on-site blending of chemically compatible wastes. On-site blending of the material is an alternative to shipping each container separately for disposal. This "bulking" of chemically compatible materials prior to shipment will take advantage of the more cost effective bulk disposal prices rather than the more costly individual shipment and disposal costs. The formation of Bulk Groups from individual hazard characterizations minimize the number of disposal wastestreams that have to be dealt with. Bulk Groups are typically chosen based on the disposal alternative available for the waste material on-site. Bulking Groups typically are chosen during the development of the site waste disposal plan. All waste materials that are proposed to be disposed of utilizing the same alternatives such as wastewater treatment, fuels blending or landfilling, can be placed in the respective Bulking Groups.

The "bench-scale" blending or bulk test will monitor the procedure for possible reactions that could occur from combining high concentration wastes. By combining proportional volumes of waste from chemically and physically similar hazard characterizations the blending can be monitored for temperature increase, polymerization and gaseous emissions that may occur. A bulk test should be completed for each "Bulking Group" that is proposed. An example of such a grouping is Flammable Solids. This bulk group would include all solids that were found to be flammable or combustible and do not exhibit any other chemical characteristics that would disallow the material to be incinerated. A pictorial example of this is presented below:



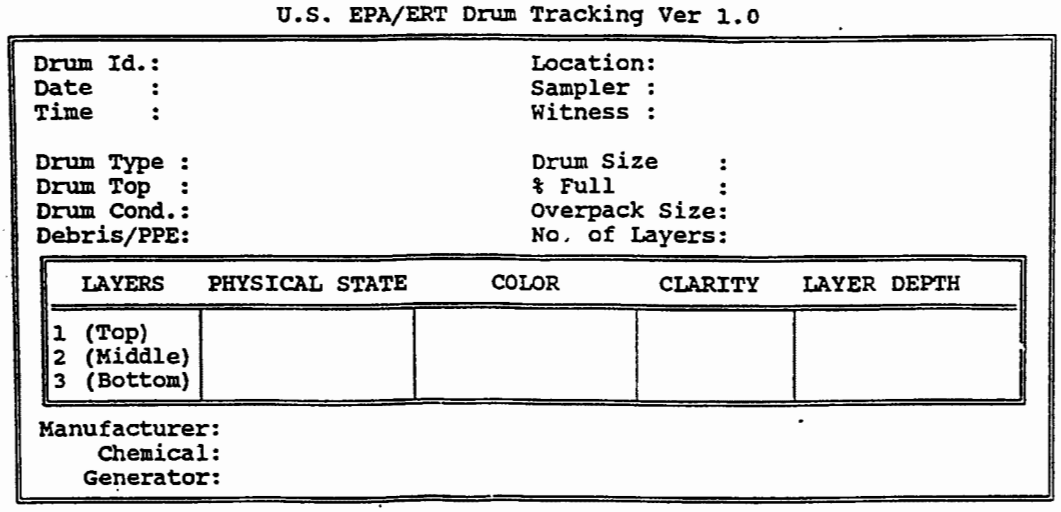
After the bulking test has been completed, further, more extensive testing is usually completed to further identify the chemical composition of the waste. This includes performing analyses such as volatiles, semivolatiles, metals and pesticides. These analyses will help complete the disposal facility requirements such as profile sheets that are required by various disposal facilities for approval of waste into the respective facility.

Characterization and bulk testing can be conducted at a project site utilizing an on-site mobile laboratory or the samples can be transferred to a fixed based laboratory for the analyses. There are several advantages to an on-site laboratory, however the biggest advantage is easy access for interaction between the site supervisory personnel and the chemists in the laboratory. The on-site laboratory is dedicated to the project and as a result, turn-around-times are quicker and communications become easier and clearer. The project is also not delayed by the downtime involved with transferring the samples to the fixed based lab as well as the analyses. All of these items contribute in the overall cost savings for the project.

While this approach of testing, characterization and bulking is very cost effective and timely, the organization and cross-checking involved with this process is sometimes very detailed. Attempts to place this information into a standard computer database program can be somewhat limited to allowing the user to generate a hard copy of the data. In order to facilitate the entire process, the U. S. EPA has recently developed in conjunction with Kiber Environmental Services, Inc. a computer software program that allows the user to track these unknown waste containers from initial inventory and sampling through the characterization and ultimate off-site disposal.

This computer software program is actually a compilation of four different databases which track physical container data and Hazscan or Hazcating results as well as generate hazard Characterizations and Bulking Groups. Each of these four databases are programmed to function as an entire program that allows the user to manipulate and generate a multitude of individual reports. The DrumTrack Program (Program) was designed to be utilized on large drum sites that are following the process described previously. Each phase of this process, including Inventory and Sampling, Hazscan Testing, Hazard Characterization, Bulk Group Selection, Disposal and Shipment of waste off site, can be tracked.

On most drum sites, during the sampling and inventory process various information is recorded on a "drum log" which aids the tracking of the actual container as well as the waste inside. This can be transferred to the first screen in the program in the format presented below:



The Program continues by allowing entry of all the Hazscan test results. Once the test results have been recorded, the Program will automatically classify each container and place each one into a Hazard Characterization category. The user can then generate proposed Bulk Groups for the site and assign each Hazard Characterization category to its respective Bulk Group. Finally, the program allows for tracking disposal of each container by the manifest number.

The true benefits of this Program can be appreciated once all information has been entered into the database and the full application of the Program can begin. Over twenty-five different pre-set reports can be generated to aid the user and other on-site personnel in dealing with the waste. These reports include the following:

Individual Drum Log Sheet With Data
Numerically Arranged Hazscan Test Results
Drum Marking by Drum ID Number
Drums by Location
Drums by Manifest
Drums Missing Hazscan Results
Inventory of Empty Drums
Inventory of Drums Containing Personnel Protective Equipment
Drums By Hazard Characterization
Drums By Bulk Group
Summary of Hazard Characterization
Summary of Bulk Groups
Bulk Groups by Target Volume (listing of drums up to a user chosen target volume)
Disposed Drums by Bulk Group

Quite simply what this Program does for its user is automate all of the tasks which were once required to be completed by hand. These include sorting current paperwork to find containers that did not get analyzed, categorize and generally interpret hazscan results, assign drums to Bulk Groups, generate a list of drums for a tankerload of bulk waste and finally print a listing of all drums assigned to a particular manifest.

This Program becomes especially important to any transportation and disposal coordinators involved with the project, by having all of the containerized waste information regarding the physical and chemical characteristics available at "the touch of a key". Transportation and disposal coordinators can minimize the time required to coordinate and arrange disposal for the waste on-site by utilizing the Program to generate information about the classification and bulking of the waste.

The overall benefit of the Program is that it reduces the time and personnel commitments which are normally required to process and track the vast amount of information that is generated during the project and eventually used to dispose of the material. By utilizing the Program, in conjunction with an on-site laboratory, two full time personnel can easily process and track approximately 100 to 200 samples in a twelve hour work shift.

An additional time saving application of the program is the field data entry system that is computer pen-based. This "Drum Pen" Program allows the user to take a pen-based computer into the field and enter the data as the samples are being collected. This eliminates the need to generate a hard copy of the drum information while sampling and then enter this information later in the database. The elimination of this "double-handling" of the data can save a considerable amount of time in both sampling and data entry. The program can even be used to later generate hard copies of all drum information formatted in a "drum log" sheet.

SUMMARY

Application of the Hazscan or Hazcat testing regime along with U. S. EPA new DrumTrak Software Program can save considerable time, money, and resources on any project requiring the management of numerous unknown containers. This approach provides an alternative to the extensive analytical testing and overwhelming amount of paperwork utilized today and can be easily applied to any large-scale project containing large quantities of unknown wastes.

ON-SITE LABORATORY SUPPORT OF OAK RIDGE NATIONAL LABORATORY ENVIRONMENTAL RESTORATION FIELD ACTIVITIES

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ABSTRACT

A remedial investigation/feasibility study has been undertaken at Oak Ridge National Laboratory (ORNL). Bechtel National, Inc. and partners CH2M Hill, Ogden Environmental and Energy Services, and PEER Consultants are contracted to Lockheed Martin Energy Systems, performing this work for ORNL's Environmental Restoration (ER) Program. An on-site Close Support Laboratory (CSL) established at the ER Field Operations Facility has evolved into a laboratory where quality analytical screening results can be provided rapidly (e.g., within 24 hours of sampling). CSL capabilities include three basic areas: radiochemistry, chromatography, and wet chemistry. Besides environmental samples, the CSL routinely screens health and safety and waste management samples. The cost savings of the CSL are both direct and indirect. Direct cost savings are estimated based on comparable off-site quick-turnaround analytical costs. Indirect cost savings are estimated based on: reduction of costs and liability associated with shipping for off-site analyses, preparation for sampling, assistance to Health & Safety staff, use of CSL results to focus further sampling efforts, and sampling crew downtime. Lessons learned are discussed.

INTRODUCTION

A remedial investigation/feasibility study (RI/FS) began at Oak Ridge National Laboratory (ORNL) in 1987 for ORNL's Environmental Restoration (ER) Program. Bechtel National, Inc. and partners CH2M Hill, Ogden Environmental and Energy Services, and PEER Consultants are the RI/FS subcontract team. In 1989 the project established the Close Support Laboratory (CSL) to provide rapid radiological ($\alpha/\beta/\gamma$) and volatile organics screens on samples to determine DOT classifications before shipment to the off-site CLP laboratory. The advent of the *Observational Approach* and *SAFER* led the RI/FS team to shift the main use of the CSL from preshipment screening to screening to help in technical decisions (e.g., delineating the extent of contamination). Basic wet chemistry techniques were added to assist in rapid and cost-effective sample characterization. CSL scope is now changing further to support other groups performing environmental restoration activities for ORNL ER.

TECHNICAL SUPPORT

The CSL provides the quality, quick-turnaround data needed to support results-based field decision making. Also, CSL staff assist RI/FS project geologists with planning,

interpretation, and application of sampling and analysis plans and associated support documents. The staff currently support ER field efforts with analytical planning, cost estimating, and data interpretation.

We interact with various ER project staff to provide pre- and post-field-support activities including preparation of sampling kits, sample screening for DOT transportation/packaging and radioactivity checks, analytical planning and coordination with off-site confirmatory-level laboratories, receiving excess sample from off-site labs, and archiving or disposing of sample remnants (thus closing the chain-of-custody).

*Im*mobile laboratory trailers at the ORNL ER Field Operations Facility (FOF) house the CSL. This location is convenient for sampling teams to pick up sample kits or to deliver samples since the FOF is the starting and stopping point for most ER field activities. We routinely screen environmental, health and safety, low-level decontamination and decommissioning and waste management samples. Our sample screening results are used by off-site labs to guard against instrument contamination and detector saturation.

ANALYTICAL TECHNIQUES

The analytical scope of the CSL covers basic radiological and volatile organics screening, and basic wet chemistry. Analyses can be performed rapidly, and results from complementary techniques are reviewed to provide a more complete technical understanding. Method detection limits are comparable to off-site confirmatory labs. Minimum detectable activity values for radiological samples may be adjusted by changing sample sizes and count times to meet the customer's needs. Radiochemical analyses include gamma spectroscopy, tritium and carbon-14 screens using liquid scintillation analysis, and gross alpha and beta counting. Cerenkov counting and crown-ether-based separation are the two rapid methods used for determination of radiostrontium in water samples.

Gamma spectroscopy is performed via an intrinsic germanium detector with a computer-based multichannel analyzer. Due to the lack of an autosampler and the long count times often required, the gamma detector system is a bottleneck in sample throughput. A second detector will soon be on-line to increase our capacity.

Liquid scintillation is used to perform ^{3}H and screening ^{14}C analyses. Samples are not distilled; instead, soils are DI water extracted (1:1 w/v) and instrumentation software corrects for quenching effects in all samples. Carbon-14 can be excluded based on negative screening results but cannot be confirmed based on positive results (other weak or quenched β particles may cause 'false' positives).

Gross α and β are measured using proportional counters. Low-activity samples are analyzed on a low-background gas-flow proportional counter. Higher-activity samples

are analyzed on scalers because higher-activity samples might contaminate the low - background counter, and the ZnS solid scintillator probe is immune to the β->α cross-talk observed in the α signal from the gas-flow proportional counter.

The CSL analyzes ^{90}Sr in water samples using one of two methods. Strontium may be separated from unfiltered or filtered samples using SrSpec columns (EiChrom), then immediately counted for ^{90}Sr as gross β before substantial ^{90}Y ingrowth. Alternatively, after a two-week ^{90}Y ingrowth, ^{90}Sr Cerenkov counting may be performed on filtered samples using the liquid scintillation counter (and *no* scintillation cocktail). Strontium-90 Cerenkov counting also requires gamma spectroscopy to provide $^{137}Cs/^{60}Co$ correction to the Cerenkov-determined activity.

Volatile organics screens are performed by gas chromatography (GC) using photoionization (10.2 eV) and Hall electrolytic conductivity detectors and a CSL-specific method based on EPA 601 and 602. A sixteen-port purge-and-trap autosampler introduces samples onto the GC column. The primary volatile organic contaminants of concern are fuel-based aromatics and solvent-based chlorinated hydrocarbons.

Basic wet chemistry for environmental waters includes alkalinity, dissolved and suspended solids, ion chromatography (IC), and, (for various matrices) pH and resistivity. IC is used to analyze both cations and anions following a CSL-specific method based on EPA 300. Together, IC and alkalinity provide an ionic profile of water samples.

QUALITY ASSURANCE

The mission of the CSL is to provide rapid screening (EPA level II) for the ORNL ER program. The lab delivers these results, using lab-specific methods, without time-consuming deliverable requirements. Controlled CSL procedures and the laboratory quality assurance plan document quality requirements for each analysis and general laboratory practices. QA staff from Bechtel, ORNL Oak Ridge Reservation, and DOE Oak Ridge routinely audit the lab's procedural conformance and good lab management practices. The CSL has used commercially prepared performance evaluation (PE) samples to fine tune method accuracy. The radiological PE samples were obtained from Analytics and the chemical from Environmental Resource Associates. Recently, we have begun to take part in EPA-sponsored radiological (EMSL-LV) and chemical water pollutant (EMSL-Cinci) PE studies. Participation in these studies will verify our accuracy and interlaboratory comparability.

COST EFFECTIVENESS/SAVINGS

The CSL is saving dollars both directly and indirectly. Direct cost savings are based on comparable off-site quick-turnaround analytical costs; premium charges for rapid response from off-site laboratories make the CSL especially cost-effective. The RI/FS team has documented CSL savings estimated to be greater than $1 million for each of the last two fiscal years.

Indirect savings are difficult to quantify. They are based on reduction of costs and liability associated with shipping samples off-site for analysis, preparing for sampling and sample shipping, assisting Health and Safety (H&S) staff, and sampling crew downtime. CSL data provides for proper DOT classification of environmental samples. Sample container procurement, sample kit preparation, and sample chain of custody are all centralized through the CSL for most samples analyzed by the CSL. CSL staff also generally prepares and packages samples for shipment to off-site labs for further analysis. H&S staff uses the CSL to analyze monitoring samples to minimize personnel risk, and field sampling crews are more productive because of the rapid turnaround of data from H&S and sampling based on results of previous sampling. The RI/FS team has made extensive use of CSL data in the Remedial Investigation for Waste Area Group 5 at ORNL and other site characterization projects.

LESSONS LEARNED

Several lessons learned at the CSL may apply to similar screening laboratories.

- Participate in the initial scoping or DQO Process activities to identify data uses and opportunities to use CSL data.

- Determine a general prioritization scheme for samples and analyses *before* competing deadlines or customers require one. This planning should include holding time, data end-use, and lab staffing considerations. Lab customers should be aware of and agree with this scheme.

- Establish appropriate sample selection guidelines to identify possible further analyses (e.g., perform γ spectroscopy only when β activity is greater than x) within the screening lab or at an off-site confirmation lab. Setting up a formalized analytical decision tree will save money by reducing unnecessary analyses and documentation requirements.

- Invest in an expandable data handling system and integrate data handling into the appropriate project data management plan. Data quality can be undermined by a poor or 'make-do' handling system.

- Stagger staffing hours. Varied schedules reduce overtime, improve morale, and serve both the first-of-the-day customers (generally technical staff) and end-of-the-day customers (generally field sampling staff).

FUTURE DIRECTIONS

The mission of the CSL will likely stay the same as the CSL continues under another subcontractor to Energy Systems, although with the recent appointment of a technical interface, Energy Systems will take a more active role in CSL activities. An upgrade to the database is under way to ensure seamless electronic data delivery to CSL customers and the Oak Ridge Environmental Information System. As quick-turnaround screening data are more broadly accepted, the analytical capability and sample capacity of the CSL will likely expand.

SUMMARY

The ORNL RI/FS team established the CSL to provide rapid radiological ($\alpha/\beta/\gamma$) and volatile organics screens for ER. Basic wet chemistry techniques were added to assist in rapid and cost-effective sample characterization. The CSL provides its RI/FS and other ER customers with technical and analytical support, and lessons learned may have potential application for similar sites or labs. ER is expanding the CSL's scope to support general environmental restoration/waste management activities at ORNL.

4

A DECISION ANALYSIS APPROACH TO DETERMINING SAMPLE SIZES FOR SITE INVESTIGATION

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INTRODUCTION

A current problem in environmental restoration work is the lack of a detailed and complete definition of the overall site investigation and remediation process. A generic process has been created under the RCRA and Superfund laws but it has many gaps. A number of individual tools have been developed to deal with individual parts of the site investigation and remediation process, but very little has been done to connect these parts into a contiguous whole in which site investigation parameters (e.g., sample plan design) can be clearly and traceably related to the identified risk goals.

This paper is an attempt to remedy at least a small portion of that problem. The connection between a desired post-remediation condition of a waste site and the data to be collected during the site investigation is identified. To portray the connection, the following information is developed and presented:

- the data necessary to describe a contaminated waste site
- the structure of the decision process
- the relationship of the site data to risk estimates
- the basis for designing a sampling plan
- the required information about a proposed remediation process.

This paper does not concern itself with variations on a theme for how to perform the risk assessment. It will be assumed that the risk assessment methodology is defined and is linear with concentration. In addition, only soils are dealt with.

OVERVIEW

The fundamental decision to be made at a waste site is whether or not to remediate the site. Secondary considerations include choosing a specific remediation technology, where to remediate, and how much to remediate. Once the basic mechanism for arriving at the fundamental decision is established, the secondary considerations can be addressed as optimization parameters.

This analysis is based on the following logic:

- Describe the model of waste site contamination used most commonly in site investigations.

- Describe the parameters used in statistical decision making.

- Structure the decision process based on the contamination model and statistical decision parameters.

- Use the decision process structure to establish the expected outcome of the decision as a function of the contamination model parameters, sample plan parameters, and associated decision error rates.

- Optimize on the expected outcome of the decision process to obtain the best combination of sample plan parameters and error rates for a given range of contamination conditions.

DESCRIBING CONTAMINATION

The U.S. Environmental Protection Agency (EPA) describes the statistical tools to be used for designing sampling plans and identifying contamination at facilities. The model of contamination used (EPA 1994) is as follows:

- Some portion of the facility may be contaminated. This portion is identified as epsilon (ϵ) and may range from 0 (uncontaminated) to 1 (all of the facility contaminated).

- The contaminated portion of the facility has had a constant amount, so that the overall average concentration for the site is above the background levels of analytes of concern, by a quantity identified as delta (δ).

In addition to the above description of contamination, the uncontaminated conditions of the facility are assumed to contain the analytes of concern at concentration levels that vary naturally across the facility.

The value of ϵ and δ that is important to detect depends upon the nature of the background distribution, the risk calculation methodology, and the acceptable post-remediation risk levels. The risk methodology is assumed constant and will not be further considered. A relatively direct linkage can be made between the desired post-remediation risk and critical values of ϵ and δ. These critical values represent the conditions for which the sampling plan must be designed in order to achieve the expected level of acceptable risk.

PROBABILISTIC DECISION MAKING

The decision process for whether or not the waste site is contaminated is usually based upon a quantifiable decision rule (i.e., a statistical hypothesis test) that may or may not yield the "correct" decision given the true waste site conditions. In a site investigation, the accuracy of a decision is measured in terms of the probabilities associated with the two possible decision errors, false positives and false negatives.

The null hypothesis being tested (EPA 1994) is "The reference-based cleanup standard achieved." The alternative is "The reference-based cleanup standard not achieved." In more common terms, this amounts to asking if the waste site is clean or dirty. Using the null and alternative hypothesis, the nature of the decision errors can be identified:

		TRUE CONDITION OF WASTE SITE	
		CLEAN	CONTAMINATED
DECISION ABOUT WASTE SITE CONDITION	CLEAN	$1-\alpha$ CORRECT DECISION	TYPE II ERROR, ß
	CONTAMINATED	TYPE I ERROR, α	1-ß CORRECT DECISION

The decision rule will have two probabilities associated with it, α and ß. These quantities indicate the probability of committing each of the two possible errors in making the decision. The first kind of decision error (false positive, also called type I error in the statistics literature) is denoted by α and is the probability of declaring the waste site contaminated when it is not. Because the probabilities of declaring the waste clean or contaminated, given the true condition is clean, must add to 1, the probability of making a correct decision under this condition is $1 - \alpha$.

The second kind of decision error (false negative, also called type II error in the statistics literature) is denoted by ß and is the probability of declaring the waste site clean when the true condition is contaminated. Because the probabilities of declaring the waste site clean or contaminated, given the true condition is contaminated, must add to 1, the probability of making a correct decision under this condition is 1 - ß. The term "power" is used to denote the quantity 1 - ß. ß depends on the number of samples taken from both the background (n) and waste sites (m), the extent and magnitude (ϵ and δ) of the contamination at the waste site, and the value of α chosen.

ERROR RATES AND SAMPLING PLAN DESIGN

The usual procedure in designing a sampling plan is to specify the value of α and one or more combinations of ß, ϵ, and δ. From this information, the number of samples from both the background and waste site areas can be determined by consulting the appropriate power tables. The main problem is in determining the necessary and appropriate combinations of ß, ϵ, and δ. This is where the connection to the risk assessment process must be made.

POST-CLOSURE RISK

We structure the sampling design problem in terms of a decision tree, to bring out all the relevant steps involved and all possible decisions in facing a variety of uncertain scenarios and the consequent outcomes. This is particularly useful in computing probabilities associated with various final outcomes of a complex process and thereby computing the expected value of a potential decision taken.

Use of such tree diagrams and computation of probabilities associated with final outcomes is described in many statistics books. See, for example, Bernardo and Smith (1994). Using the decision tree construct, we develop the concept of post-closure risk. Post-closure risk provides a quantitative measure for describing the goal of a site investigation, thereby providing a means for choosing from among various sampling designs and parameters for the site investigation.

The use of a decision rule based upon the outcome of a statistical hypothesis test is a node in the decision tree. The outcome of the test is either remediate or stop. Figure 1 shows a simplified decision tree for the choice of sampling plans. The decision "Use Sample Plan X_i" is followed by two binary nodes in sequence for a total of 2^2 possible outcomes.

The first node in the sequence describes the possibilities for the true condition of the waste site. The variable δ_o is used to create the binary nature of the node. δ_o may be arbitrarily specified as a detectable difference above background, or it may be interpreted as a regulatory limit, such as a maximum permissible concentration. The probability ϕ embodies the uncertainty in the knowledge about the true state of nature. In Bayesian terms, ϕ is the prior estimate of probability of the waste site being dirty ($\delta_o \leq \delta$), while $1 - \phi$ is the probability of the waste site being clean ($\delta_o > \delta$).

The second node in the branch is the hypothesis test used to trigger a remediation action. The power of the test ($1 - ß$) is the probability of accepting H_a when H_a is true. Similarly, when H_0 is true, $1 - \alpha$ is the probability of not performing a remediation action.

The expected risk in the waste site after closure will depend upon

1. the residual risk (R_{c2}) if the site is determined clean
2. the risk from contamination (R_{c1}) if the site is determined contaminated
3. the power of the decision rule to detect the contamination ($1 - ß$)
4. the risk levels achievable by the remediation process (R_{r2} , R_{r1}).

The expected post-closure risk can be constructed as follows. The pre-

closure waste site risk is divided into two parts, the risk from a clean site and the risk associated with a contaminated site. The expected post-closure risk, R_f, will be the weighted average of the risk after remediation, R_r, and the baseline (current) risk. The weighting factors are the values 1 - ß and ß, respectively:

$$
\begin{aligned}
R_f = E(Risk) &= \phi[\beta R_{c1} + (1-\beta)R_{r1}] + (1-\phi)[(1-\alpha)R_{c2} + \alpha R_{r2}] \\
R_{c1} &= \textit{Waste site risk, given } \delta_o \le \delta \\
R_{r1} &= \textit{Residual risk after remediation, given } \delta_o \le \delta \\
R_{c2} &= \textit{Waste site risk, given } \delta < \delta_o \\
R_{r2} &= \textit{Residual risk after remediation, given } \delta < \delta_o
\end{aligned}
\qquad (1)
$$

The connection to the sampling plan design is made by replacing ß with the functional form of the power curve, ß = $f(\epsilon,\delta,n,m)$. In practice, the functional form of $f(\epsilon,\delta,m,n)$ may not be known. What will be known are discrete values from a power table. The tabular values can be entered into the equations and R_f calculated.

The value of ϕ in Equation (1) is unknown and, as described above, must be estimated *a priori*. A reasonable estimate of ϕ may be obtained by looking at the proportion of a site contaminated, ϵ. Thus, ϕ may be interpreted as the probability that a randomly chosen grid location is contaminated. Consequently, we may estimate ϕ with ϵ. This viewpoint allows us to use an estimate based on historical information. The substitution yields

$$E(R_f) = \epsilon[\beta R_{c1} + (1-\beta)R_{r1}] + (1-\epsilon)[(1-\alpha)R_{c2} + \alpha R_{r2}] \qquad (2)$$

The risk variable in Equation (2) can easily be replaced by the appropriate cost variable, with the caveat that the costs must be converted to commensurable units.

Equation (2) incorporates all of the critical Data Quality Objectives information that must be established before a sampling plan can be specified. The prior information about the site and the remediation method performance is included in the expected outcomes of the decision tree and in the specification of the true condition. The hypothesis test is implicitly required in the determination of the type I and II error rates.

DETERMINING A SAMPLE SIZE

Given a single equation such as Equation (2), optimization procedures can be directly applied to generate the sample plan design, thus

simultaneously optimizing not only the number of samples but also the type I and II error rates. Not only can the optimum sampling plan for a given waste site condition be determined, but the critical (i.e., worst case) waste site conditions for which a sampling plan should be designed to detect can be determined. The critical condition would be that waste site condition that results in the highest expected risk for a given sampling plan.

Equation (2) can be used to plot the expected post-closure risk (R_f) against δ.[a] Figure 2 is an example set of such curves of R_f plotted against the baseline risk. To generate such curves, the analyst must make several decisions:

1. What statistical hypothesis test will be used?
2. What type I error rate will be used (α)?
3. What remediation option will be considered?

The first two decisions are necessary to establish the power of the hypothesis test for a specified number of samples. The third decision is necessary to establish the performance level(s) of the remediation process (R_{r1}, R_{r2}).

The decisions made for this analysis are listed below:

- Use the Wilcoxon Rank Sum Test (WRS, EPA 1994).
- Use a significance level (α) of 5%.
- Use a value for ϵ of 1.0, consistent with the usage of the WRS test to detect a uniform contamination in the waste site.
- Remediate by removal of soil and replacing with clean backfill, i.e., background material ($\delta_0 = 0$).

Several characteristics of the curves in Figure 2 should be noted. For the baseline risk equal to very large values, the power of the WRS test approaches 1.0. Thus, the remediation will almost certainly be performed, achieving a post-closure risk equal to the background risk. For very small values of the baseline risk, near background, the power of the WRS test is also small, thus failing to trigger a remediation. Because the baseline risk is small to begin with, this is acceptable. At intermediate levels of baseline risk, there is a maximum in the expected post-closure risk. Where this maximum occurs is a function of the shape of the power curve. Different sample sizes have been used to obtain different power curves and, hence, different curves of R_f.

The peak of each curve represents the critical waste site condition leading to the maximum value of R_f. All other possible waste site conditions will lead to lower values of R_f. Selecting the number of samples that yields a maxima less than the stakeholder determined target risk will assure the stakeholders that, *regardless of the initial waste*

site conditions, the expected result is less than the target risk. Should the actual waste site conditions differ from the critical values, then the expectation is that the final post-closure risk, R_f, will be lower, perhaps significantly so, than the target risk. This establishes the basis for selecting the optimum sampling plan for the critical waste site conditions.

Figure 3 shows the process repeated for different ϵ. An interesting result of these curves is that for the WRS test, the reduction in power for decreasing ϵ is slower than the reduction in risk due to the reduced exposure area of the waste site. This is evidenced by the fact that the peak value for $\epsilon = 1$ is the largest and the peaks decline as ϵ declines. It is not until ϵ reaches very small values and the contamination is very large with respect to the background conditions that R_f begins to increase and approach the $\epsilon = 1$ maxima. This indicates a condition in which a change should be considered in the hypothesis test used.[b]

DISCUSSION

The examples above were based upon the Wilcoxon Rank Sum test. Any defined decision rule can be used, provided that the power of the decision rule is known or can be estimated. The analysis for the critical values ϵ, δ and the optimum values m, n requires that

- the decision rules be defined
- their power be determined
- the remediation method performance be defined
- the acceptable maximum expected post-remediation outcome (risk, dose, or cost) be established by the stakeholders.

The design of the sample plan can be performed generically and applied to many different waste sites. Site-specific changes may occur if a predetermined decision rule is sensitive to area (i.e., hot spot detection), a decision rule is changed (e.g., moving from a statistically based decision rule to a subjectively based decision rule), or the acceptable maximum expected post-closure risk is changed (e.g., a change in risk scenarios from a change in proposed land use).

Decision rules based upon professional judgment are also possible. In this instance, α and ß become subjective probabilities. A discussion of the determination of subjective probabilities is beyond the scope of this paper, but is compatible with the above development. The "Sample Plan X_i" branch may be replicated, and the probabilities α and ß replaced with the subjective estimates of α' and ß' for the error rates.

The analysis presented does not guarantee that every waste site will be cleaned up to less than the target risk for which this analysis is used to establish sampling plans. It does guarantee that, *on average*, all of the

waste sites will be remediated to acceptable conditions. If the stakeholders desire to guarantee that every waste site meets the acceptable risk criteria, then each site must be remediated, thus eliminating the decision errors. However, the cost of achieving this level of certainty may be unacceptable to the stakeholders.

A spreadsheet can easily perform the analysis for a few likely combinations of ϵ, δ, m, and n. The sample plan designer can then pick out the combination that results in the expected post-closure, R_f, being equal to or less than the stakeholder target risk. However, for performing a comprehensive optimization of the sampling plan, the development of software to specifically perform the calculations and display the curves should be pursued.

SUMMARY

A simple process has been defined for developing soil sampling plan parameters based upon the power of the decision rule being used and the stakeholder-defined acceptable post-closure risk levels. The output of this process may be performed generically and applied to many waste sites simultaneously, thus reducing the amount of effort involved in sample plan generation.

ENDNOTES

(a) δ may also be converted to other scales and units of measurement such as baseline (initial) risk or P_r as described in EPA (1994).

(b) The Quantile test recommended in EPA (1994) was designed specifically to detect this condition. Overlaying the curves of the Quantile test and the WRS test will allow the analyst to establish a balance between the two tests based upon comparable performance in achieving R_f.

ACKNOWLEDGMENTS

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Figure 1.

SIMPLIFIED DECISION TREE FOR SITE INVESTIGATION AND REMEDIATION

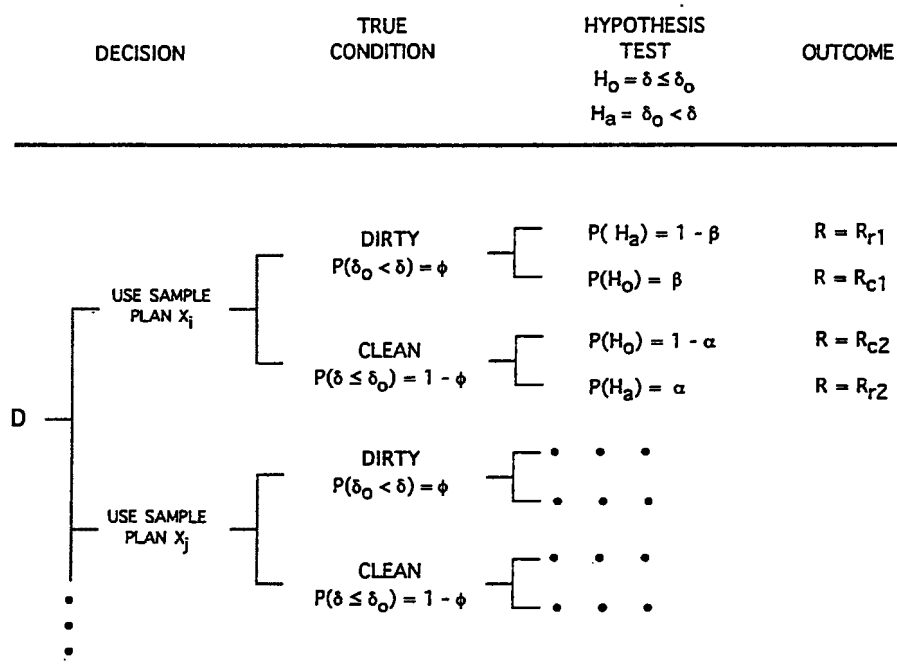


Figure 2.

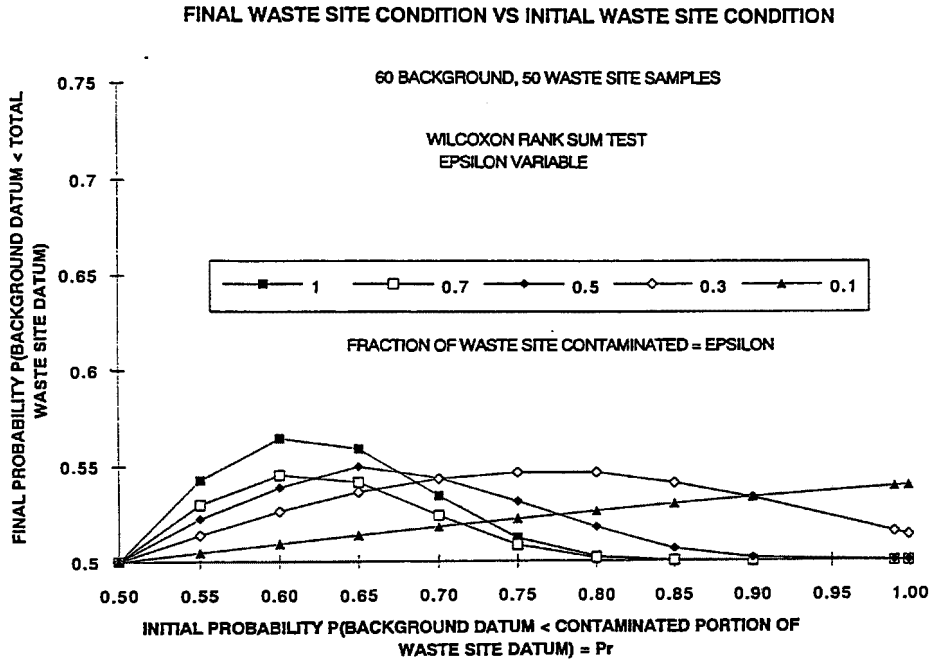
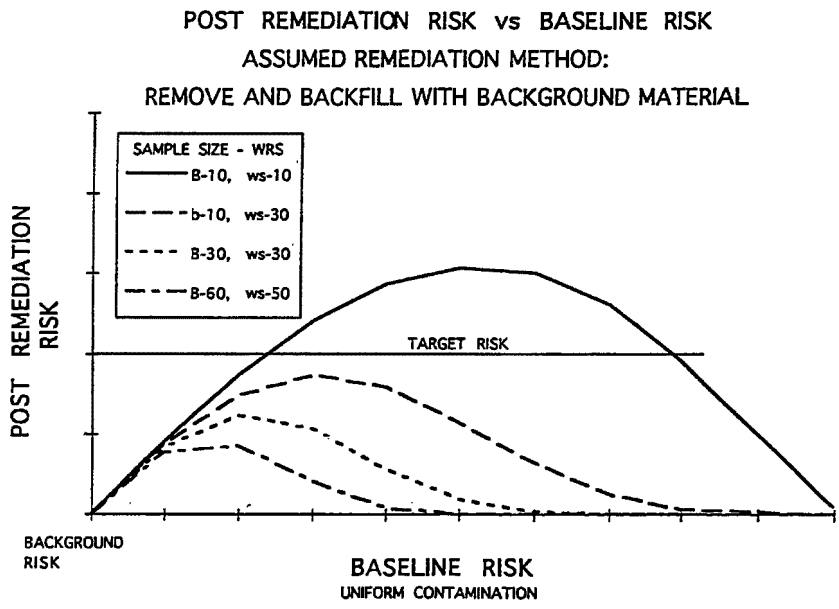

FINAL WASTE SITE CONDITION VS INITIAL WASTE SITE CONDITION
60 BACKGROUND, 50 WASTE SITE SAMPLES
WILCOXON RANK SUM TEST
EPSILON VARIABLE
1
0.7
0.5
0.3
0.1
FRACTION OF WASTE SITE CONTAMINATED = EPSILON
FINAL PROBABILITY P(BACKGROUND DATUM < TOTAL WASTE SITE DATUM)
0.75
0.7
0.65
0.6
0.55
0.5
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
INITIAL PROBABILITY P(BACKGROUND DATUM < CONTAMINATED PORTION OF WASTE SITE DATUM) = Pr

Figure 3.


POST REMEDIATION RISK vs BASELINE RISK
ASSUMED REMEDIATION METHOD:
REMOVE AND BACKFILL WITH BACKGROUND MATERIAL
SAMPLE SIZE - WRS
B-10, ws-10
b-10, ws-30
B-30, ws-30
B-60, ws-50
TARGET RISK
POST REMEDIATION RISK
BACKGROUND RISK
BASELINE RISK
UNIFORM CONTAMINATION

REFERENCES

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5

Cost Effective Statistical Sampling: Composting, Double Sampling and Ranked Sets

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Several cost effective methods of statistical sampling will be presented. These methods; compositing, double sampling and rank set sampling allow for more effective site specific coverage patterns for detecting contamination and at the same time reduce sampling costs. The cost savings are achieved by reducing the number of necessary laboratory analysis, which is a major cost in environmental data collection for site investigations, rather than by reducing the number of site samples taken. Each of these statistical methods are appropriate for a site decision making under varying assumptions. A discussion of each method will be given along with an example data set. Ways of combining these methods to achieve greater cost savings will also be discussed.

THE DEVELOPMENT OF AN INNOVATIVE PROGRAM TO MONITOR THE EFFECTIVENESS AND PERFORMANCE OF REMEDIATION TECHNOLOGY AT A SUPERFUND SITE

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ABSTRACT

An innovative monitoring program was developed to assess the effectiveness and performance of remediation systems at a former organic chemical manufacturing facility, known as the Ott/Story/Cordova Superfund Site near Muskegon, Michigan. The groundwater contains an estimated 80 mg/l of ammonia-nitrogen and 1500 mg/l of COD. Thirty percent of the COD is composed of a mixture of 50 Appendix IX compounds that include aromatic and halogenated organics. The remaining COD consists of a complex mixture of known organic compounds and unidentified chemical process intermediates and degradation products. Many of the unidentified chemicals were phenolic and aromatic nitrogen based compounds related to historical pesticide production. A two-stage PACT*(Powered Activated Carbon Treatment) system was evaluated at bench and pilot scale levels.

The monitoring program developed for the remediation system evaluation had to address Appendix IX constituents in addition to the large group of unidentified organic compounds. This was accomplished by the following steps; conventional treatment performance parameter analysis, GC/MS analysis by 8240 and 8270 expanded to include spectral libraries of influent and effluent compounds and mass spectral interpretation, and biological whole effluent toxicity testing.

Conventional parameter analysis and GC/MS methods were used to monitor the operation of the treatment systems. Influent and effluent mass spectral libraries were developed for each chromatographic peak detected above threshold. Forward

searches using these libraries were then conducted to determine whether unidentified influent organics were effectively removed by the system. Mass spectral interpretation of the unidentified effluent organics was performed to provide structural information. In order to provide an overall indication of treatment performance, acute and chronic whole effluent toxicity testing was conducted.

Based on the results of the monitoring program for the bench scale system, the two-stage PACT technology was found to effectively remove organics and ammonia. A 9.5 liter/minute pilot PACT* system was then constructed on site and operated for five months. The only Appendix IX compound found in the pilot system effluent was 1,2-dichloroethane. Comparisons of the mass spectra for influent and effluent samples showed that only three unidentified compounds passed through the system; these were low molecular weight degradation products with little environmental significance. The effluent was also found not to be acutely toxic to aquatic organisms in the whole effluent tests. The data from the monitoring program was used to demonstrate that the remediation system effectively removed the unidentified compounds and produced an effluent that would not impact the environment. As a result of the on-site pilot study, a 4,600 cubic meter per day, two-stage PACT* system is being implemented at the site. Operation of the two-stage PACT* system represents a potential cost saving of $20,000,000 over the project life as compared to the several technologies originally recommended.

INTRODUCTION

The Ott/Story/Cordova Superfund Site, located in Muskegon, Michigan, has been extensively studied and evaluated for remediation for almost 20 years. The Ott/Story Chemical Company produced a variety of pesticides and specialty organic chemicals in a remote area from 1958-1974. Production wastes were equalized and stored in unlined ponds prior to discharge in a small stream. The site is located on sandy soils with a shallow aquifer 5-10 feet from the surface. A plume of contaminated groundwater extends 4,000 feet down gradient from the site and is intercepted by Little Bear Creek.

The Ott/Story Chemical Company generated phosgene and methyl isocyanate on site to produce a variety of carbamate and

urea based pesticides. Azo coupling reactions were also used in the synthesis of dyes such as chlorazol chloride. In addition, a number of specialty chemicals based on camphor and glycine were also manufactured. PCBs and chlorinated hydrocarbon pesticides were not detected in the site soils or groundwater. The major chemicals produced and used at the facility are listed in Table 1.

With the exception of a few chlorinated and aromatic solvents, polycyclic aromatics, and phenols, the groundwater contained a limited number of HSL compounds. Appendix IX analysis plus TICs (Tentatively Identified Compounds) however identified over 50 compounds including aromatic amines, substituted phenols, and camphor related materials. This analysis only accounted for 30% of the chemical oxygen demand. A listing of groundwater characteristics is given in Table 2.

The design considerations for remediation at this site are itemized in Table 3. The complex chemical composition of the groundwater in addition to the environmental health concerns related to phosgene, methyl isocyanate, and pesticide production resulted however in the design of a very elaborate and costly remediation system. The EPA mandated system contained a series of biological and physical/chemical processes including:

air stripping	activated sludge
clarification	lime softening
ammonia stripping	aerobic digestion
sludge thickening	recarbonation
sand filtration	carbon adsorption
thermal oxidation	

A detailed analysis of the chemicals and their environmental fate however supported the use of enhanced biological treatment. An evaluation of remediation alternatives found the PACT*(Powdered Activated Carbon Treatment) System to be the most effective process due the combination of activated carbon with aggressive biological treatment. This alternative was not initially acceptable to the EPA due to concerns related to the unidentified chemicals and the perceived "fragility" of biological systems when treating concentrated organic influents. Bench scale testing of a 2 stage PACT* System found the technology effective in removing influent organics. Based on these results, a 9.5 liter/minute pilot system was constructed on site to evaluate the technology. A key component to this evaluation

Table 1.
Chemicals Produced and Used at the
Ott/Story Chemical Co.

Chemicals Produced

Methyl isocyanate
Propyl isocyanate
Ethyl isocyanate
Butyl isocyanate
Chlorophenyl isocyanate
Pentachloronitrobenzene
Dimethyl carbamoyl chloride
Camphor sulfonic acid
Glycerol chlorohydrins
Ethyl centralite
Chlorophenyl-n-methyl carbamate
Tetramethyl urea
Amylphenyl-n-methyl carbamate
Phosgene
Phenyl Glycine
Ethyl chloroformate
Isopropylphenyl methylcarbamate
Tolyl methylcarbamate
Butyl phenyl methylcarbamate
Chlorazol chloride
Diuron
Monuron

Major Chemicals Used

1,2 Dichloroethane
Amyl Phenol
Aromatic Naptha
Ammonia
Substituted Anilines
Substituted phenols
Camphor
Nitric Acid
Glycine

Table 2.
Ott/Story Chemical Company
Groundwater Characteristics

- 1500 mg/l chemical oxygen demand
- 81 mg/l ammonia nitrogen
- 87 mg/l organic nitrogen
- 50 EPA Appendix IX Compounds including halogenated and aromatic solvents, chlorinated and alkyl phenols, polycyclic aromatic hydrocarbons, phthalate esters, nitro aromatics. (500 mg/l)
- 100 other organic compounds including aromatic amines, substituted ureas, ethoxy compounds, aldehydes, camphor derivatives, and alcohols. (300 mg/l)
- 200 unidentified organic compounds (200 mg/l)
- 800 mg/l of organic compounds that do not chromatograph

Table 3.
Remediation System Design Considerations

- Effectively remove a variety of polar and non-polar organic chemicals
- Address concerns related to unidentified organic compounds
- Produce an effluent acceptable for discharge to surface water
- Remove ammonia
- Cost effective
- Easy to operate

was the design and implementation of a monitoring program that would address unidentified organic compounds and document a stable treatment process that produced an effluent acceptable for discharge to the receiving stream. This paper discusses the remediation system monitoring program and presents the results.

THE REMEDIATION SYSTEM MONITORING PROGRAM

The monitoring program developed for the PACT* pilot system had to address conventional wastewater parameters, Appendix XI constituents, TICs, unidentified organics, and whole effluent toxicity. The monitoring program is summarized in Table 4. While traditional monitoring programs can be readily designed around a parameter list, the large number of TICs and unidentified organics in the site groundwater presented a problem that required resolution. Gas chromatography/mass spectrometry (GC/MS) methods had to be modified in an innovative manner to include this group of chemicals. A project specific target list was first developed that included Appendix XI volatiles and semivolatiles in addition to significant site compounds such as camphor, N,N-dimethyl aniline, N-ethyl aniline, tetramethylurea, and 1,1-dichloro-2,2-diethoxyethane. Mass spectral libraries were then constructed for all chromatographic peaks in both the influent and effluent samples for each sampling event. The influent library was used to search the effluent samples to monitor the removal of TICs and unidentified compounds by the PACT* System. As a further check of removal, the effluent library was used to search the influent samples to document the absence of compound overlap in the chromatogram. Finally, mass spectral interpretation was used to characterize the unidentified compounds in the effluent. Even though the exact identity of these compounds could not be determined, the mass spectra and retention times clearly showed the chemicals to be of low molecular weight. In addition, it was evident that the effluent compounds did not contain halogens or aromatic rings. This was a significant determination because most of the environmentally hazardous chemicals contain halogens and or aromatic ring structures.

A diagram of the two-stage PACT* system is presented in Figure 1.

Table 4.
Remediation System Monitoring Program

• Conventional Parameter Analysis	Oxygen Demand Nitrogen Series Solids Sulfate Total Phosphorus Alkalinity
• Organic Analysis by GC/MS	Volatile Organics Semivolatile Organics Spectral Libraries of Each Peak Library Searches Mass Spectral Interpretation
• Toxicity Testing	Acute and Chronic Fish and Invertebrates

EARTH TECH Designed PACT Process Treatment Schematic

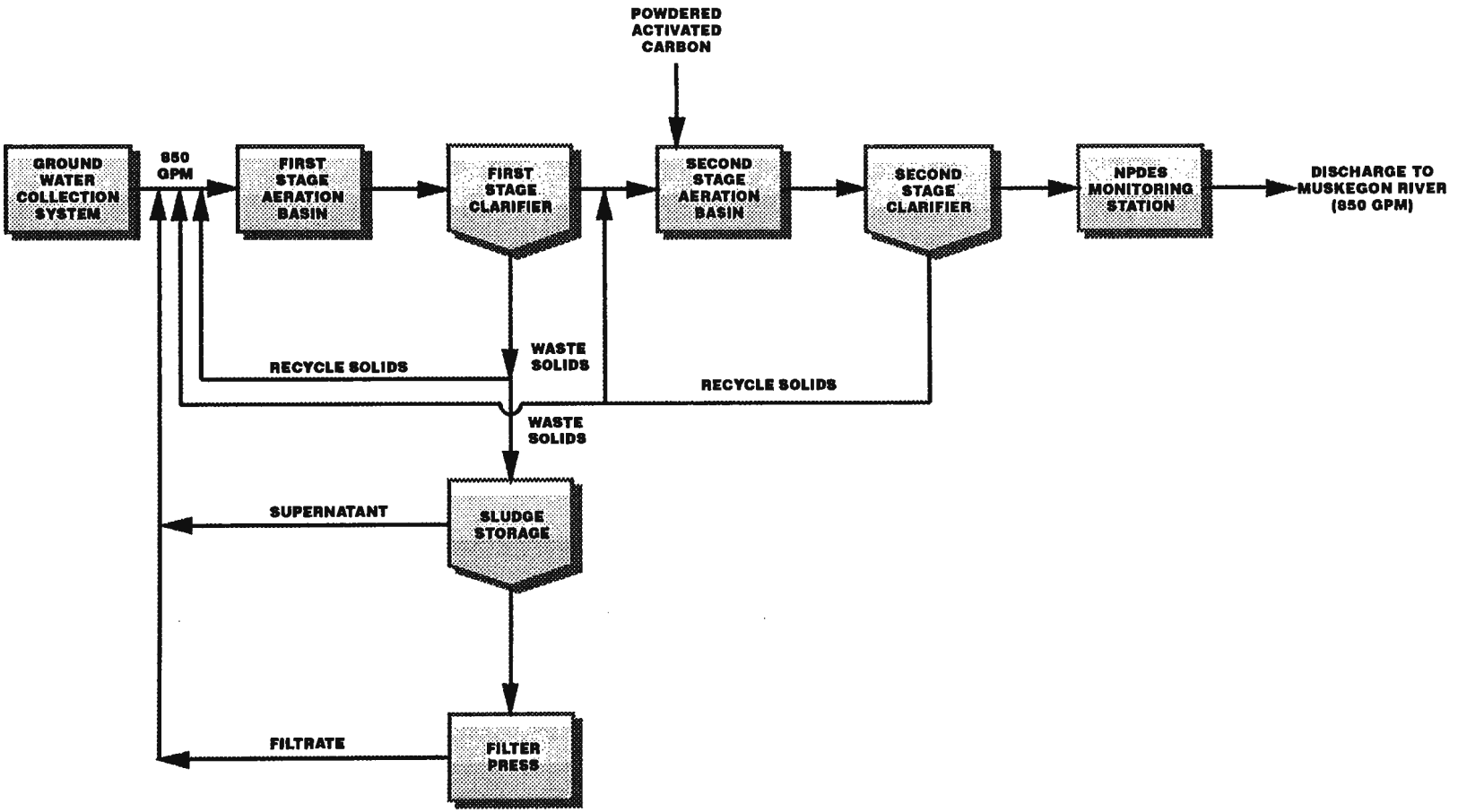


Figure 1.

Samples were collected from the influent, stage-one effluent, and stage-two effluent. A five month monitoring program was initiated. Program components are given in Table 5. Conventional parameters were analyzed during the first month for start-up purposes. Volatile and Semivolatile organics were added during months 2 and 3 to document steady state. All parameters were analyzed during months 4 and 5. As a further verification of performance, 3 sets of samples were sent to an EPA contract laboratory. All methods were performed according to EPA approved methods (EPA, 1992).

MONITORING PROGRAM RESULTS

The results of the monitoring program are presented in Figures 2, 3, and 4. The only Appendix XI compound found in the effluent was 1,2-dichloroethane. This compound was detected at concentrations consistently below the proposed discharge limit of mg/l. The system was also found to effectively remove BOD, ammonia, and total phosphate. Only three unidentified compounds remained in the effluent. Two of these compounds were low molecular weight degradation products which had spectra similar to alcohols and esters. The remaining compound had structural similarities to camphor and was probably an oxygenated metabolite. There was no evidence of halogenated or aromatic compounds in the semivolatile analysis. The effluent was also found not to be toxic to fish or invertebrates in the whole effluent toxicity tests.

SUMMARY

Based on the results of the remediation system monitoring program, the EPA accepted the two-stage PACT* system as the appropriate remedy for the site. A 4,600 cubic meter per day system is currently under construction. Operation of the two-stage PACT* system represents a potential cost saving of $20,000,000 over the project life as compared to the original remediation alternative. The innovative use of GC/MS in the monitoring program was a key factor in

Table 5.
Ott/Story Remediation System Monitoring Program

Parameter	Frequency				
	Month 1	Month 2	Month 3	Month 4	Month 5
BOD	5/wk	5/wk	5/wk	5/wk	5/wk
COD	5/wk	5/wk	5/wk	5/wk	5/wk
Nitrate	5/wk	5/wk	5/wk	5/wk	5/wk
Nitrite	5/wk	5/wk	5/wk	5/wk	5/wk
Ammonia	5/wk	5/wk	5/wk	5/wk	5/wk
Total Organic Nitrogen	5/wk	5/wk	5/wk	5/wk	5/wk
Total Phosphate	5/wk	5/wk	5/wk	5/wk	5/wk
Sulfate	5/wk	5/wk	5/wk	5/wk	5/wk
Alkalinity	5/wk	5/wk	5/wk	5/wk	5/wk
TSS	5/wk	5/wk	5/wk	5/wk	5/wk
Volatile Organics	*	1/wk	1/wk	5/wk	5/wk
Semivolatile Organics	*	1/wk	1/wk	5/wk	5/wk
TICs and Unidentified Organics	*	*	*	5/wk	5/wk
Whole Effluent Toxicity	*	*	*	1/mo	1/mo

* sample analysis not performed

Figure 2.

Ott/Story/Cordova
Remediation System Performance

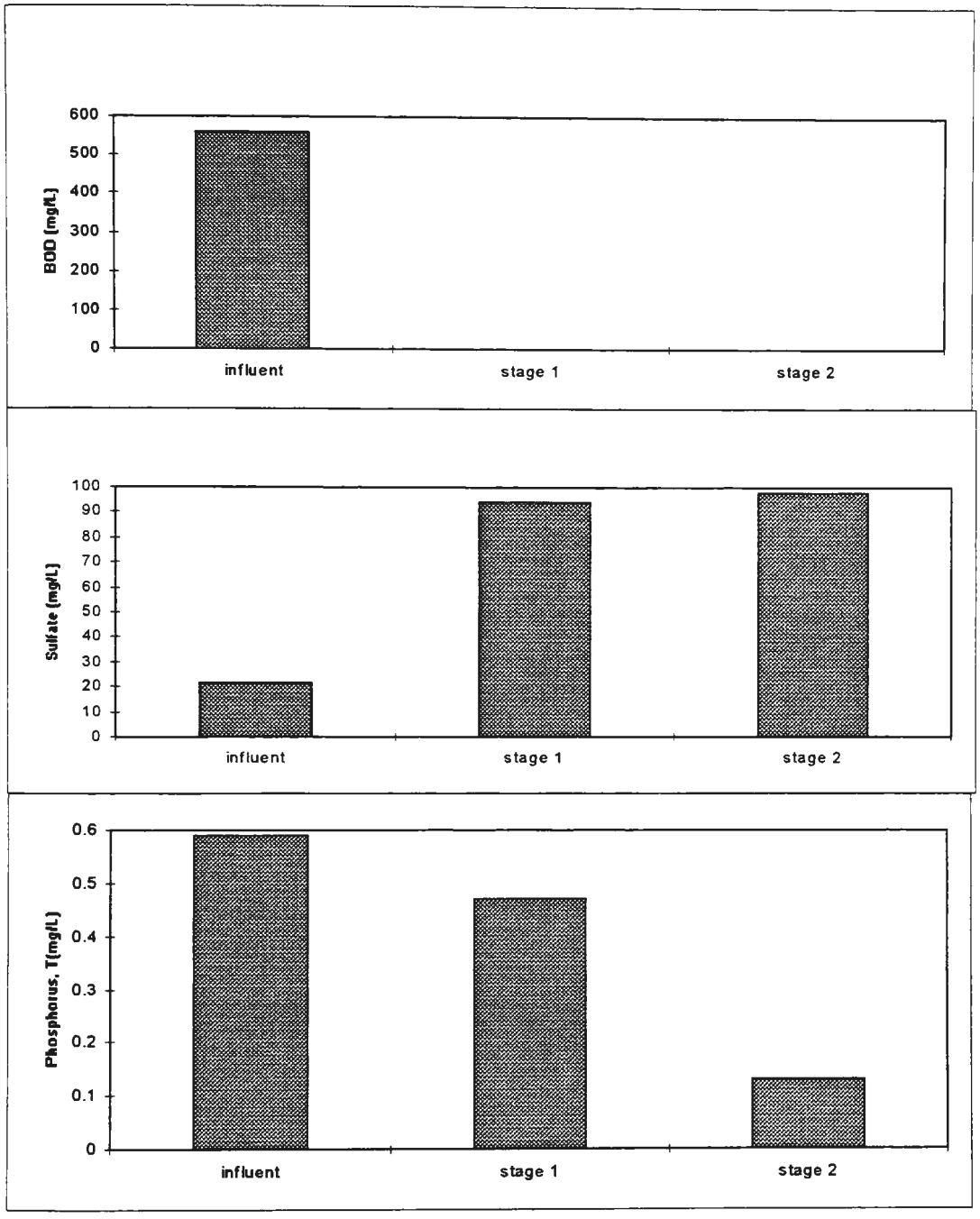


Figure 3.

Ott/Story/Cordova
Remediation System Performance

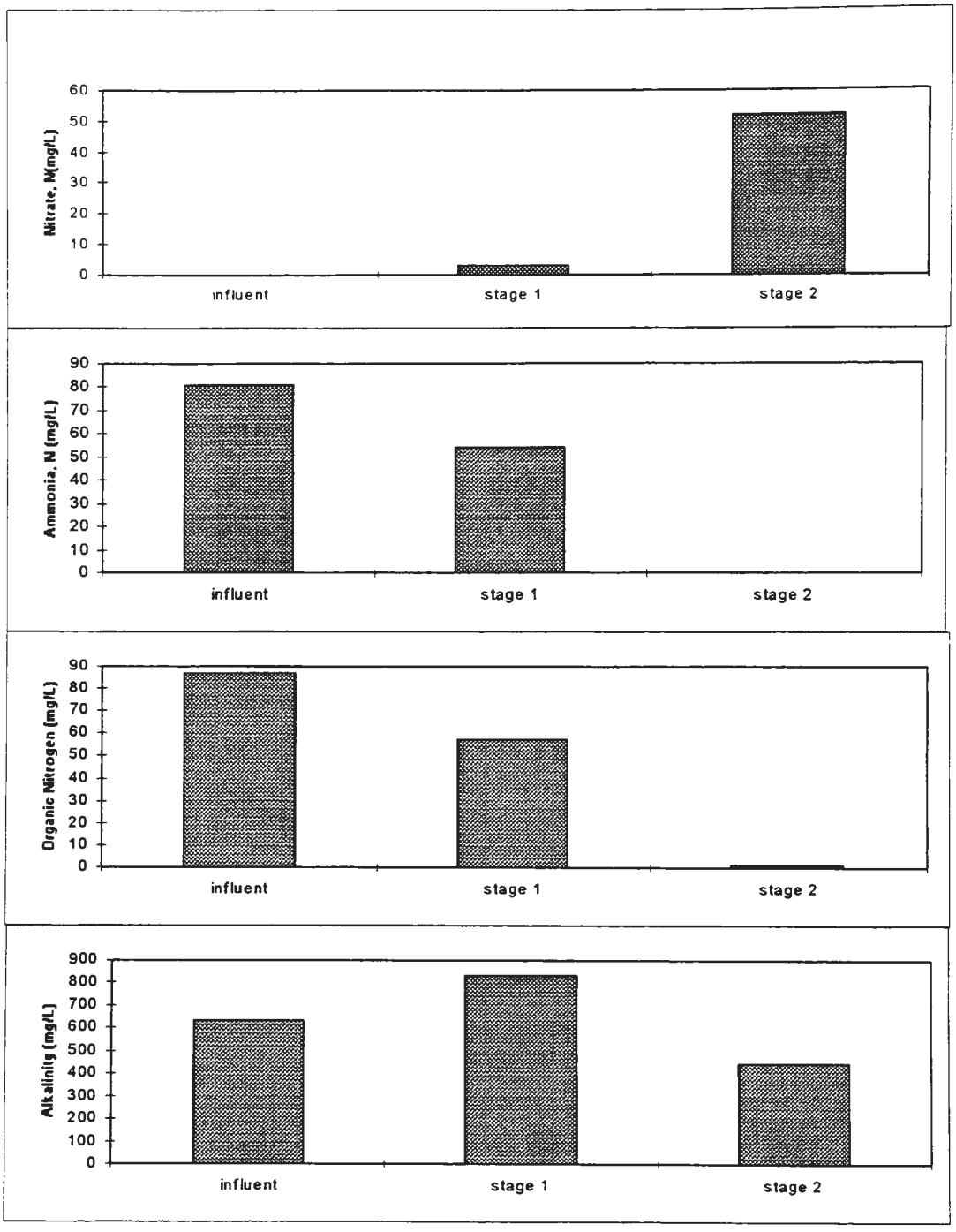
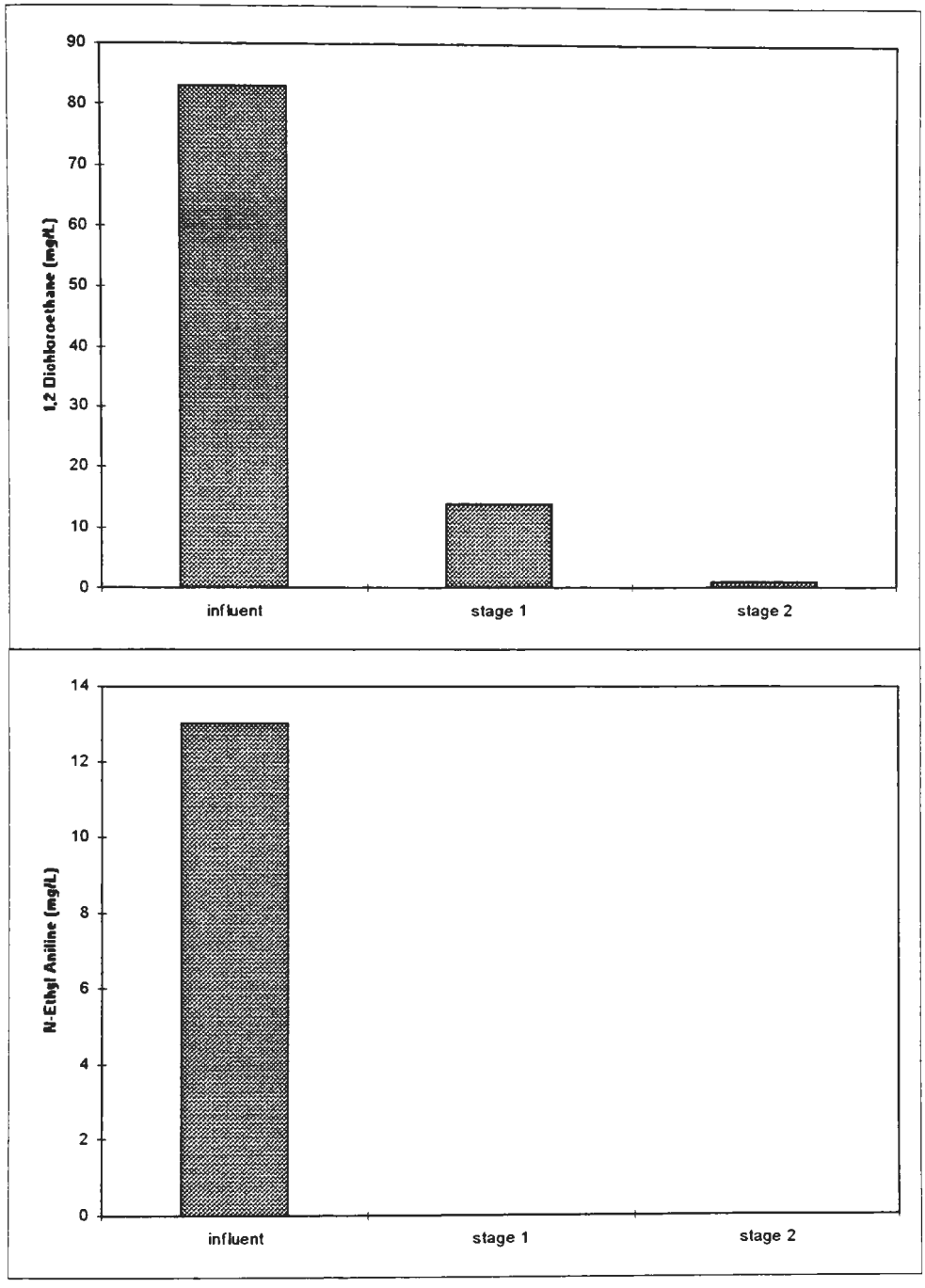


Figure 4.

Ott/Story/Cordova
Remediation System Performance



obtaining EPA approval for a more cost effective remediation technology.

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COMPARISON OF ALTERNATIVES FOR SAMPLING AND STORAGE OF VOCS IN SOIL

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ABSTRACT

The search for an effective alternative to SW 846 Method 5030 for preparing Volatile Organic Compounds (VOCs) in soil must overcome the limitations that were inherent in that method, i.e., the method must show minimal volatilization and/or biodegradation losses. Other issues such as method sensitivity and waste handling also become important depending upon the particular regulations for which testing is required. This study was undertaken to study several alternatives which are currently being promoted by various state/federal regulations: 1)Brass Tube; 2)Dynatech Soil Vial; 3)Methanol Preservation; 4)En Core Sampler. The Dynatech soil vial is a 40 ml glass vial with two teflon-sealed caps and a glass frit on the bottom. The soil is sampled directly into the vial and the vial is analyzed without subsampling. This is the basis of EPA SW 846 Method 5035 for VOCs. The EnCore sampler is a stainless steel volumetric sampling device which has a sealed sample chamber that can store the sample immediately after sampling.

The results of this study indicate that only methanol is completely effective at preventing both volatilization and biodegradation. The brass tube showed significant losses of benzene and other target compounds as early as 12 hours after sample preparation. The Dynatech soil vial and the EnCore sampler did not show significant volatilization losses over the 14 day test. However, if a microbiologically active soil was spiked with VOCs, then losses could occur within 1-2 days of sample preparation. The same soil, after sterilization, regained its ability to retain VOCs. This provides strong evidence that the Dynatech and En Core systems are not prone to volatilization loss but may not be suitable for samples which have the potential for biodegradation unless the method is modified.

Results will be presented using a sampling and sample storage scheme which tests the efficacy of adding a preservative, such as 80% ethylene glycol in water, sodium bisulfate or sodium azide, to the soil. The method recommended here may meet all of the criteria necessary to provide a unified, effective soil VOC method.

INTRODUCTION

Samples taken for soil VOCs under EPA protocol are packed into glass jars in such a manner as to minimize headspace. The jars are routinely shipped offsite and held for up to 14 days before the laboratory prepares the sample for analysis. The preparation involves a subsampling of the soil in order to collection a 5 gm sample into a purge and trap tube. The tube, when attached to the purge and trap instrument, is no longer subject to any further exposure to the environment. This method of storage has been shown by a number of investigators to be deficient to the point where the length of storage time after collection can be the major variable in the analytical results (See the EPA Symposium reference, 1993).

This study was undertaken to compare alternatives to the currently accepted method. Very few studies have been published which compare alternative sampling and storage methods for soil VOCs. This is partly due to the fact that it is very difficult to sample soils with a high sampling precision so that different methods can be statistically compared. A soil mixing device based upon the mixing system developed by Paul King (1993) was used for this study to compare four primary alternatives for soil sampling and storage. The purpose of this study was to determine whether recommendations could be made about which method or method combination might be used to provide precise and accurate results.

EXPERIMENTAL

Clayey sand taken from the field and mixed with sand as necessary to create a finely mixed soil. The soil was mixed in a 35 gallon steel drum into which were welded a series of mixing blades which facilitated the mixing. The chamber was turned on its side and rotated at 5-7 rpms by means of a motorized belt assembly. The drum was kept inside an

insulated box which was cooled to 40-45 degrees Centigrade by means of a refrigerated circulating pump.

The soil was precooled and water was added to achieve a 10% final moisture content. The soil was spiked with a synthetic gasoline standard which contains ten major components of gasoline and, in several instances, also with a spiking mixture of 1,2-dichloroethane, trichloroethylene and tetrachloroethylene. The starting concentration was adjusted so that, after 16-20 hours of mixing, the final concentrations were of sufficient concentration to be in the middle part of the calibration curve. All samples were analyzed using a Hewlett-Packard 5890 GC with either a PID/FID tandem for BETX and Gasoline analysis or a PID/ELCD detector for BETX and chlorinated compound analysis.

All experiments were run over multiple time points and each time point was done with five replicates. In some instances, not every sample was useable due to instrumentation or quality control problems. Once the experimental setup was designed, a computer program was used to set a randomized sampling order to control for sample order bias.

On the day of sampling, a team of samplers were arranged so that the sampling could be completed in less than 10 minutes. It was determined that over 100-120 samples could be collected within this time frame without creating a significant bias due to time delays.

For methanol preservation, twenty five gms of soil were preserved immediately upon sampling and analyzed at the indicated storage times. For brass tubes, twenty five gms of soil were subsampled into methanol and the samples were analyzed within one week of preservation. A twenty five gram version of the EnCore sampler was used as third comparison method. For these three methods, the soil to methanol ratio was 1:1. One hundred microliters of methanol was analyzed in a 5 ml purge volume.

For the Dynatech soil vials, a 5 gm plug of soil was sampled into each vial using the EnCore volumetric sampler. The vials were capped and stored at 4 degrees C until the specified storage time and then analyzed immediately on a Dynatrap autosampler. For the EnCore sampler, the samples were taken and stored at 4 degrees C until the specified storage time, then sampled into the Dynatech vial and analyzed immediately. After the initial experiment, the soil was spiked with manure and the experiment repeated. A sample of the soil was taken for analysis of petroleum-degrading bacteria. After this experiment, the same soil was sterilized, re-spiked and the study repeated a third time. Again, a sample of the soil was analyzed for

petroleum-degrading bacteria.

Results were analyzed using the SPSS for Windows statistical package.

RESULTS AND DISCUSSION

Table one shows the stability of methanol-preserved parameters over a 28 day period against the brass tube over a two day period and the EnCore sampler over a five day period for benzene which was the compound most susceptible to losses. The brass tube was ineffective after 12 hours and the EnCore sampler was stable after 48 hours. Benzene in methanol-preserved soils was stable over the 28 days.

Table two shows the results of a comparison study between the Dynatech soil vial and the EnCore sampler over 14 days for benzene. The upper set of data is on the original soil. The middle set of data is for the bacteria enriched soil. The bottom set of data is for the sterilized soil. In this last case, only data for day six was generated.

Table three shows the same data pattern for 1,2-Dichloroethane. As can be seen, benzene in both the Dynatech and EnCore vial is stable for somewhere between two to four days, then begins to show a decline in concentration. After spiking with manure, the benzene was essentially gone after two days. After sterilizing with soil, the benzene levels where close to zero time concentrations. Bacterial counts from the soil at the second experiment were 5×10^8 and declined to non detectable counts after the sterilization procedure. This is strong evidence that biodegradation rather than volatilization is occurring in the Dynatech vial and EnCore sampler. Table three shows that the 1,2-dichloroethane was stable within 30% over all three experiments. This was added as a control since it is not very susceptible to aerobic biodegradation. This also supports the contention that these methods do not lose significant concentrations due to volatilization. A final set of experiments will be reported where soils sampled into the Dynatech vial are preserved immediately and after two days with solutions of ethylene glycol, sodium azide or sodium bisulfate. Results of these experiments will be the basis of recommendations for a sampling protocol for soil VOCs.

CONCLUSIONS

Methanol preservation of soils prevents both volatilization and biodegradation. The brass tube method is not stable and should not be used for more than a few hours storage. The Dynatech and EnCore methods are effective for longer term storage if the soil does not contain petroleum-degrading microbes. However, a water-based preservative may overcome the limitations of the Dynatech method and allow real hold times approaching 14 days.

A sampling and storing scheme will be discussed which takes advantage of the benefits from the different methods studied here.

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TABLE 1
Comparison of Hold Time by Method
Percent of Zero Time for Benzene

Method	Zero Time	12 Hours	48 Hours	14 Days	21 Days	28 Days
Methanol	100	———	———	94	89	98
Brass Tube	100	47	43	———	———	———
EnCore	100	100	100	———	———	———

TABLE 2
Comparison of Hold Time by Method
Percent of Zero Time for Benzene

Method	Zero	24 Hours	48 Hours	4 Days	6 Days	10 Days	14 Days
Dynatech	100	97	97	47	23	48	7
EnCore	100	87	81	52	15	7	15
		Manure	Spiked				
Dynatech	100	27	8	0	0	0	0
EnCore	100	16	5	0	0	0	0
		Sterile	Soil				
Dynatech	100				89		
EnCore	100				67		

Table 3
Comparison of Hold Time by Method
Percent of Zero Time for 1,2-Dichloroethane

Method	Zero Time	24 hours	48 Hours	4 Days	6 Days	10 Days	14 Days
Dynatech	100	107	102	93	71	91	93
EnCore	100	104	97	93	95	85	79
═══	═══	═══	Manure	Spiked	═══	═══	═══
Dynatech	100	90	90	78	78	78	75
EnCore	100	82	82	74	76	81	77
═══	═══	═══	Sterile	Soil	═══	═══	═══
Dynatech	100	———	———	———	76	———	———
EnCore	100	———	———	———	74	———	———

A Comparison of Response Factors For Weathered Petroleum Standards

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Leaking underground storage tanks represent an increasing environmental concern. Identification and quantitation of petroleum products in the environment can be troublesome for environmental laboratories since the composition of these products is changed in the environment due to weathering. This weathering may be caused by evaporative loss, migration through natural matrixes, or bio-degradation.

Various evaporative loss weathered petroleum products, both laboratory controlled environment weathering and real world weathering, were analyzed to determine their composition. These standards are compared to determine how weathering affects the petroleum products identification and quantitation.

9

A Simple, Accurate Field Test for Crude Oil Contamination in Soil

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Abstract

Crude oil has been pumped out of the earth in the United States for over 100 years. As a result of the commercial exploration of petroleum reserves, the soil in the immediate areas of production, storage and transportation facilities are contaminated with high levels of crude oil. In areas that have been used for these purposes for decades, the concentration of crude oil in the soil frequently exceeds 10%. Many of the oil producing states and oil production companies are working to reduce the level of crude oil contamination surrounding these facilities and return the soil to levels of crude oil less than 1%.

Existing methods for the determination of crude oil concentration in soil are usually done in a laboratory. Those tests that are adaptable to field use are not necessarily easy to use and suffer from the same interference problems experienced by the method in the laboratory.

This paper will introduce a field analytical product called the Crude Check™ Soil Test which can be used simply and accurately in the field by personnel otherwise unfamiliar with chemical analysis.

Introduction

A test has been developed to accurately determine the concentration of crude oil in soil at contaminated areas of production, storage, and transportation facilities. The test was designed to meet the requirement for crude oil testing imposed by the Texas Railroad Commission (Statewide Rule 91) in the field to expedite delineation and remediation of crude oil contaminated soil.

Current Analytical Methods

With thousands of crude oil sites to evaluate, clean-up, and monitor, the task of measuring the extent of the problem is a serious, costly one. Existing methods for the determination

of crude oil concentrations in soil are usually performed in a laboratory. They are based either on the direct gravimetric determination of crude oil extracted from soil by a solvent mixture (Method 9071) or by the measurement of the hydrocarbon content of a Freon extract of soil using IR spectrometry (Method 418.1). While it has been feasible to adapt Method 418.1 to field use with a portable instrument, the field protocol is not ultimately easy-to-use and suffers from some of the same interference problems experienced by the method as practiced in the laboratory. In addition, the use of Freon will not be permitted past the end of 1995, requiring the use of an alternative solvent.

Crude Check™ Soil Test System

The need for a simple, accurate test that can be used in the field by personnel otherwise unfamiliar with chemical analysis methods has resulted in the development of a field analytical product called the Crude Check™ Soil Test System. The test allows the user to test a small sample of soil for crude oil in less than 5 minutes. The test results in a quantitative indication of crude oil concentration over the range of 0.5% to 6%. The analysis of soil samples for crude oil can be performed over a wide range of ambient temperature (40°F - 110°F) and humidity conditions (5% - 95% RH) and the test materials have a storage shelf life of 1 year. To provide accurate quantitation, the test requires the use of a simple piece of field equipment, while complicated solvent extractions, and the large volume of waste solvent they generate, are avoided.

The method is based on the principle that crude oil will form a stable emulsion in water solution under certain conditions. A simple procedure is employed to place any crude oil that may be present in the soil into conditions where emulsion formation will occur. A sample of the soil (5g) is first extracted with a small volume of a proprietary solvent and the extract is subsequently mixed with a water solution that causes the emulsion to form. The turbidity of the final solution is directly proportional to the crude oil concentration. A portable, battery-powered turbidimeter is used to measure the turbidity of the solution and a conversion table is provided in the test instructions to convert to percent oil concentration by weight.

Test System Performance

Sensitivity

Quantitative methods used for environmental purposes must have the minimum sensitivity necessary to measure the analyte at concentrations that are lower than the regulatory action levels. The minimum sensitivity is usually expressed in two ways: 1)

method detection level, which is a quantity of crude oil equivalent to three standard deviation increments of turbidity above a mean negative sample result; 2) reliable quantitation limit, which is the quantity of crude oil derived from four times the turbidity measurement calculated for the method detection. The method detection limit is usually regarded as the lowest concentration that could be measured under ideal circumstances and for the Test System is 0.11% crude oil. The reliable quantitation limit reflects the minimum sensitivity that can be reasonably obtained under most circumstances. The Test System has a reliable quantitation limit of 0.33% crude oil.

The maximum concentration that can be reliably measured is 6% crude oil. Above this concentration, the turbidity response is no longer proportional to crude oil concentration.

Accuracy and Precision

The Crude Check™ Soil Test System is designed to deliver accurate, precise quantitative results over the range of regulatory interest. The accuracy and precision of the test was determined using a silty loam soil fortified with 15 different crude oils at two different crude oil concentrations. Using the conversion table in the User's Guide to obtain concentration results from turbidity data, the test characterisitics in Table 1 were found. These results indicate that the test is both accurate and precise.

Furthermore, the recovery of one crude oil (Prudhoe Bay) was evaluated following fortification of 9 different soil types at a concentration of 1%. The mean recovery of crude oil from these soils was 116±14%, indicating excellent consistency of recovery, with little effect of different soil matrices.

Selectivity

The Crude Check Test accurately determines the concentration of crude oil in soil. In addition, the test also measures the concentrations of diesel fuel, fuel oil #2, bunker C, grease, and motor oil in soil. These petroleum products are detected with somewhat more sensitivity than crude oils and, therefore, correction factors must be applied to the results generated using the conversion table in the User's Guide. These correction factors are given in Table 2. The Crude Check test does not give a useful response to either gasoline or brake fluid.

Correlation with Standard Analytical Methods

The Crude Check Test has been evaluated with field samples and has been shown to give results comparable to the laboratory methods commonly used to evaluate crude oil contamination in soil. The results of a trial conducted with crude oil contaminated soil samples provided by a large oil company are shown in Table 3. Each sample was analyzed by Method 9071, Method 418.1, and the Crude Check Test System. The

correlation between the Crude Check results and the results from either laboratory method is as good as the correlation between the two laboratory methods. The variability seen in any of these results is attributable partially to sample heterogeneity.

Robustness

The ability of technically unsophisticated individuals to run the test will be a key to getting representative data in the field. A set of samples from a variety of locations was tested by two different operators using the Crude Check test. These results are given in Table 4.

Many methods perform well in the laboratory, but fail to perform to the levels expected when taken out into the field and subjected to field conditions. There are many possible reasons for performance shortfalls in field trials of field analytical methods. The variablility of field conditions may have an effect on the performance of a method. These conditions include temperature, humidity, wind, sunlight, and precipitation. It is important to determine if these environmental factors seriously effect the method to understand its limitations. Other circumstances such as sample heterogeneity, sample matrix, and user training can have an impact on test performance.

The Crude Check Test system is currently undergoing field trial evaluation.

Conclusions

An accurate, rapid, easy-to-use field test has been developed that quantifies crude oil contamination in soil. The results from this test correlate well with those obtained for the same samples analyzed by the standard laboratory methods. The test allows the user to quickly assess the achievement of clean-up of crude oil contamination at wellheads and storage and transportation facilities without sending samples to a laboratory and incurring the delays inherent in the laboratory analytical process. This facilitates the clean-up with a minimum number of trips back to the site.

Table 1

Bias and Recovery for Crude Check

Characteristic	1% Spike	5% Spike
Recovery (accuracy)	109%	97%
Precision (RSD)	12%	7%

Table 2

Correction Factors for Other Petroleum Products

Petroleum Product	Correction Factor
diesel fuel	0.94
fuel oil #2	0.94
bunker C	0.83
grease	0.83
motor oil	0.83

Table 3

Comparison of Results from Crude Check with Laboratory Methods

	Field Sample Results % OIL		
Sample ID	Crude Check	Method 418.1	Method 9071
L	1.7	ND	1.2
C	1.1	ND	2.9
K	4.6	ND	3.9
D	4.9	ND	5.2
F	> 6.0	ND	9.9
1	< 0.5	0.2	0.9
2	> 6.0	66.1 / 73.5	44.2
3	> 6.0	9.9	14.2
4	5.8	6.7	7.5
5	> 6.0	6.4	8.5
6	< 0.5	< 0.1	0.4
7	1.6	1.2	2.3
8	> 6.0	9.4	19.6
9	> 6.0	19.6	31.6
10	< 0.5	0.1	0.6
11	< 0.5	0.1	0.6
12	2.4	2.9	2.6
13	4.6 / > 6.0	7.9	7.9
14	5.5 / 3.6	7.6	13.1*
15	< 0.5 / < 0.5	0.2	1.0
16	3.7 / 3.0	5.5	12.2*
17	1.6	0.3	1.5
18	1.4	4.8	1.2
19	> 6.0	12.0 / 11.1	12
20	0.5	2.6	1.5
21	4.4	7.2	3.9
22	> 6.0	22.2	17
23	> 6.0	14.3	18.7
24	> 6.0	8.7 / 8.6	8.3
25	> 6.0	11	13.2
26	2.6	3.6	2.5
27	1.9	2.9	1.5
D	3.5	< 0.1	20.3*
I	2.6	< 0.1	9.3*
J	1.0	< 0.1	0.6
M	0.9	0.2	1
P	< 0.5	< 0.1	0.3
S	< 0.5	< 0.1	0.4

* Contained material in extract which did not appear to be crude

Table 4

Operator-Induced Variability

Sample ID	Crude Check Results Operator 1 (% oil)	Crude Check Results Operator 2 (% oil)
1	> 6	> 6
2	2.7	3.4
3	3.7	3.6
4	2.7	2.7
5	4.3	4.3
6	> 6	> 6
7	1.1	1.3
8	1.0	0.9
9	0.6	0.8
10	0.9	0.7

10

A Practical Field Application of Medium Level Soil Extraction/Headspace GC Screening for VOCs in Soil Samples

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A site for a confidential client consists of approximately nine (9) acres in the Upper Peninsula of Michigan. Since the 1930's, the site was used for the disposal of wood tar wastes from the production of charcoal briquettes and chemicals derived from wood. Following evaluation of several remedial alternatives; excavation, removal, shipment by rail and landfilling of the wood tar materials was selected as the most viable solution. The recommended approach was reviewed by Michigan Department of Natural Resources (MDNR) and ENSR was the designated engineer and construction manager for this project.

The major task of the interim response required removal of all visibly contaminated material (over 70,000 tons) while minimizing potential community impacts. Toxic Characteristic Leaching Procedure (TCLP) regulatory levels for volatile organic compounds were used as guidelines for loading the tar waste.

In order to assure that material being loaded into railroad cars met the waste characteristic requirements of the landfill to which it was being sent and to assure that it was properly manifested as non-hazardous; ENSR successfully employed a Photovac Model 10SPlus field GC with a Photoionization detector (PID) to screen large quantities of soil samples. The screening method is a modification of the EPA medium level VOC soil analysis and includes soil sample preservation and extraction into methanol with subsequent analysis of an aliquot of the extract headspace equilibrium over 30 ml of water in a 40 ml VOA vial. Total analysis time per sample was under 20 minutes. Analytical protocol will be presented with associated quality assurance/quality control data for samples from this site. Ten percent of the samples were sent for laboratory confirmation by EPA method SW846/8240. This comparison data will also be presented.

Use of this field screening during one of the most severe winters in the Upper Peninsula saved the client over $ 200,000 in laboratory costs and enabled work to progress in a timely fashion with minimal impacts on the surrounding community.

USE OF A PORTABLE, FIBER-OPTICS, CCD SPECTROPHOTOMETER TO MEASURE FRIEDEL-CRAFTS PRODUCTS IN THE DETECTION OF CRUDE OIL, FUEL, AND SOLVENT CONTAMINATION OF SOIL

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ABSTRACT

The utilization of a test kit employing Friedel-Crafts alkylation reactions to produce intensely colored products of aromatic compounds in the analytes (typically carbon tetrachloride) has facilitated removal of contaminated soils and provided an extremely accurate and rapid analysis of remediation processes. The extraction/colorimetric method has employed visual comparison of results with photograph standards. Testing of a new, portable spectrophotometric read-out device has been completed on a selected group of crude oils, fuels, and solvents. This paper describes results of the use of the device in determining concentration of a typical West Texas crude oil, a gasoline, and a diesel fuel in soil. The extremely small size (5" x 7" x 3") of the device is made possible by the use of a recently-developed single-fiber optic/CCD spectrometer "bench". The instrument is interfaced to a 486 SX "notebook" PC. An algorithm for software development using color values developed by the International Commission on Illumination (CIE) was incorporated to provide quantitative analytical data.

INTRODUCTION

Since the discovery, in 1986, of the technique of extracting soil and water samples with various solvents and then causing the extracts to undergo Friedel-Crafts reactions by the addition of stoichiometrically great excess (>100x) amounts of appropriate Lewis acid catalysts, the procedure has been utilized as a field method to provide extremely accurate quantitative analyses of these substances on site in thousands of cleanup and remediation projects around the world. Optimization of this procedure in order to maximize the visual detection sensitivity has typically involved the use of various amounts of an alkyl halide, carbon tetrachloride, which is, although an extremely good Friedel-Crafts reactant, high on the list of chemical "betes noïrs". The subsequent search for solvents which would serve to provide sufficient reactivity and color via this method, coincident with a general focus by the EPA and other regulatory agencies on the larger scale environmental problems such as leaking underground fuel tanks, crude oil production, storage and processing areas, pipelines, etc., led to the realization that these substances of concern were generally composed of the requisite chemical

species, e.g. aromatics, alkenes, ketones, to allow high level (ca. 100 PPM) detection without the use of an alkyl halide solvent. This, however, further spurred efforts to develop a spectrophotometric read-out device which would alleviate the problems of subjective interpretation of the colors obtained in the precipitates which are the determining parameters in the method. That is, in comparing the colored products of the FC reaction caused by the sample extract in the test tube to the photograph standard, visual acuity, lighting and other uncontrollable factors played a part in determining the result.

Two relatively important technical considerations had stymied successful development of a suitable, field-portable, spectrophotometric instrument for this method: 1) an appropriately sized and focused optical viewing device, and 2) an appropriately sized and powered detector. The first technical problem centered on the fact of the powered reflective surface composed of the excess catalyst and the F-C precipitates. Numerous researches on these reflection/scattering phenomena have pointed to the considerable effects of parameters such as particle size, packing, interstitial fluid, etc. A solution to many of these problems seemed to be offered in the technique understood by printers and Post-Impressionist painters for many years: optical integration of a large area. Just as a too-close inspection of a Seurat painting or a photograph reveals a confusing jumble of dots, a microscopic look at the color in the Hanby method test tubes showed a wide variation in the color of the catalyst/precipitate catalyst/precipitate mixture. The unreacted catalyst particles ($AlCl_3$) and hydrated catalyst ($AlCl_3 - 6H_2O$) were typically white while those particles of the F-C reaction, or adsorbed product were colored to an extent indicative of the relative amounts of the reactants (analytes).

The solution to the second technical problem, i.e., size and power requirements, lay in the utilization of a charge-transfer device of some type. In the fall of 1994 the author was introduced to a group, Ocean Optics, Inc. who had developed a technology in 1992 which seemed ideally suited to the needs of the method. In the development of optical technologies diversely used for pH and spectrophotometric applications, this group had produced an extremely small optical detector employing charge coupled devices and single fiber optic transmission. Essentially all that was necessary in the development of the present device was the design and manufacture of the appropriate optical cell (test tube) holder. This was accomplished by the author after experiments with various materials indicated that, probably due to the rather inconsistent reflection characteristics of relatively inexpensive, commercially-available test tubes, a non-reflective material should be utilized. After the completion of the test tube/fiber optic probe module, a series of test were run to determine the correct distance the probe should be placed from the sample tube. This would optimize the view area and the signal strength. In effect, probe distance would primarily determine the signal to noise ratio (SNR).

For the initial trials of the instrument a particularly appropriate algorithm was available for the conversion of input to output, i.e., the tri-stimulus values established by the International Commission on Illumination (CIE). Essentially, the defined wavelength/color relationships of Red (700nm), Green (546.1), and Blue (435.8) are used in the computation of values in the CIE-derived colour space such as: L*, a*, b*, xtri, ytri, and ztri. As the primary indicator of quantitative analytical results with the method, as heretofore used as a visual method, had been lightness/darkness of precipitated color, it was assumed that the L* (color intensity from white to total saturation) value would be the more indicative parameter, however the data was to prove otherwise. In more spectrophotometrically familiar (to a chemist) terms this was of benefit as the chromophoric effect various functional groups have is a long-established body of chemical knowledge, and using other parameters, namely the tristimulus values: xtri, ytri, and ztri, a simpler translation to wavelength/absorption numbers would be available. Hence, the expansion of the method in terms of a qualitative technique for identification of substances would be enhanced.

EXPERIMENTAL

Selection of substances to be utilized in the initial trials of the instrument was prioritized roughly be production and environmental importance. Thus, crude oil, gasoline, diesel fuel, and toluene were chosen. Of course, an extremely wide range of crude oils exists, and the definition of a "standard" gasoline or diesel fuel is not chemically available. Hence the use of the various terms to describe these substances, e.g., "heavy, medium, light" or, "high or low" octane or cetane numbers, etc. This lack of exact chemical definition, of course, is understandable and perhaps has given rise to the often denigrated term "Total Petroleum Hydrocarbon". Give the site-specific, and, often, substance-specific uses this method has found it was appropriate to prepare exact mass/solvent concentration standards of various "typical" samples of crude oils, gasolines, and diesel fuels which were ampoulized as reference materials for the procedure. All standards were prepared using HPLC grade n-Heptane or a 20% (v/v) solution of carbon tetrachloride in heptane (Fisher Scientific). Two ranges were established according to the solvent selected: 1. (CCl_4/Heptane--low range--) 2, 10, 25, 50, 75, 100, 200, 500, 750, 1000 mg/Kg and, 2. (Heptane--high range--) 500, 2500, 10,000, 25,000, and 50,000 mg/Kg.

INSTRUMENTAL

The L-shaped test tube/probe holder was fabricated from black Delrin to configure the fiber optic probe orthogonally to the test tube at a distance of 7.0 mm. This resulted in a focused viewing area of 3.4 mm in diameter. The reflectance probe/fiber optic used was the R-200-7-LR; tungsten-halogen source, LS-1; spectrometer optical bench, PS1000 (Ocean Optics, Inc., Dunedin, FL). An aluminum housing for the complete assembly was

manufactured by Preferred Stampings of Texas, Inc., Round Rock, TX. The spectrometer was interfaced via a ribbon cable/A/D card (DAQCard-700, National Instruments) to an AST 486 SX/25 notebook PC. Data and graphs were printed on a portable printer (HP DeskJet 310). The portability of the complete system: Field test kit, spectrophotometer, computer and printer is such that it can easily be carried on-site and operated, and complete reports can be generated by the analyst.

EXPERIMENTAL PROTOCOL

Solutions were prepared in the ranges listed above corresponding to the amount of analyte extracted from a 5.0 gram soil sample using 10 ml (C_7/CCl_4) or 20 ml (C_7). One gram catalyst amounts were added to 4.2 ml aliquots of these solutions in the standard 100 mm x 15 mm test tubes according to the Hanby Field Test Kit protocol, and the solutions were hand shaken intermittently for 4 minutes, allowed to settle for 1 minute, and then read in the instrument. Four readings (with ca. 30 degree rotation of the tube between each) were taken for each concentration. The tristimulus value ztri was found to correlate extremely well with concentration for each set of readings. Virtually all readings were found to lie within five percent of the mean of the four readings. This verified the fact of the optimization of the tube/probe module configuration, and corresponded well with the typical test kit weighing and extraction error of +/- 5%.

DISCUSSION

The primary aim of this research was to test the application of the new instrument to this field test kit method of analysis. as illustrated by the data, confirmation of the applicability is proven. In the course of the experimental work, another desirable feature of the method was demonstrated. The utilization of this application of Friedel-Craft chemistry now extends to the "other" branch of this time-honored discovery, i.e., acylation. That is, previous employment of the method primarily exploited the intense colors produced by strong alkylation reactions promoted by use of very high ratios (>100:1) of the Lewis acid catalyst employed, and the use of the very reactive F-C solvent, carbon tetrachloride. Acylation reactions as well as reactions in which other alkylating agents, e.g., alkenes, are available in substances such as crude oils and fuels. Again, the fundamental principle of the Hanby method, i.e., the use of stoichiometrically very large proportions of the aluminum chloride catalyst which serve to dehydrate the extract and enhance the Friedel-Crafts reaction, is certainly key to the successful use of this procedure for the high concentration (ca. 50,000 PPM) ranges that are being allowed as interim soil contamination levels at designated sites. Implementation of these regulatory limits has been carefully considered by a number of oil-producing states and was recently effected by the Texas Railroad Commission. As stated in a classic text of analytical chemistry, "In the broadest sense, an instrument for chemical analysis converts an analytical signal that is usually not

directly detectable and understandable by a human to a form that is. Thus, an analytical instrument can be viewed as a communication device between the system under study and the scientist." This development can be regarded as a practical combination of the two divisions of analytical chemistry, classical or "wet" analysis and instrumental analysis.

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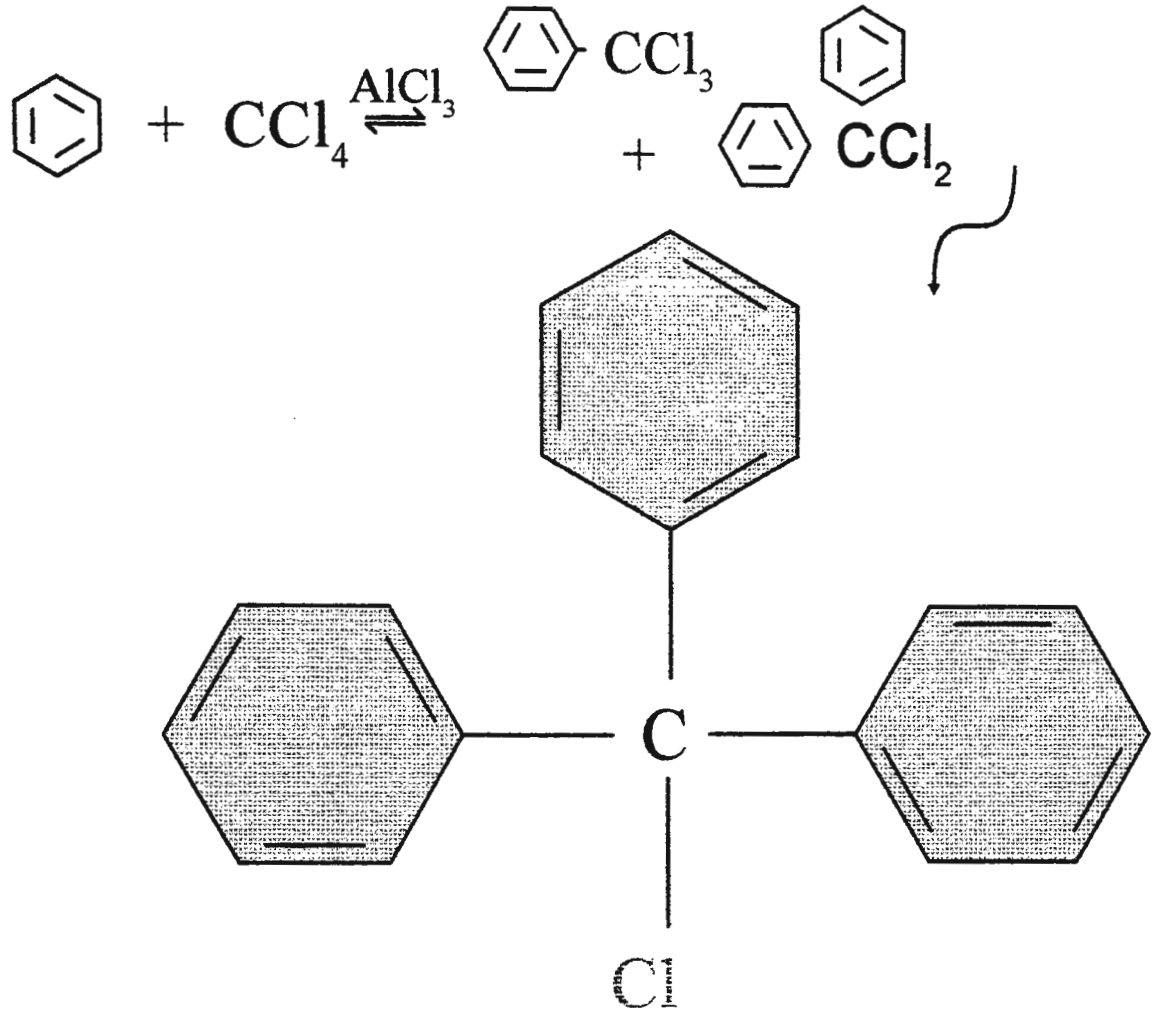
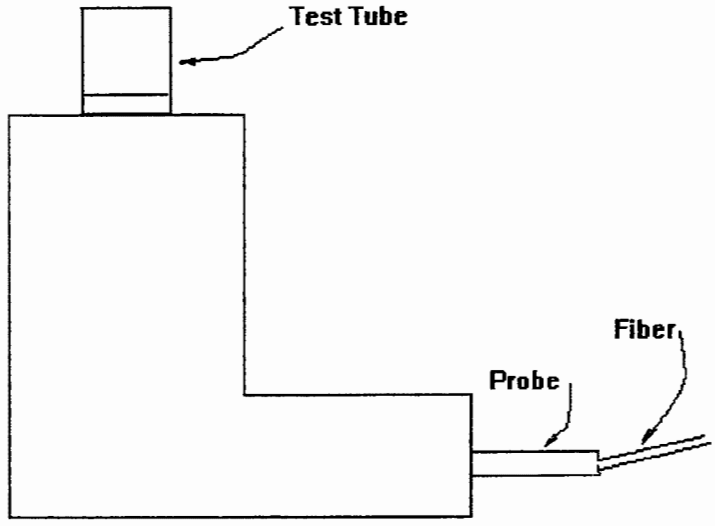


Friedel-Crafts alkyation reactions :

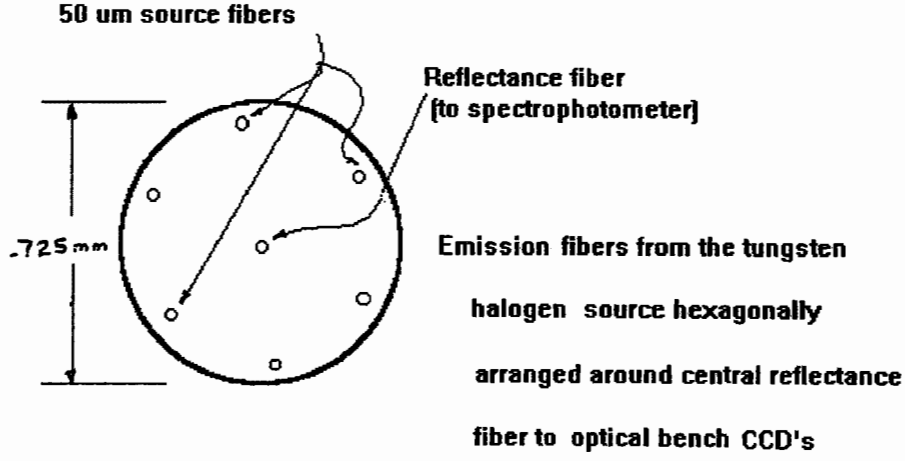
Formation of Mono- , Di- , and Tri-

Arylalkylhalide Structures

Intensely colored, UV-unstable

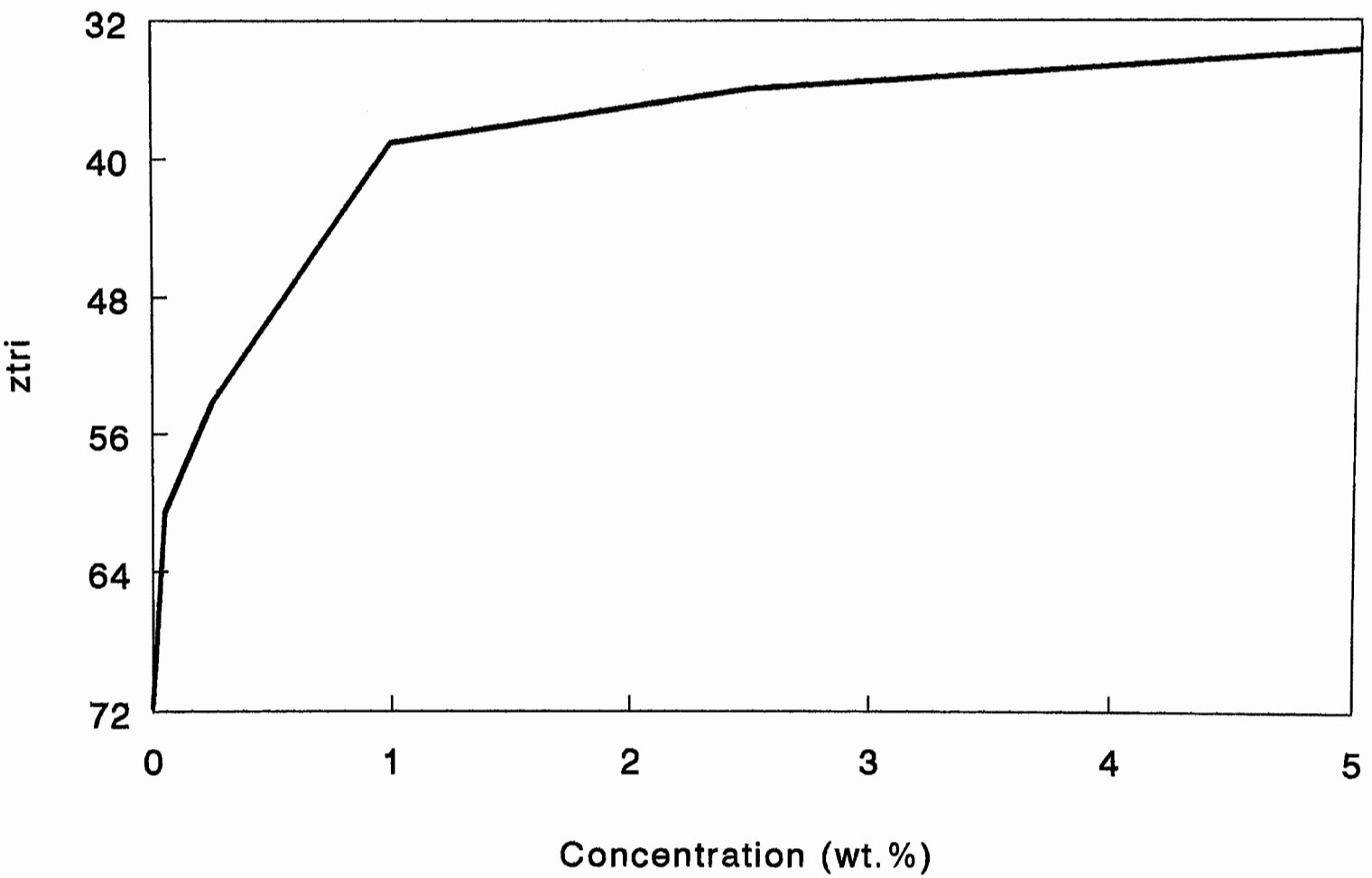


Test Tube Holder

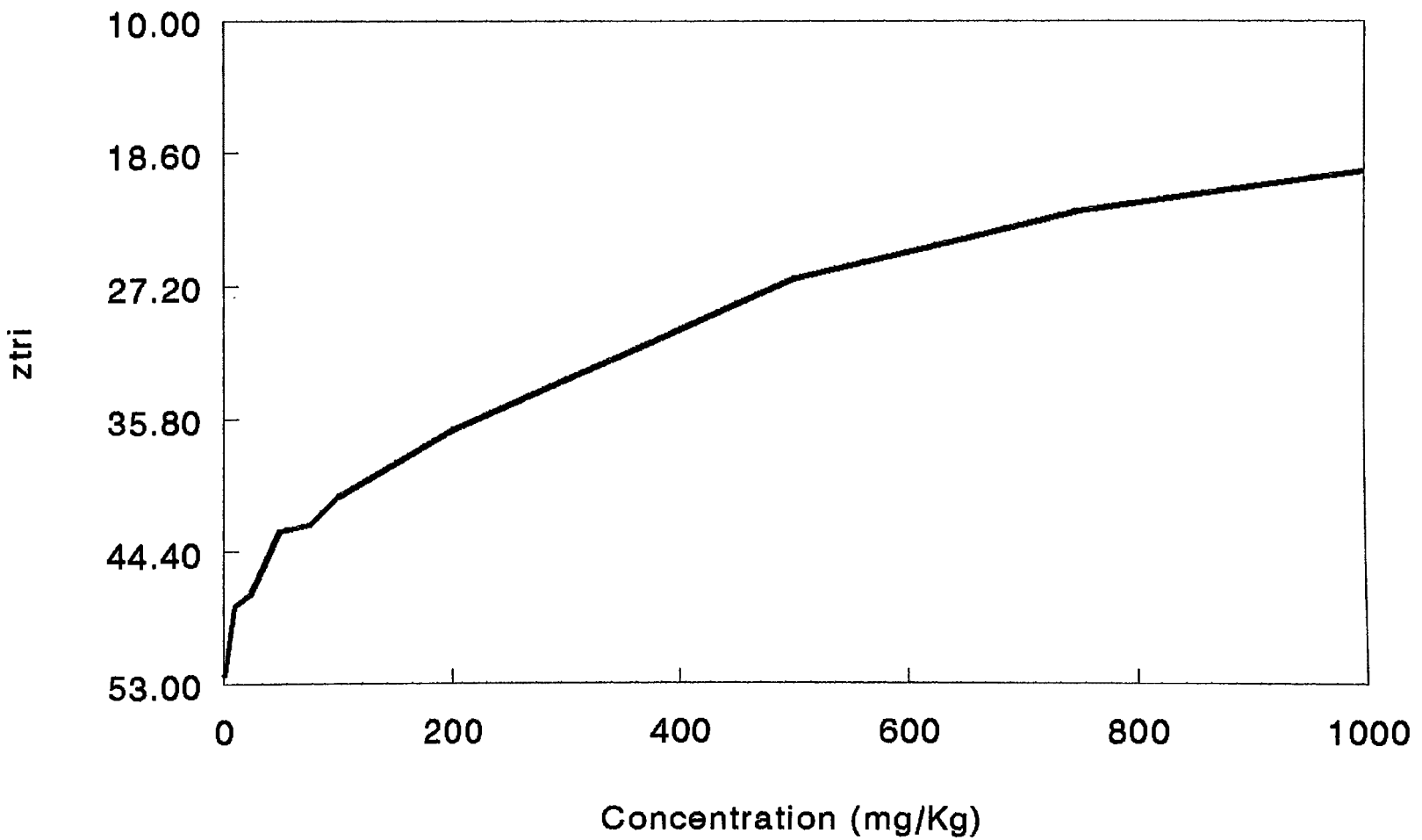


Fiber Optic Probe End Window

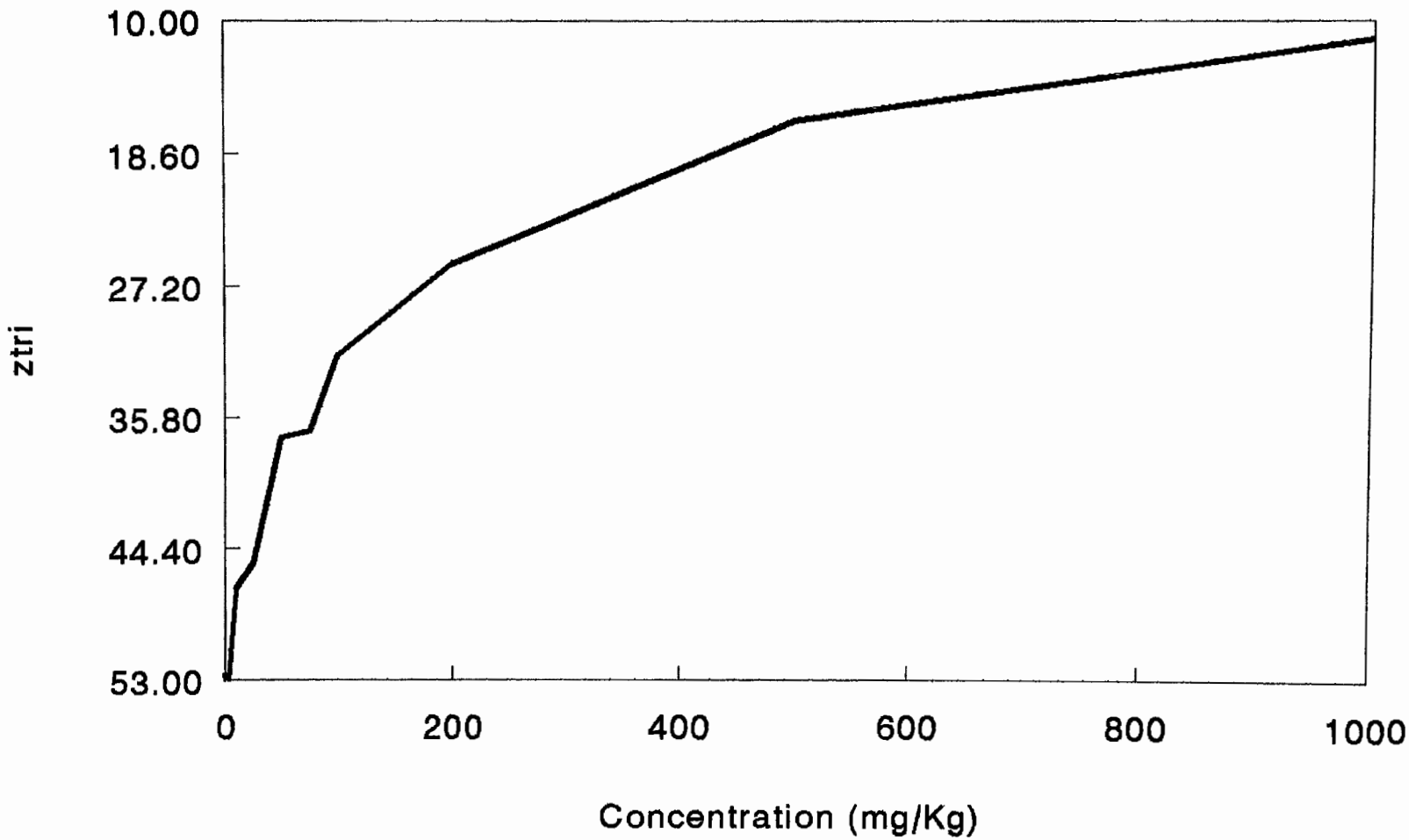
West Texas Crude Oil in Soil



Diesel in Soil



Gasoline in Soil



12

IMPROVED METHOD FOR SOIL ANALYSIS SCREENING BY HEATED HEADSPACE/ION TRAP MASS SPECTROMETRY

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Screening techniques generally offer a cost-effective alternative to conventional total analysis by GC/MS when determining organic contamination in soil. A semi-quantitative heated headspace screening method using deuterated internal standards and GC/ion trap mass spectrometry has been developed and successfully applied in a RCRA facility investigation (RFI). The method optimizes purge conditions to maximize sensitivity and enable detection of components not generally thought of as volatile materials. Possibly the most unique feature of this method is that quantitation is performed by addition of deuterated analogs of the analytes for most components. This approach greatly enhances the overall accuracy and precision of the method by virtually eliminating matrix effects that could change the relative responses of the internal standards and analytes in different samples. Our method of using isotopically labeled compounds for internal standards reduces to a minimum differences in relative responses since, chemically and physically, the internal standards and the analytes are almost identical, except for minor isotope effects.

The method has been used in a RFI to determine if any releases to the soil have occurred along several miles of process waste sewers. Twelve analytes that were typically found in the sewer were selected as indicator compounds which could be analyzed with the method quantitatively to determine if a release had occurred. With this selected list of analytes, the detection sensitivity ranged from sub-ppm to a few ppm depending on the compound.

As a part of the QA/QC protocol, about 10% of the screened samples were analyzed for volatile and semivolatile organics by conventional GC/MS analysis. This poster presentation gives the technical details of the developed method including the QA/QC protocols and the results of the application of this method to the analysis of approximately 200 RFI soil samples along with the details of the associated cost savings.

FIELD SCREENING OF VOLATILE CHLORINATED HYDROCARBONS BASED ON SONOCHEMISTRY

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ABSTRACT

A proof-of-principle was recently established of using ultrasound in combination with relatively simple electrochemical devices for monitoring volatile chlorinated hydrocarbons in water. The idea is to use sonochemistry to decompose pollutants such as trichloroethylene (TCE), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) into compounds or ions, such as Cl^-, which can be more easily detected than the parent compound. For example, one minute sonication of aqueous solutions containing ppm concentrations of TCE gives sufficient Cl^- which can be measured using commercially available Cl^- ion selective electrodes. Increases in Cl^- as a result of sonication indicates the presence of the chlorinated hydrocarbons. This method is not meant to replace laboratory methods. Rather it is meant to be used as a rapid field analytical method. Excellent correlation coefficients were obtained in Cl^- changes versus concentration of TCE, $CHCl_3$ and CCl_4 in low ppm ranges. Humic substances at concentrations up to 400 ppm did not adversely affect the Cl^- sonochemistry yield. Some lowering was noted at 800 ppm. It is concluded that none of the parameters investigated to date seriously impact on plans to develop miniaturized ultrasound chemical monitoring cells and to perform operational testing in the field.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has been examining the potential of combining ultrasound with other technologies for monitoring specific classes of organic pollutants in water. This is a new concept for field screening applicable to hazardous waste sites with particular emphasis on *in situ* groundwater monitoring. Ultrasound is defined as any sound of frequency beyond which the human ear can respond, i.e., above 16 KHz. Excellent summaries of the fundamentals of ultrasound are available[1,2]. Ultrasound in the range of 20-100 KHz affects chemical reactivity. Tiny bubbles are formed in liquids through ultrasound processes. The energy generated on collapse of these bubbles is given as the underlying reason for chemical transformations and enhancements (sonochemistry)[2].

The concept of using ultrasound in chemical analysis is illustrated in equation 1 using

$$CCl_4 + H_2O \xrightarrow{\text{Ultrasound}} Cl_2 + HCl + CO \qquad (1)$$

CCl_4 in water. Sonication of a solution containing the chlorinated target analytes yields ions or other products that can be measured using for example, ion selective electrodes (ISEs). Sonication of chlorinated hydrocarbons usually leads to the formation of Cl^-. Increases in Cl^- are an indication of the presence of the analyte. Initial experimental results were very promising[3,4]. Chloride ion was detected in aqueous solutions containing low ppm concentrations of CCl_4, $CHCl_3$, and TCE, after one minute of sonication. Chloride ion increases were accompanied by increases in conductivity and decreases of pH. Aromatic and polyaromatic chloro compounds (chlorobenzene and polychlorobiphenyls) did not form chloride ion as readily as did CCl_4, $CHCl_3$, and TCE. Changes in anion concentrations via sonication would be used in monitoring the target pollutants. The purpose of this paper is to present additional results on the use of sonochemistry in monitoring CCl_4, $CHCl_3$ and TCE in water with special emphasis on the potential for quantifying results in the field, and possible impacts due to the presence of humic substances.

EXPERIMENTAL

Chemicals and Test Solutions: The chlorinated hydrocarbons were obtained from Aldrich Chemical Co., Inc. in high purity grade (99%). Stock solutions were prepared in methanol and used for preparation of the test samples (1:100 dilution) with deionized water or a humic substance solution. Humic acids were obtained as follows: sodium salt of humic acid, technical grade from Aldrich Chemical Co.; humic acid from Fluka; and peat humic acid from International Humic Substances Society, Colorado School of Mines. Stock solutions were prepared by first mixing weighed amounts of the humic substance with 500 mL of deionized water in a 1 L volumetric flask. The solution was shaken for 2 minutes several times during the day and occasionally during the next two days. The volume was then adjusted to 1 L. The concentrations of the humic acids in the test solutions (weight/volume) were: sodium salt of humic acid (Aldrich)(**HANa**), 100 ppm, 200 ppm, 300 ppm, 400 ppm, humic acid (Fluka)(**HA**), 100 ppm, 200 ppm, 3000 ppm, 400 ppm, 800 ppm, and peat humic acid (**Peat**), reference grade, 400 ppm. The concentrations of CCl_4, $CHCl_3$, and TCE in the test samples were 40 ppm, 37 ppm, and 37 ppm, respectively.

Equipment and Procedures. A Branson Ultrasonic Corp. Sonifier Model 450 (20 kHz)was used for sonication of the sample solutions. The unit was equipped with a power supply, a soundproof box, a converter, and a 1/2" horn probe. There was also a cup horn which was not used in the present sonication experiments; however, because of its design, it served both as a convenient holder for reaction tubes and as a cooling

bath. Sonication was performed in borosilicate vials. Coolant was passed through the cup horn using a peristaltic pump in conjunction with a cooling bath. The output temperature of the cooling bath was set at -10°C. The optimum sample volume for use with the 1/2" horn probe was 15 mL. This allowed proper immersion of the probe. The horn probe was operated at the maximum output control setting i.e., 10, during the experiments. The average output power in the 1/2" horn probe was 120 W. A pulse mode of 80% was used. In the pulse mode, ultrasonic vibrations are transmitted to the test solution at a rate of one pulse per second. The pulse mode can be adjusted from 10 to 90%, enabling a solution to be processed at full ultrasonic intensity while limiting temperature build-up. The temperature of the samples after 1 minute sonication under the conditions of the present experiments was 30°C. Readers are referred to reference 3 for additional details on experimental procedures.

RESULTS AND DISCUSSION

Changes in Cl^- Concentration. An increase in Cl^- after sonication of an aqueous solution suspected to contain chlorinated hydrocarbons is taken as a positive test. Changes in Cl^- concentration for aqueous solutions of TCE (37 ppm), $CHCl_3$ (37 ppm), CCl_4 (40 ppm), and chlorobenzene (Ph-Cl)(94 ppm), were reported previously[3]. The greatest increase was noted for CCl_4; smaller changes were noted for $CHCl_3$ and TCE. The smallest changes were for Ph-Cl. We have now found that changes in Cl^- vs. concentration of CCl_4, $CHCl_3$, and TCE in the range of 3-80 ppm are linear with excellent correlation coefficients i.e., 0.995, 0.987, and 0.957, respectively. The same order of reactivity is evident as found earlier[3].

Perhaps the most important chemical parameter which needs to be taken into account in developing ultrasound monitoring methods is pH. Cheung and coworkers[5,6] recorded pH data in destroying organochlorine compounds in water as part of a remediation feasibility demonstration. The pH decreased rapidly in all cases. Using 1 minute sonication times and working with 15 mL samples of water containing various ppm amounts of chlorinated hydrocarbons, we confirmed that pH decreases. The relationship was found to be nonlinear.

Effect of Humic Acids. One of the important parameters that needs to be investigated in the use of sonication for chemical monitoring in ground water is the effect of dissolved humic substances. Soil organic matter is the source of humic materials which are divided into fulvic acids (soluble in acids and bases), humic acids (soluble in bases but not in acids), and humins (insoluble in acids and bases). Humic acid (50 to 80% by mass) and polysaccharides (10 to 30% by mass) may constitute up to 90% or more of the total humus in soil[7]. Formation of complexes between pollutants and dissolved humic substances may have a significant effect on the chemical reactivity and fate of the contaminants in natural systems (see reference 8 and citations therein). It was of interest to determine whether sonication of aqueous humic acid will lead to its decomposition. It was also necessary to establish whether humic substances will inhibit or accelerate Cl^-

formation in the sonolysis of chlorinated hydrocarbons. For example, the presence of humic acid was found to increase the reductive dehalogenation of chlorinated hydrocarbons in aqueous solutions containing ferrous ion by factors up to 10 (reference 9). Three different humic acid substances were examined. It is known that the structure of dissolved humic substances is affected by pH, ionic strength, and electrolyte cation valence (see citations in reference 10). These factors were not investigated in our sonochemistry studies. Instead, "high" concentrations of the humic acids were utilized in an effort to discover major effects.

The Cl^- concentrations, as determined by an ISE using the 400 ppm solutions of HANa, HA, and Peat, were found to be 2.0, 13, and 1.0 ppm, respectively. The pH values were 8.1, 6.1, and 6.0, respectively. The conductivity values (μS/cm) were 135, 91, and 6, respectively. It was noted that the solutions were cloudy. Filtering the humic acid sodium salt and the Fluka humic acid solutions with either WVR qualitative filter paper or Micropore 0.45 μm filter paper did not change the results. It is clear that the peat humic acid is much less ionic in water in comparison to the other two samples. *Sonication of the humic acid solutions for one minute did not affect the values within experimental limits, indicating stability to ultrasound.* If measurable decomposition occurred, one would have at least expected changes in conductivity.

A number of experiments were performed to compare changes in Cl^- concentration in the sonolysis of TCE, $CHCl_3$, and CCl_4 in the presence of humic acids. No significant changes with humic acid sodium salt and Fluka humic acid (100 - 400 mg/L), and peat humic acid (400 mg/L) were noted in comparison to deionized water alone. No significant effect was noted as a result of filtering the Fluka humic acid (400 mg/L). However, it was noted that the presence of humic acid sodium salt at 800 mg/L did reduce Cl^- formation.

Conductivity increases and pH decreases were much smaller in the presence of humic acids than in their absence (peat humic acid gave the greatest changes among the substances examined). Generally, it appears that the presence of humic substances such as the ones examined, at least up to 400 mg/L, will not be a problem in Cl^- monitoring using ultrasound.

Another important question for sonolysis experiments in the real world for monitoring applications relates to the effect of suspended particles. Kotronarou[11] studied the effect of large sand particles (500 μm average) and fine particles (7 nm average) on the sonication rate of sulfide oxidation. Large particles might be expected to decrease the rate because of sound attenuation. The fine particles might enhance the rate by providing additional nuclei for bubble formation. The effects of sand particles at the sizes and concentrations studied were insignificant. This implies that no problems should be encountered in chemical monitoring scenarios. Also, as mentioned above, filtering humic acid solutions containing very finely divided material, made no difference in the sonication yields of Cl^-.

SUMMARY

The use of sonication in combination with measuring changes in Cl^-, in real time is a very simple approach in monitoring organochlorine compounds in water. However, there are many parameters that may affect the rate of Cl^- production. One may not necessarily be able to provide controls in a field situation to optimize the course of sonochemical reactions. For field screening, in situations in which the potential contaminants are known and in which the water system characteristics are understood, optimization may not be needed. Sonication experiments with water from a particular location using potential pollutants of interest should allow an understanding of what to expect in monitoring the water and what the data obtained from that source means. As mentioned above, it appears that the presence of humic acids will not cause problems.

Design of the ultrasound system and equipment options are very important; they affect sonochemistry performance. The ultimate goal for field measurements is to design an ultrasound system which would allow a probe to be placed into 2" and 4" diameter monitoring wells. Preliminary engineering designs were not considered under the scope of this work, but the possibility of miniaturized ultrasound systems appears feasible. For example, tapered microtip horns are commercially available with diameters of 3.2 mm. These can be used for volumes ranging from 1-2 mL. The design of a cell system compatible for both sonolysis and reaction product measurements present technical challenges, but these do not appear insurmountable.

The sonication approach is applicable to organic compounds which contain other halides, phosphorus, nitrogen, and sulfur that, when released as anions, could be easily quantified. It is judged that ultrasound may be very useful as an *in situ* technique for monitoring the effectiveness of remediation processes and for post-closure monitoring. The potential of ultrasound systems for monitoring chemicals in water is judged to be high. Predicted attributes include:

Adaptabitity to miniaturization,
User friendliness,
No sampling requirements,
No solvents,
No wastes,
Self-cleaning,
In situ generation of reagents, and
Adaptability to networking.

ACKNOWLEDGMENT

Parts of this work were performed at the Harry Reid Center for Environmental Studies, University of Nevada - Las Vegas.

NOTICE

The U.S. Environmental Protection Agency (EPA, through its Office of Research and Development (ORD), partially funded and collaborated in the research described here. It has been subjected to the Agency's peer review and has been approved as a publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The U.S. Government has a non-exclusive, royalty-free license in and to any copyright covering this article.

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THE ENVIRONMENTAL RESPONSE TEAM'S (ERT's) ON-SITE (MOBILE) ANALYTICAL LABORATORY SUPPORT ACTIVITIES

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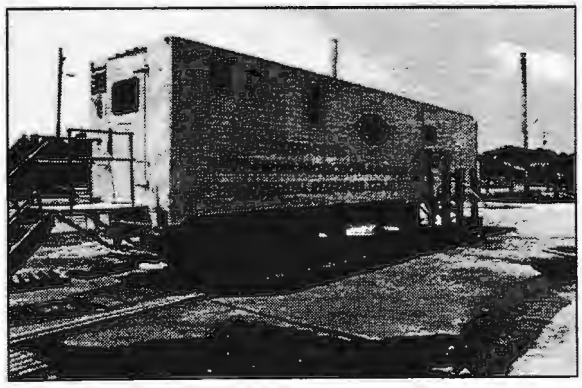
ABSTRACT

One of the critical factors for successfully conducting site evaluation/removal activities is immediate and appropriate analytical laboratory response. The United States Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT) is at the forefront of efforts to utilize on-site analytical laboratory support (mobile laboratories) to provide rapid turnaround of analytical results, the flexibility to meet changing requirements, and immediate interpretation of complex results during emergency response and removal activities.

On-site analytical support has proven to be a viable, cost-effective approach in providing quick turnaround of environmental sample analysis results for site evaluation/characterization, especially during emergencies and removal actions.

INTRODUCTION

The EPA/ERT's mobile laboratory fleet has grown from one unit to five units in the last ten years. Sample results which previously took site managers days or even weeks to receive from fixed laboratories are now available from real-time to within a few hours. Through the Response Engineering and Analytical Contract (REAC) and the Technical Assistance Team (TAT), the U.S. EPA/ERT has successfully implemented and utilized mobile laboratory support at over 200 sites, saving over two million dollars in sample analysis cost and unaccounted field personnel hours.



The U.S. EPA/ERT mobile laboratory is fully equipped with state-of-the-art instrumentation to provide analysis support.

BACKGROUND

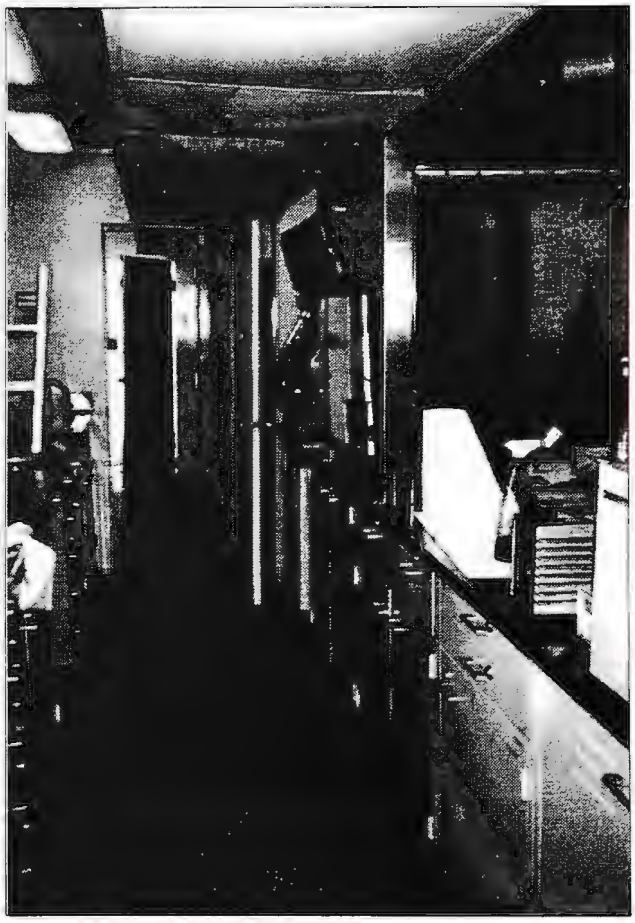
The U.S. EPA/ERT was established in October 1978 to provide technical assistance to federal On-Scene Coordinators (OSCs), Regional Response Teams (RRTs), the National Response Team (NRT), U.S. EPA Headquarters and regional offices, and other federal/state government agencies. The U.S. EPA/ERT also provides environmental emergency assistance to foreign governments during such environmental emergencies as chemical spills, chemical fires, and oil spills.

CAPABILITIES

The mobile laboratories combine state-of-the-art instrumentation with U.S. EPA/ERT approved methodologies and rigorous Quality Assurance/Quality Control (QA/QC) procedures to provide immediate and accurate data analysis.

Some of the procedures include holding time, frequency of blank and matrix spikes required, and expected recovery ranges for surrogates and matrix spikes as specified in the U.S. EPA methodologies. Instrumentation is also required to meet all the criteria for tuning, initial calibration, continuing calibration, and check (or verification) standards. Detection limits are established before the methodologies are adapted and verified as needed. Blind [performance evaluation (PE)] samples are occasionally included with field samples collected. All of these procedures are employed to ensure the reliability of the analytical data.

Furthermore, on-site laboratory operations conform to all relevant U.S. EPA and Occupational Safety and Health Administration (OSHA) regulations to ensure the safety of personnel operating the analytical equipment. The analytical laboratory



Mobile laboratories can be equipped with fume hoods, gas chromatographs, gas chromatograph/mass spectrometer, atomic absorption spectrometers, glove boxes, dependant on the analyses required at each site.

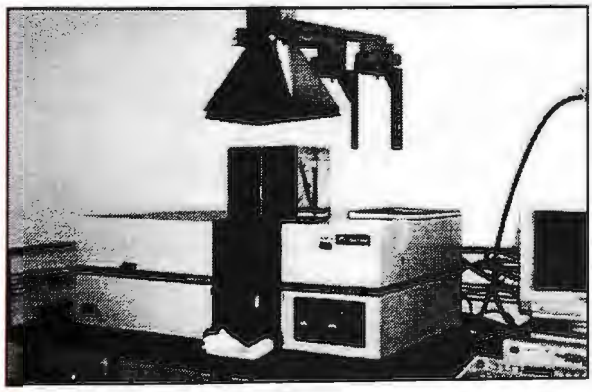
capabilities can be used for on-site characterization of pollutant levels in soil, water, and complex sample matrices, including:

- Atomic absorption (AA) spectroscopy for inorganic metal analyses of water, soil and other media.
- Gas chromatograph (GC) for analysis of pesticide/poly-chlorinated biphenyls (PCBs), pentachlorophenol (PCP), and creosote in environmental samples.
- Gas chromatography/mass spectrometry (GC/MS) for analysis of base neutral/acid extractables (BNAs), volatile organics (VOAs), PCP, and creosote in environmental samples.
- Gas chromatograph/photo ionization detection (GC/PID) of volatiles in water, soils, and soil gas in bags and acetate sleeves.
- X-ray fluorescence (XRF) for analysis of metal contaminants in soil and nonroutine elements in other media.
- Extraction and analysis of nonroutine pollutants (such as dicamba and benzonitrile), as necessary, using GC electron capture detector (ECD) and flame ionization detector (FID).

CASE STUDIES

Aladin Plating

The Aladdin Plating site, located in Chinchilla, PA, was an abandoned "backyard" chrome-plating operation located on top of a hill. Plating waste was dumped on the ground and concentrated near the operation but also had spread downslope toward nearby properties. Based on earlier characterization studies, remedial activities were undertaken to clean up the site. The soil contaminant of concern was total chromium (Cr), however, hexavalent chromium (Cr^{6+}) was also suspected as a groundwater contaminant. The action level set by the site manager was 50 parts per million (ppm) total Cr.



Atomic Absorption (AA) unit.

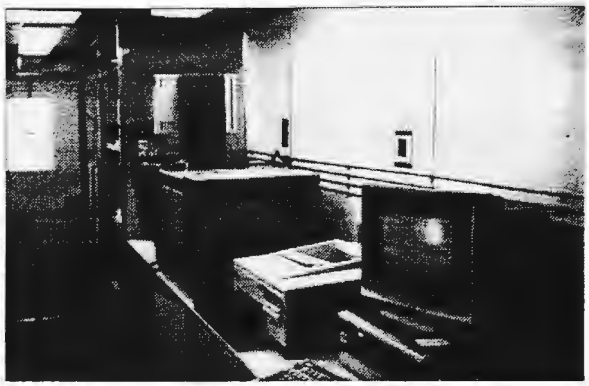
An on-site laboratory was set up in a trailer to provide Cr/Cr^{6+} analysis for the months of October and November 1990 and during the spring of 1991. Analytical instrumentation included a portable AA unit for Cr analysis and a portable spectrophotometer for determination of Cr^{6+}. Samples were prepared and analyzed

using standard U.S. EPA methodologies, including PE samples, to satisfy rigorous QA/QC protocol. The majority of samples were analyzed for total Cr with less than five percent for Cr^{6+}. Typically, 10-15 samples/day were analyzed over a 3- to 5-month period, providing reliable same-day results to guide additional remedial activities.

The availability of on-site analytical laboratory support facilitated efficient removal actions by providing the RPM cost-effective, same day turnaround with no compromise in data quality or reliability.

Shavers Farm

Shavers Farm, an abandoned farm site in Chicamauge, GA, was used as an industrial waste landfill between 1973 and 1974 and was an approved landfill by the state of Georgia. Many of the drums deposited in the landfill had corroded and leaked their contents contaminating the surrounding grounds. Soil and drum contaminants of concern included dicamba and benzonitrile.



Computer systems are utilized to track data.

A mobile trailer laboratory was set up in May 1990 to support site excavation/removal actions. Laboratory instrumentation included two dedicated GC systems: one to analyze benzonitrile using an FID, and one to analyze dicamba using an ECD. U.S. EPA-approved methods were modified for field analysis of soil and drum samples. The modified methods provided quick extraction times and low detection levels; 2 milligram per kilogram (mg/kg) for dicamba and 5 mg/kg for benzonitrile. These detection levels were well below the 25 mg/kg action level set by the OSC. Typically, 15-20 samples/day were analyzed over a 5-month period, providing fast results to guide next-day excavation/removal activities. Reliability was ensured by analyzing PE samples in accordance with strict QA/QC criteria.

On-site analysis of dicamba and benzonitrile contaminant levels provided the OSC with critical data for field decisions on appropriate removal actions. Fast (24-hour) turnaround incorporating rigorous QA/QC protocol guaranteed reliability of analytical results used in that decision process.

Petrochem

The Petrochem site, located in Salt Lake City, UT, was utilized (prior to 1987) as a hazardous waste storage facility and a hazardous waste incineration/waste oil recycling facility. Storage tanks and drums were in poor condition and numerous spills of oil, acid, and caustic had been documented. Soil and water pollutants of concern included PCBs, BNAs, VOAs, and polyaromatic hydrocarbons (PAHs).

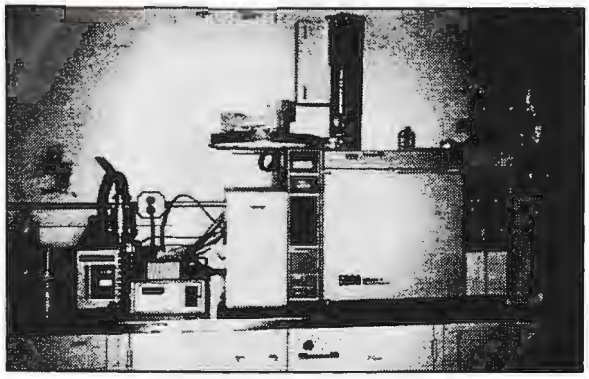
Mobile laboratory: Sample preparation.

A laboratory was set up at the Water Resource Center in Salt Lake City to support site assessment/characterization activities during the months of May and June 1990. Instrumentation included a GC with dual detectors (ECD and FID), a GC/MS, and a separate portable GC with a PID. Analyses performed on samples included: pesticide/PCBs by GC/ECD methods; BNAs, PAHs, and Oil fingerprints by GC/FID with GC/MS confirmation; and VOAs utilizing the portable GC/PID. U.S. EPA methods were modified for field analysis while maintaining high data quality in accordance with strict QA/QC protocol. Approximately 150 samples were analyzed over a 1-month period, providing fast (24-hour) turnaround and high quality results to the OSC.

Mobile-analytical-laboratory support provided fast turnaround on high-quality analyses of several critical pollutants to assist the OSC in the assessment and characterization of site contamination.

Escambia Woodtreating Sites

The Escambia Treating Company operated four woodtreating facilities located in Pensacola, FL; Brookhaven, MS; Camilla, GA; and Brunswick, GA. Wooden telephone poles and foundation pilings were manufactured and treated at these facilities from the 1940s until they were closed between 1982 and 1991. Poor handling practices in the treating facilities resulted in PCP and creosote contamination of soil throughout each site.



A gas chromatograph/mass spectrometer (GC/MS).

It was necessary to analyze samples containing dioxin waste material which could not be analyzed at the ERT/REAC Edison laboratories. Therefore, an on-site High Hazard laboratory was established in May 1991 at the Brunswick, GA site to provide fast turnaround on PCP and creosote analyses for dioxin-contaminated samples, using modified U.S. EPA methods while maintaining high quality of analytical results. This laboratory provided analytical capabilities for all Escambia locations. Instrumentation included GC/FID systems in operation since the laboratory was mobilized in 1991. Over 1,000 samples were analyzed using GC/FID. GC/FID was replaced by GC/MS in 1992 and a GC/MS method was established which provides 24-hour turnaround for analyses of 15-20 samples per day. Large sample batches for PCP analysis have also been processed and analyzed by GC/MS, resulting in 240 samples analyzed within a 2- to 3-week period. Over 4,000 samples have been analyzed by GC/MS between 1992 and 1995.

Ongoing operations at this High Hazard laboratory continue to provide high-quality, fast, cost-effective analyses for site characterization, treatability studies, and remediation/removal activities at several hazardous waste sites. Capabilities are continually updated and improved as new analytical technology becomes available.

OTHER SITES

In addition to the case studies discussed above, the U.S. EPA/ERT has utilized on-site analytical laboratory support at over 200 sites in the United States (Figure 1). For example, PCBs were analyzed at Pagano Salvage in Los Lunas, NM, Beck Street Salvage in Salt Lake City, UT, and Raymark site in Statford, CT; PCP contamination was determined for Rocky Boy Post and Pole in Box Elder, MT and at the Blackfeet Pencil Factory site in Browning, MT; and, Toxaphene levels were determined by GC/ECD at the FCX site in Washington, NC.

ENVIRONMENTAL RESPONSE TEAM (ERT) FIELD SUPPORT

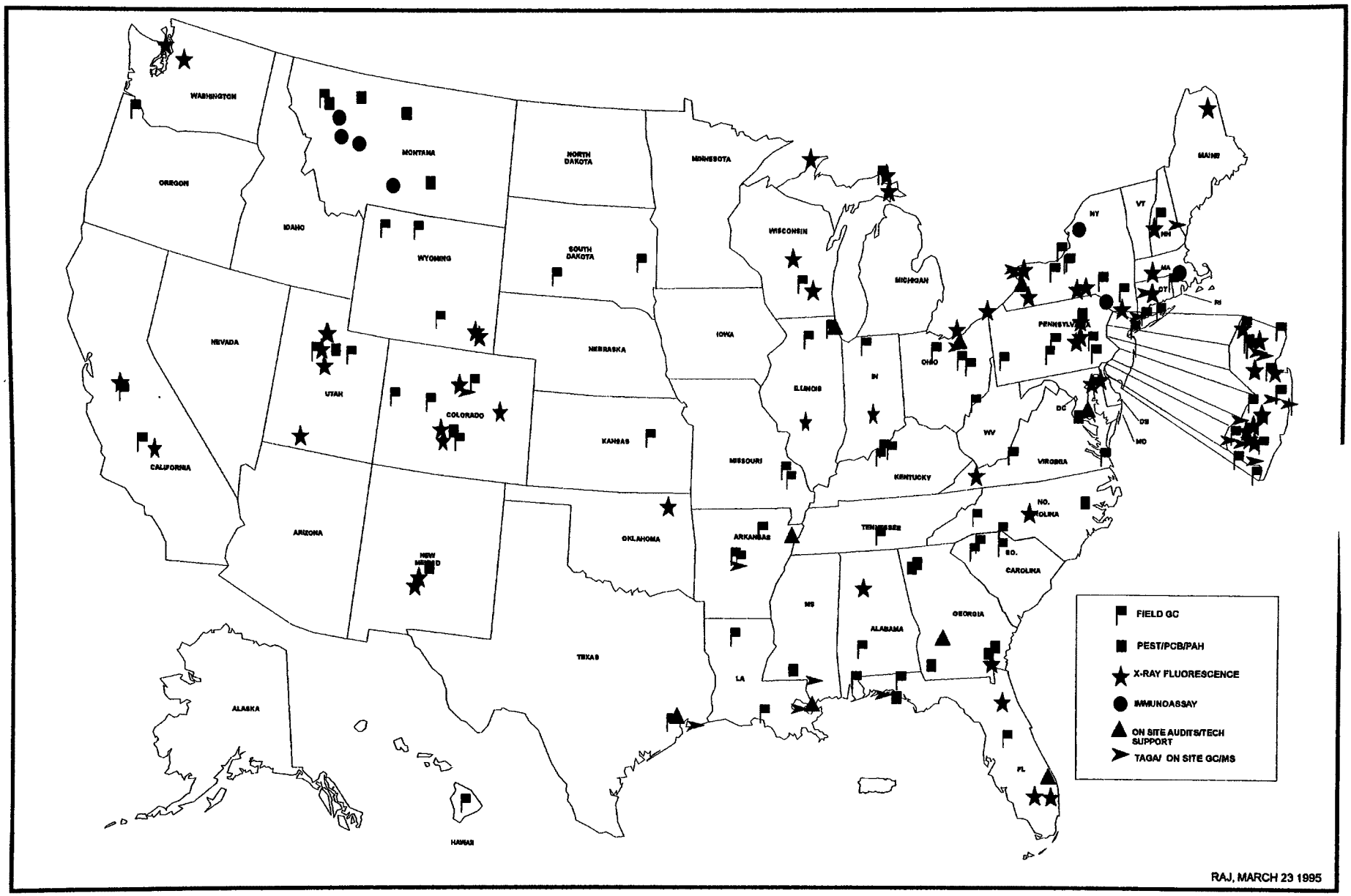


FIG-1

CONCLUSIONS

On-site mobile laboratory analytical support has proven to be a viable, effective approach to meet pollutant analysis needs in many U.S. EPA/ERT hazardous waste evaluation/removal programs. High-quality results are achieved with quick turnaround using U.S. EPA-approved analysis methodologies incorporating rigorous QA/QC procedures. The availability of highly reliable on-site laboratory analyses provides site managers with the data needed to guide critical field decisions concerning remediation/removal actions while at the same time realizing cost and time savings compared to analysis associated with outside laboratories. The scope of the U.S. EPA/ERT mobile laboratory functions and capabilities spans the United States and continues to broaden.

ACKNOWLEDGEMENTS

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A NEW SOIL SAMPLING AND SOIL STORAGE SYSTEM FOR VOLATILE ORGANIC COMPOUND ANALYSIS

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ABSTRACT

The design and performance of a new stainless steel coring device, the EnCore sampler will be presented. This device is made in two sizes, a 25 gm version for methanol preservation, and a 5 gm version made for EPA SW846 method 5035. The sampler is designed to both sample and hold a plug of soil for an interval of time so that the limitations of using other methods in the field are overcome. The data shows that the sampler can hold the target Volatile Organic Compounds for a minimum of 48 hours. This will allow the field personnel to bring the sample to the laboratory for either preservation in methanol or for preparation into a soil vial.

INTRODUCTION

Wisconsin implemented methanol preservation for soil BETX and GRO and is in the process of implementing the method of VOCs. A new sampler, called the EnCore sampler, was developed to overcome the need for using methanol in the field. This stainless steel device is designed to sample a 25 gm soil core. The sampler has a cap containing a Viton O-ring and when the cap is attached, the chamber forms an air-tight seal. The back of the chamber has a moveable plate which is held in place by a nut. The moveable plate is sealed to the back of the chamber with a small Viton O-ring. When the sampler is filled with soil and sealed, the sampler can be used as a sample container and can be sent back to the laboratory on ice. The laboratory detaches the nut and extrudes the soil into the methanol. Recently, a 5 gm version became available which performs exactly the same way but extrudes a soil plug into a 40 ml VOC vial. A disposable sampler is also in development and its performance relative to the stainless steel samplers will be discussed.

EXPERIMENTAL

A soil mixing system as described in another paper in these proceedings was used to generate samples for testing different methods of sampling and various methods for storing the samples for VOC analysis. Common methods such as using a spatula, brass tube, plastic syringe, plastic baggy and the EnCore sampler were compared when sampled and handled immediately versus holding on ice for up to 48 hours.

RESULTS AND DISCUSSION

The results indicate that the method of sampling is not as critical as the method of storage for obtaining reliable VOC results. If sampled quickly, all methods tested provided equivalent results. If samples are held two hours, however, only the brass tube and the EnCore sampler provided results equivalent to results with no storage. When the brass tube and the EnCore sampler were compared to 48 hours, only the EnCore sampler showed high recovery. When stored more than 48 hours, the EnCore sampler shows a steady decline in BETX compounds, probably due to biodegradation.
Based upon these results it is recommended that 3 EnCore samplers be taken per sample location. A 48 hour time limit is placed on samples in the EnCore device. One of the samples is used to screen for high/low level VOCs. If the sample is low level, then the other two soils are extruded into 40 ml vials or into Dynatech soil vials for low level analysis. If the sample is high level, at least one sample is extruded into methanol. In this way, limitations that exist with both methanol and the soil vial method can be overcome, i.e., methanol can be eliminated from the field and low level detection limits are possible and expensive, breakable glass vials are not needed for the field and high level samples will be identified so they do not "overload" the low level system.

CONCLUSION

The EnCore sampler may provide a simple, short term method for hold soil VOC samples until the proper preparation method is determined.

PERFORMANCE EVALUATION OF A NEW LOW-COST FIELD TEST KIT FOR ANALYSIS OF HYDROCARBON-CONTAMINATED SOIL AT A DIESEL FUEL RELEASE SITE

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ABSTRACT

Dexsil Corporation's new low cost PetroFLAG™ field test kit was used in conjunction with a mobile laboratory to field test soil contaminated by diesel fuel. This innovative new technology uses no CFCs and is completely field portable. Initially the PetroFLAG field test results were compared directly to sample splits analyzed by an on-site mobile laboratory using EPA method 8015 for diesel. The field generated PetroFLAG results proved to be very accurate when compared to the mobile laboratory results. The first time PetroFLAG users required only 5 minutes of training to become proficient enough at using the test kit to achieve this high degree of correlation. Due to the excellent correlation between PetroFLAG results and the mobile laboratory results, the PetroFLAG test kit was used exclusively in the field to find the zero line of contamination in the soil. When the PetroFLAG test indicated that no hydrocarbons were present in the soil, the sample was given to the mobile laboratory for confirmation analysis. By using the PetroFLAG test, site work including lateral and vertical definition of the contaminated area and excavation and removal of the contaminated soil could proceed without delays caused by lack of test data. The mobile laboratory was spared the inconvenience of "hot" samples that might otherwise overload the laboratory equipment necessitating a time consuming recalibration, thus saving time and expense. Overall, the use of the PetroFLAG test kit allowed more samples to be tested at a low cost, freed up the mobile laboratory to perform confirmation analysis only, provided an accurate method for locating the zero line of contamination so that additional volumes of uncontaminated soil were not excavated, accelerated the project, and helped to keep the project, equipment and manpower working without delays.

INTRODUCTION

Releases of petroleum hydrocarbons to surface and subsurface environments are an unfortunate reality in todays world. These releases can result in significant degradation of the quality of our soil and water resources and may result in substantial health risks to people, plants, and animals in the vicinity of the release. Environmental professionals are typically called upon when a release of petroleum hydrocarbons is reported to assess the nature and extent of the release and to formulate a remedial action plan to address the problem. The characterization work is frequently conducted on an emergency response basis, requiring rapid turn around of data to support remedial decisions in the field.

A common problem with characterizing the nature and extent of petroleum hydrocarbons in soil at a release site has been the lack of a quick, easy to use and accurate method of measuring the concentration of petroleum hydrocarbons in soil at the site. Typically, soil vapors are measured using a field photoionization detector (PID) or other similar device to test for the presence of gasoline in soil, while observations of staining and odors are used to check for the presence of "heavier", less volatile petroleum hydrocarbons (i.e., diesel, motor oil, kerosene, jet fuel, crude oil). These semi-quantitative field data are often used to direct soil excavation activities and to determine where confirmation samples are to be collected and sent to a state-certified laboratory for analysis.

Use of these semi-quantitative field methods typically results in the following problems: false positives (field methods indicate the presence of petroleum hydrocarbons where they are not present) resulting in unnecessary excavation, excessive confirmation sampling and lost time and money; false negatives (field indicators do not indicate the presence of petroleum hydrocarbons where they are present above the target concentration) resulting in re-excavation of areas presumed to be "clean" and lost time and money; uncertainty in the data, resulting in excessive confirmation sampling and down time.

Dexsil Corporation, recognizing the need for a fast, low cost, quantitative field test for determining the concentration of a full range of hydrocarbon contaminants in soil, recently developed the PetroFLAG field test kit. The PetroFLAG test is inexpensive, fast, easy to learn and yields quantitative results for a full range of hydrocarbons in soil. The PetroFLAG analyzer displays sample results directly in parts per million (ppm). The test kit can be used to analyze one sample, or multiple samples at a time.

Correlation between PetroFLAG test results and standard EPA Laboratory methods 8015 and 418.1 is excellent. The PetroFLAG test kit provides environmental professionals with a new tool to perform quantitative on-site sample analysis quickly and inexpensively. PetroFLAG test results can be used to determine when and where to collect soil samples for (more expensive) laboratory confirmation analysis, thus eliminating subjective observations such as soil color and soil odor for the process.

This paper presents a case study involving the use of the PetroFLAG test kit at a diesel fuel release site where excavation was the selected remedial measure.

BACKGROUND

Several thousand gallons of diesel fuel were released from an underground pipeline beneath the roadway in a residential neighborhood in California. The diesel fuel was released under pressure from the top of the pipeline at approximately 3 feet below ground surface, resulting in the upward migration and lateral spread of the diesel beneath the asphalt road. Some of the diesel emerged from the seams between the asphalt road and the concrete sidewalk and subsequently flowed above ground into an adjacent storm drain.

Levine•Fricke, Inc. was called in to assess the nature and extent of the release and to formulate a remedial action plan for the site. Levine•Fricke is a nation-wide full-service environmental consulting firm and is recognized as an industry leader in the characterizing and remediation of petroleum-affected sites.

Due to the residential setting of the site and the specific concerns of the local residents, the responsible party agreed to excavate the diesel-affected soil beneath the road to a concentration below laboratory detection limits (i.e., less than 1 ppm for total petroleum hydrocarbons as diesel [TPH/d]). The excavated diesel-affected soil is to be treated using bioremediation at an off-site location. A mobile laboratory was dispatched to the site to provide real-time on-site data to help direct the excavation. In addition, Levine•Fricke arranged for an on-site demonstration of the PetroFLAG test kit by a representative of Dexsil Corporation to help assess whether PetroFLAG would be appropriate for use at the Site.

The following sections discuss how the PetroFLAG test kit was used on the project.

FIELD PROCEDURES

Training and Confirmation Sampling;

A representative of Dexsil Corporation provided Levine•Fricke personnel with a demonstration on the morning of the second day of the excavation activities. The demonstration consisted of calibrating the PetroFLAG analyzer using two prepackaged calibration standards. The calibration standards consist of a blank and a 1000 ppm spike, and are provided with every ten pack of soil test reagents used in the PetroFLAG test kit. The on-site calibration took approximately 10 minutes to perform.

A ten gram sample of the soil from the site was weighed directly into the extraction container and a premeasured ampulized extraction solvent mixture was added to the soil sample. A timer was set, and the soil and extraction solvent were then shaken vigorously several times during the first four minutes of the five minute extraction period. The mixture was allowed to settle during the final minute. The solvent/soil mixture was then decanted into a filter syringe and the sample extract was filtered directly into a cuvette containing the pre-measured color development solution. The digital timer was then set for ten minutes (the color development quantification period). The cuvetted contents were then mixed thoroughly during this period. At the end of the ten minute quantification period, the cuvette was placed into the calibrated PetroFLAG Analyzer and analyzed for diesel. The total demonstration including analyzer calibration took approximately 25 minutes.

Upon completion of the demonstration, Levine•Fricke personnel collected a soil sample near the excavation and split the sample into two sub-samples. One sample split was analyzed by the on-site mobile laboratory for TPH/d using EPA method 8015; the other split sample was analyzed for TPH/d using the methods described above. The short demonstration period was sufficient for Levine• Fricke personnel to conduct the analysis using the PetroFLAG kit. Results from both analyses were below detection limits (e.g. less than 1 ppm) for the mobile laboratory. The PetroFLAG result was zero. Based partially on these results, and the quick and easy nature of the PetroFLAG analysis method, PetroFLAG was selected for use at the site.

Excavation and Sampling Procedures

The objective of the remedial action plan was to excavate petroleum-affected soil with a concentration of TPH/d greater than the laboratory detection limit (1 ppm) from the site. To meet this objective, soil samples were collected from the bottom and sidewalls of the excavation using a slide-hammer sampler fitted with clean brass liners. Subsamples were collected from the brass liners and analyzed for TPH/d using the PetroFLAG test kit.

Results of the PetroFLAG analyses were used to assess whether additional excavation would be required in the area sampled and to assess where confirmation samples were to be collected. If the results from the PetroFLAG analysis indicated the presence of petroleum hydrocarbons above 1 ppm, additional excavation was conducted in that area. When the results of the PetroFLAG analysis indicated that petroleum hydrocarbons were not present, the subject sample was sent to a state-certified laboratory for confirmatory analysis and excavation in that portion of the site was stopped. After results were received from the state-certified laboratory confirming the PetroFLAG results, the area was backfilled with clean fill, compacted and paved. This procedure was followed until the entire portion of the road was remediated.

Approximately 210 samples were analyzed on-site using the PetroFLAG test kit during the excavation work (approximately 8 weeks). Of the 156 samples that were sent to the state-certified laboratory for confirmation, only 3 samples had results greater than the detection limit (at 3, 4 and 17 ppm, respectively). Based on the excellent agreement between results from PetroFLAG analysis and analysis results from the state-certified laboratory, the mobile laboratory was sent off of the Site after two weeks and confirmatory samples were sent to a (less expensive) stationary laboratory.

RESULTS AND DISCUSSION

Training

The on-site training session for Levine•Fricke personnel took approximately 25 minutes to complete,10 minutes of that time consisted of calibrating the PetroFLAG analyzer. From this short training session,

Levine•Fricke personnel were able to use the PetroFLAG test kit with confidence on the same day, immediately after the training session. Levine•Fricke personnel operated the PetroFLAG test kit several times a day during the excavation project with virtually no problems or delays.

Results of Confirmation Analysis

Of the 156 samples analyzed using PetroFLAG and sent to the state-certified laboratory for confirmation, only 3 had results greater than the detection limit (at 3, 4, and 17 ppm, respectively). It is possible that the disagreement in the results associated with these samples may have been the result of soil heterogeneity's within the collected soil sample volume. In any case, the data collected during this study indicate an excellent agreement between PetroFLAG results and results from a stationary, state-certified laboratory using EPA method 8015.

Use of the PetroFLAG Test Kit at the Excavation

The PetroFLAG test kit was used exclusively at the site to assess when the lateral and vertical extent of the diesel-affected soil had been reached. Based on the excellent agreement between the PetroFLAG results and the results from the mobile laboratory, the mobile laboratory was sent off of the Site after two weeks and confirmatory samples were sent to a (less expensive) stationary laboratory. The confidence in the PetroFLAG data was sufficiently high to allow for use of the PetroFLAG data only to direct the excavation.

Use of the PetroFLAG test kit in this manner resulted in substantial savings of both time and money. The quick turn-around time for PetroFLAG results (approximately 10 minutes) made it possible to make decisions regarding where to excavate and where to halt excavation and collect confirmatory samples rapidly, resulting in efficient use of manpower and excavation equipment. This resulted in an accelerated progress of the excavation project and completion of the excavation ahead of schedule. Also, use of the PetroFLAG test kit to screen samples for confirmatory analysis prevented "hot" samples from being submitted to the mobile laboratory that might overload the mobile laboratory equipment, resulting in costly downtime.

Use of the PetroFLAG test kit at the Site also resulted in substantial

savings of money. Perhaps the most significant cost savings was realized in the overall savings of time described above. Other more direct cost savings realized through the use of PetroFLAG included reduced volume of excavated soil and reduced total laboratory costs. The quick (approximately 10 minutes) and inexpensive (approximately $15.00/sample) nature of the PetroFLAG analysis process allowed for frequent collection and analysis of samples to assess the limits of the excavation. This increased sampling density and frequency resulted in better definition of the excavation boundary at any given place and time, thus minimizing excavation of clean soil.

The overall cost of the PetroFLAG test is $15.00 per test. As discussed above, use of the PetroFLAG test kit resulted in less samples being submitted to a state-certified laboratory (cost of $100 to $200/sample for 24-hr. turnaround) and allowed Levine•Fricke to discontinue use of the mobile laboratory (approximate cost of $1500.00 per day).

SUMMARY AND CONCLUSIONS

The PetroFLAG test kit was used at a diesel fuel release site to provide rapid, inexpensive and accurate data regarding the nature and extent of the diesel fuel in soil. Agreement between PetroFLAG results and results from a stationary, state-certified laboratory using EPA Method 8015 was excellent. Because of the excellent agreement between these methods, the PetroFLAG test kit was used exclusively at the Site to direct the excavation and to determine where confirmatory samples were to be collected for submittal to a state-certified laboratory for analysis.

Use of the PetroFLAG test kit at the subject site resulted in substantial savings of both time and money. The quick turn-around time for PetroFLAG results (approximately 10 minutes) made it possible to make decisions regarding where to excavate and where to halt excavation and collect confirmatory samples rapidly, resulting in efficient use of manpower and excavation equipment. Also, use of the PetroFLAG test kit replaced the need for an on-site mobile laboratory and reduced the total number of samples sent to a state-certified laboratory for confirmation analysis.

Based on the performance of the PetroFLAG test kit during the excavation phase of this project, Levine•Fricke is using the PetroFLAG test kit in the

bioremediation treatment phase of the project. A soil biotreatment cell has been constructed to treat the diesel-affected soil excavated from the release area. When results from the PetroFLAG tests indicate that the concentration of diesel in soil in the biotreatment cell is below the target remediation level, confirmation samples will be collected and sent to a state-certified laboratory for analysis. Additionally, the low cost associated with the PetroFLAG test kit will allow for increased sampling of diesel concentrations in soil in the biotreatment cell while the bioremediation is in progress. These on-going monitoring data will be used to track the rate and distribution of bioremediation within the biotreatment cell and to evaluate what adjustments to the biotreatment cell (e. g., increased air flow, addition of nutrients) may be warranted.

Enforcement

THE ADMISSIBILITY OF SCIENTIFIC EVIDENCE

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ABSTRACT

Time, energy, money and opportunity are wasted when environmental evidence collected by technical professionals to achieve a certain objective fails to serve that purpose. This presentation examines the basic reasons why collected data evidence fails so often to meet legal standards of proof and what the technical professional can do to ensure that specific evidence stands up to judicial scrutiny.

INTRODUCTION

Environmental statutes required the promulgation of regulations which specified detailed, highly technical procedures for handling and analyzing sample data evidence. Even now other concepts are being introduced into the process such as "performance based" methods, which will tend to shift more responsibility to the evidence generator. The use of such evidence in legal actions and the current emphasis on compliance with environmental regulations have increased the requirements placed on environmental professionals to generate admissible and defensible data as evidence in civil and criminal proceedings.

The following outline represents the topics to be discussed in the speaker's presentation:

I. Environmental Data vs. Scientific Evidence

   A. Good Sample and Poor Evidence

   B. Understanding the Rules in Two Arenas

II. The Approach used in Evaluating the Admissibility of Scientific Data as Evidence

   A. Frye Standard

   B. Daubert vs. Merrell Dow Pharmaceuticals, Inc.

III. Foundational tests for Environmental Data Evidence

A. Relevance

B. Foundation

C. Authenticity (Chain of Custody)

IV. Identifying the Language Barrier that Affects Communication between the Technical and Legal Professional

V. Using the Daubert-Blackmun Factors in Determining Scientific Validity of Testimony

VI. Establishing the Data Generation Path

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STRATEGIC CONSIDERATIONS IN PRESENTING TECHNICAL EVIDENCE IN COURT: A CASE STUDY

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Part I: The Case Study

Attached to this paper is the transcript of certain testimony by several expert witnesses in United States v. Frank, et al. No. 93-706 (ERK) (E.D. NY 1995). It will provide the reader with a bit of the flavor of how expert testimony is actually presented in court.

The case involved charges that the defendants conspired to defraud the United States, and violated several provisions of the Toxic Substances Control Act ("TSCA"), as well as the Federal Water Pollution Control Act. For purposes of this discussion, only the TSCA counts are relevant.

The facts, which are greatly simplified, are as follows: The defendants operated an oil and tank truck cleaning facility. Their specialty was cleaning out oil barges. They also cleaned oil tank trucks. They washed out the barges with high pressure water. They allowed the oil/water to separate in a large separator tank, which had heating coils in the bottom to help the separation process. They used the oil as fuel for boilers to create steam, in order to heat water for cleaning future barges. The wastewater was sent through a treatment system before being discharged pursuant to an NPDES permit.

Over a period of years, solid particles that were suspended in the oil/water that entered the separator tank, settled to the bottom of the tank, during the separation process, creating sludge. After a period of time, the sludge affected the ability of the heating coils to work, and had to be removed. The defendants moved the sludge from the tank and placed it in a barge that was not in use. The barge had four compartments that were each about 60' long, 13' wide, and 20' deep.

Over a year later, during an inspection on October 5, 1990 the U.S. Environmental Protection Agency (EPA) took one oil sample from each of the four barge compartments via an access hole. Three weeks later the EPA took one more sample (sludge, this time) from each compartment, using the same access hole. One month later they took one more sludge sample from each compartment, again using the same access hole. Testing of these samples indicated the presence of polychlorinated byphenyls (PCBs).

There were other samples taken over the next two years, mostly by private laboratories, before the material was removed from the barge. Almost all were taken from the same sampling point as the initial sets. In several instances, oil samples were tested and did not indicate the presence of PCBs. In other cases, sludge was tested, and PCBs in excess of 50 ppm were found. When the sludge was finally removed from the barge (under the direction of the EPA and the U.S. Coast Guard), the material was sampled again, as it was removed. Most of those samples indicated PCB concentrations of under 50 ppm.

TSCA mandates special handling of materials containing PCBs in concentrations of 50 ppm or more. Based on the test results, the United States obtained an indictment against the defendants that charged several of them with violations of TSCA marking, storage, and disposal requirements. The conspiracy alleged that defendants hid the fact that the storage tank contained PCB-contaminated sludge and that they were moving it to the barge.

The attached testimony includes (1) the direct and cross examination of one of the persons (Randy Braun) who took the samples from the barge (Attachment A); (2) stipulations about the testimony of two persons who assisted in analyzing the samples in the NEIC laboratory (Attachment B); (3) testimony by one of the NEIC laboratory scientists (Dr. Lawrence Stratton) who conducted or oversaw the sampling analysis in the laboratory (Attachment C); and (4) testimony by one of the persons who analyzed samples taken by a private contractor (Attachment D).

Part II: Discussion Points

A. Prefiling considerations

1. Using the Freedom of Information Act

2. Using technical evidence in prefiling negotiations

B. Pretrial considerations

1. Is this a civil or criminal case?

- Discovery differs
- Obligation to disclose differs
- Trial tactics differ
- Burden of proof differs

2. Experts (witnesses vs. consultants)

3. Finding the "qualified" expert/consultant: "I never found an expert who wasn't qualified./I never found an expert who was qualified."

   - investigatory experts
   - sampling experts
   - laboratory experts
   - toxicology experts
   - experts on the law
   - experts v. consultants

4. Reviewing the government's data

   - Who reviews it?
   - What is reviewed?
   - When is it reviewed?

5. Government protocols and procedures

   "Alice in Memoland"

B. Trial considerations

1. Who will educate the judge/jury? (Who <u>wants</u> to?)

2. Do I even want to dispute the technical evidence?

   a. Burden of proof

   b. Credibility of counsel

   c. Theory of the case

3. Did my client get and test split samples: "What goes around, comes around."

4. Calling an expert

5. Attacking technical evidence

   a. Sampling plans were flawed.

   b. The sample it isn't proof of anything (representativeness).

   c. The person taking the sample wasn't qualified.

   d. The person taking the sample was sloppy.

   e. The person taking the sample didn't follow his own agency's procedures.

   f. It's not fair to use that evidence because no private company could have known to test the way the government did.

   g. The laboratory wasn't qualified to analyze the sample.

   h. The laboratory made mistakes when it analyzed the sample.

   i. The laboratory didn't follow the right protocols when it analyzed the sample.

   j. It's not fair to use evidence against someone who couldn't have known to test the material the way the government did.

   k. "Big" attacks vs. "little" attacks

6. Using objections

7. When to use technical evidence in the defense case

8. How technical evidence is used in closing arguments.

C. Conclusions

Those who attend the enforcement session on Tuesday afternoon will receive copies of attachments at the meeting.

AVOIDING SUCCESSFUL CHALLENGES OF MEASUREMENT DATA

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ABSTRACT

This paper is presented from the viewpoint of a technical person, especially someone performing laboratory analyses, and discusses ways to thwart successful attacks on data. Good planning is the single most important preventive measure. The best planning involves all of the personnel needed to produce the data, and will address all the objectives of the measurement activities (both sampling and analysis). The people involved need to know what regulations are being enforced, any requirements placed on measurement procedures by those regulations, and what is needed to show a violation of those regulations. Shortcomings in these areas due to lack of planning are the easiest to attack. These are "legal hoops" you need to get through to defend data. If you have covered these and other basic legal requirements such as chain-of-custody, testing with a sound scientific basis should be able to withstand attacks. Having the correct answer and being able to show that fact also helps, but doesn't count if you haven't covered the basics.

INTRODUCTION

It is anticipated that this presentation will follow a presentation by a defense attorney, who among other things, outlined generic approaches to attacking data. Some general comments of my own apply to this topic. Having data good enough that it won't be attacked should be a goal, but there are ways to attack any data. Expect to have data attacked and try to be prepared. Also, there is no one correct way of producing defensible data. There are fifty states each probably having one or more laboratories which analyze samples for environmental enforcement cases, and I believe that they usually do the job successfully. I am even more confident that they have at least fifty different ways of doing things. Some of the examples I give should be thought of as things that have worked, not the only way to do things.

DISCUSSION

The first thing a technical person thinks of in connection with the term "data defensibility" is probably the scientific defensibility of the procedures used and the results obtained, including quality assurance results. In practice, unless the data really do not support the conclusions presented, these areas will not be seriously attacked. A non-serious attack might be trying to obtain victory by default - put up a weak scientific challenge and hope to prevail because nobody fights back. A serious attack would require complicated technical arguments and, if the basic conclusions of the data are correct, would have little to gain. The easier and usually more productive arguments to make are things such as: the required procedure was not used; the samples are flawed making the results meaningless; or, required items such as holding times were not satisfied. Checking the claimed credentials of the people involved to see if they are accurate is also standard practice.

If a procedure is required by regulation, that is the procedure that must be used. Regulation in this sense could be federal, state, local, or perhaps a permit. Knowing if something is required is part of the planning which should occur prior to sampling. However, it is also

essential to know what is actually required and what is an implied requirement. The implied requirement may be something done by tradition, or because it is used in another area. Implied requirements are a common area to attack because it is easy to create the impression that something wrong was done. Such attacks may be successful unless you can quickly refute the implied shortcoming, usually by explaining that it was not a requirement in this case, and often by adding that the results would have been the same using either procedure.

Communication among the personnel involved in an enforcement case is obviously helpful since each person can supply details from their specialty area, lowering the chances of overlooking a requirement unknown to persons less knowledgeable in that area. The earlier this communication takes place, the better. It is best when it takes place in the planning stages.

Communication should also address sampling. Sampling is a critical part of the measurement process, and one that often does not get its proper emphasis. Besides the importance of communication to understanding objectives, an understanding of the sample collection process can help the chemist in defending data. The chemist should know enough about the sampling to convince themselves that the procedures used were adequate to meet objectives. A chemist will give a more credible appearance if they can discuss the overall measurement, not just the laboratory analysis. In a deposition you will be questioned in your weakest and/or least knowledgeable areas, if for no other reason than to shake your confidence and perhaps get weaker answers within your areas of expertise. Also, in RCRA testing especially, the important thing often is not the data alone, but a conclusion based on the results of a test. That conclusion usually involves a knowledge of the overall measurement, not just the analytical step. However, you need to remember your limitations. Don't get into being an expert on sampling unless you are one.

Beyond using a procedure if it is required, the best way to have defensible data is to have the correct answer, and be able to show you have the correct answer. This is where the process gets down to scientific defensibility. If the results you obtained would stand up to being published in a refereed scientific journal, they will stand up in the legal process. This may mean doing a determination by alternate techniques to show you can get the same result by different methods, much the way the National Institute of Standards and Technology does in setting values for a reference material. The thoroughness of the process depends on the tests performed and on the legal venue. If standard methods meet objectives, those tests should be adequate as performed. If non-standard tests are performed, alternate procedures would probably give more confidence in the results obtained.

Quality assurance is another important part of being able to show you have the correct answer. In our laboratory, if a sample exceeds a regulatory concentration, we like to analyze the sample in triplicate to show the result is reproducible and to be able to make a more definitive statement about how confident we are the limit is exceeded. Blanks and spikes are also important in this basic scientific defensibility, but if you have one result for a sample, running a replicate gives more information than spiking the sample, especially if sample homogeneity is a question. If you get good results on a spike, you either were able to duplicate the sample result and recover the spike, or you were just lucky. If you run replicates, you find out how well you can reproduce the result. Also, what is in the sample is the issue, not how well you can recover a spike. Analyzing a reference material to verify calibration is also a good practice.

SUMMARY

The legal process can be intimidating, but that doesn't mean you should be intimidated. Knowing what is required (and not required) by the objectives of a project is the biggest single thing which can help the technical person to defend results. Being able to show you have gotten the correct answer is also important, either using a proscribed procedure or by just using accepted science. Regardless, the technical person can expect to have results questioned, and should not take it personally; attacking you is somebody's job. You should look forward to overcoming arguments based on half-truths and bad science. On the other hand, if you need to defend results based on those same things, you will deservedly be in trouble.

Organics

SOXHLET ALTERNATIVES FOR THE ENVIRONMENTAL LAB

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ABSTRACT

Accelerated solvent extraction (ASE) combines aspects of both supercritical fluid extraction (SFE) and microwave assisted extraction (MAE). The extraction is accomplished using traditional organic solvents at moderate temperature and pressure. Extraction time is faster than SFE, while labor time is comparable to automated SFE. Solvent usage and instrument cost are intermediate between automated SFE and MAE. Extraction efficiency is generally equivalent to standard laboratory extractions with Soxhlet and sonication. ASE analyte recovery from some challenging matrices was significantly higher than sonication.

INTRODUCTION

Sample preparation alternatives to Soxhlet and sonication are needed to reduce solvent and labor requirements while shortening sample preparation time. Soxhlet is the technique to which other solid sample extraction techniques are usually compared. Sonication has been a routine technique for many years. It is faster than Soxhlet, but is more labor intensive. Also, analyte recovery from some challenging matrices may be significantly less than Soxhlet.

Several new extraction technologies have been developed which shorten the extraction time (like sonication) while often maintaining the thoroughness of Soxhlet. This is usually accomplished by extracting at above room temperature and at elevated pressure. Alternative extraction fluids may also be used to improve the extraction. Most of these alternatives are more automated than Soxhlet or sonication, thus less analyst labor is required.

These new technologies for solid sample extraction are becoming viable alternatives to traditional Soxhlet extraction of solid samples for the production environmental lab. Automated and accelerated Soxhlets are available. Also, supercritical fluid extraction (SFE) and microwave assisted extraction (MAE) have been applied to environmental matrices. The latest sample preparation option for the lab is accelerated solvent extraction (ASE).

EXPERIMENTAL

Accelerated solvent extraction (ASE) will be included in SW-846 Update III as Method 3545. The extraction time is 10 minutes, with sample-to-sample cycle time of about 13 minutes. The required solvent volume ranges from 15 to 50 mL depending on the amount of sample extracted. Sample amounts from 10 to 30 g can be routinely extracted.

The ASE uses traditional solvent mixtures (dichloromethane/acetone and hexane/acetone) at moderate temperature and pressure to extract most routine semivolatile organic analytes listed in SW-846. Figure 1 shows the plumbing arrangement of the system. The weighed sample is mixed with sodium sulfate and placed in a stainless steel extraction vessel and sealed with end caps. An automatic mechanism seals the extraction vessel into

the plumbing system and moves it into the oven. The load valve opens and solvent is pumped into the vessel. When the vessel is full the static valve closes and the pump continues until the pressure reaches the set-point. As the solvent and sample warm up to the oven temperature, the pressure rises as the solvent expands. When the pressure exceeds the set-point by 200 psi, the static valve opens briefly (reducing pressure) and releases about a milliliter of solvent into the collection vial. The pump then adds a milliliter of fresh solvent and brings the vessel pressure back to the set-point. This cycle repeats many times while the sample and solvent are heating up to the oven temperature. After a total equilibration and soak time of 10 minutes, the static valve opens and all solvent in the extraction vessel is flushed out with a few milliliters of fresh solvent. Last, the purge valve opens and nitrogen gas blows the remaining solvent into the collection vial. The final extract volume ranges from 15 to 50 mL depending on sample size.

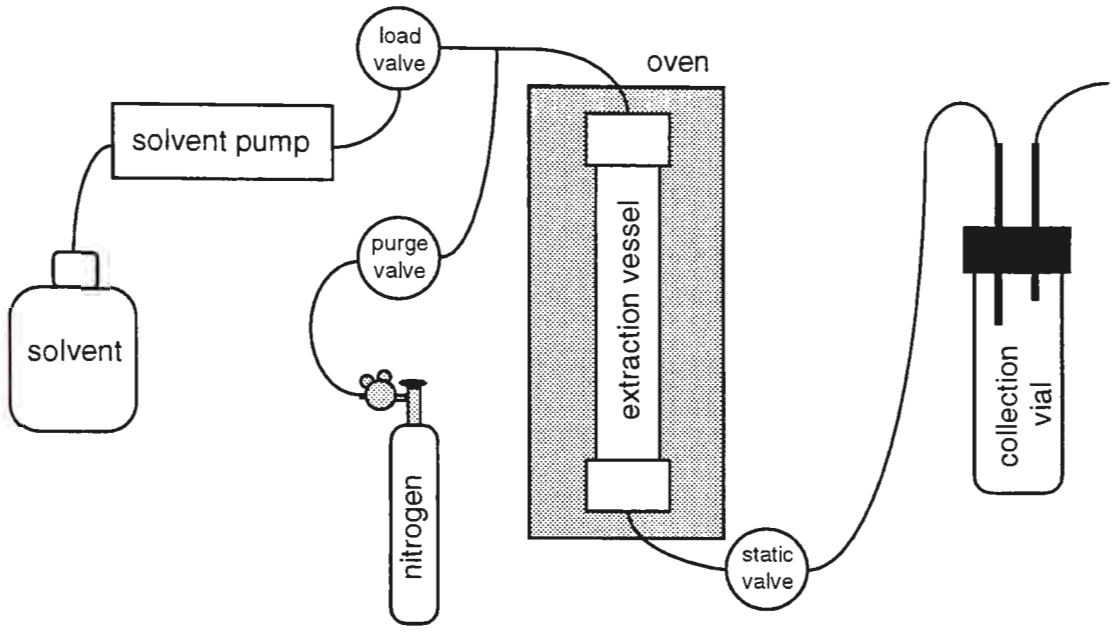

Figure 1 Accelerated Solvent Extraction System

Forty samples were examined that had been previously extracted and analyzed for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and semivolatiles (BNAs) with traditional SW-846 methods (3540, 3550, 8080, 8270). Also, a few matrix spiked samples were extracted for petroleum hydrocarbons and analyzed with infra red analysis (TPH-IR). The PCBs and OCPs were extracted with hexane/acetone (50:50) at 100°C, 1500 psi for 10 minutes. The BNAs were extracted with dichloromethane/acetone (50:50) at 100°C, 1500 psi for 10 minutes. The TPH-IR samples were extracted with tetrachloroethene at 200°C, 1500 psi in 10 minute segments.

Figures 2-4 show the results from the ASE extraction plotted relative to the results from sonication & Soxhlet extractions. The diagonal line in the center indicates the region where the ASE concentration data corresponds exactly to the sonication/Soxhlet data. The shaded region covers the area from ASE results being 50% higher to 50% lower than

the sonication/Soxhlet results. The X and Y axes are shown in log-log space since the concentration data cover many orders of magnitude.

On average the ASE PCB results (Figure 2) were comparable to the sonication/Soxhlet results but data were more scattered than one would like. Sample homogeneity was the most likely cause. The prototype ASE system was limited to 10 g samples.

The OCP results (Figure 3) show similar data scatter which was most likely caused by homogeneity limitations. Also, the ASE OCP concentrations were in general much higher than the corresponding sonication results. These OCP samples were all from the same site and were high in both clay and moisture content, which tend to be the most difficult type of *soil* to extract.

The BNA samples (Figure 4) showed good equivalence between ASE and sonication/Soxhlet extractions. The analytes determined ranged from phenol and dichlorobenzenes to 6 ring PAHs. There were 32 different semivolatile analytes detected in all. Two regions of Figure 4 deserve special note. Those analyte results that were significantly higher with the ASE were typically low concentrations of low boiling analytes. These types of analytes have been previously reported as more difficult to extract (1). Thus, the ASE may be a more efficient extractor for these analytes. Another concern raised about the ASE extraction was solvent saturation when very high level samples were extracted. The sample whose results are shown at the high end of the BNA graph was > 3% extractable hydrocarbon material. These data compare well, so solvent saturation was not a significant problem.

Figure 5 shows the results from several matrix spiked petroleum hydrocarbon samples. This test evaluated the ASE as an alternative to the Freon-113® based Soxhlet for TPH-IR analyses. Hydrocarbon recovery from wet samples is more difficult when only non-polar extraction solvents (such as Freon® or tetrachloroethene) are used. It is necessary to dry the sample either before or during the extraction to achieve good analyte recovery. Both wet and dry sample matrix spikes of diesel and motor oil were sequentially extracted until quantitative recovery was achieved. The two dry samples were quantitatively extracted with a single 10 minute extraction with tetrachloroethene at 200°C. The wet samples were more difficult to extract. The fresh diesel spiked sample required a second 10 minute, 200°C extraction to reach quantitative recovery. The aged motor oil spike although easy to extract when dry became very difficult to extract when the moisture content of this clay sample was brought to 50%. Three 10 minute extractions were required to achieve quantitative recovery. The first extraction had very little hydrocarbons recovered, but the extract contained significant amounts of water. Subsequent extractions of the same clay sample aliquot recovered more hydrocarbons and less water.

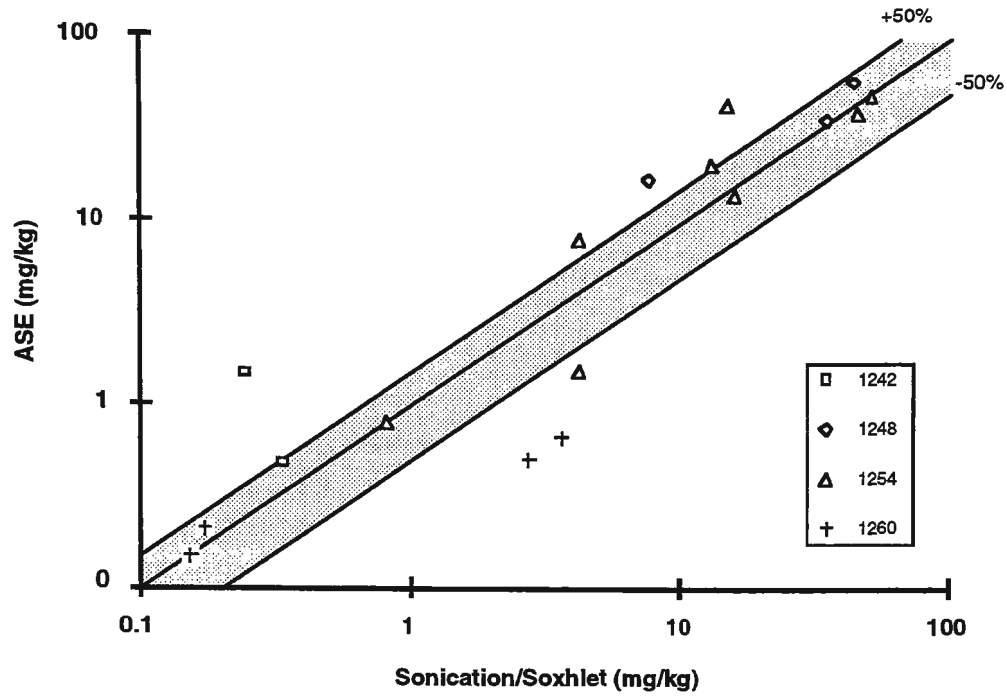

Figure 2 Comparison of Polychlorinated Biphenyl Results

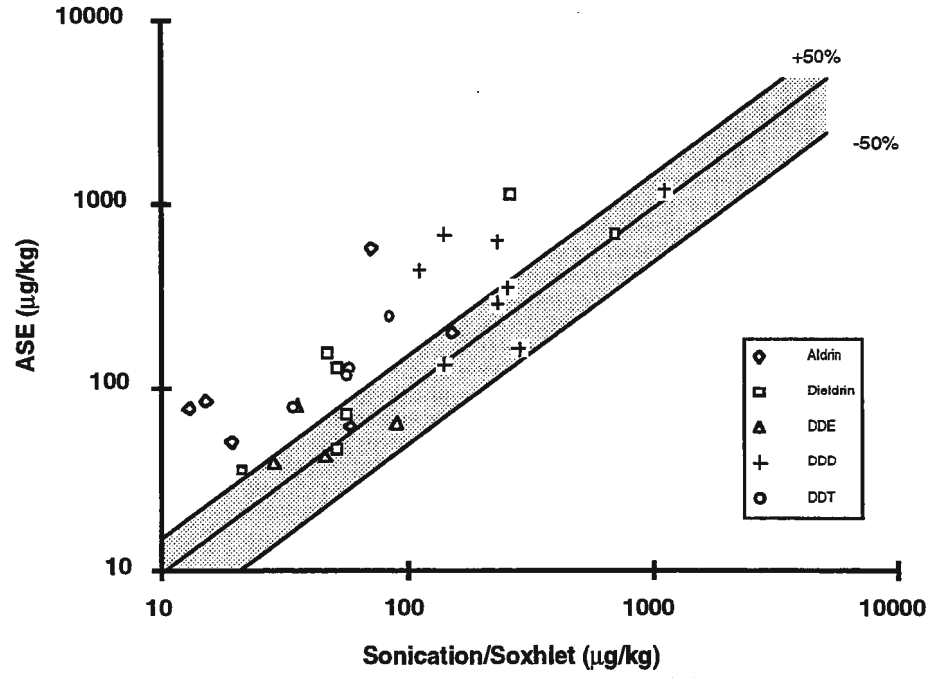

Figure 3 Comparison of Organochlorine Pesticide Results

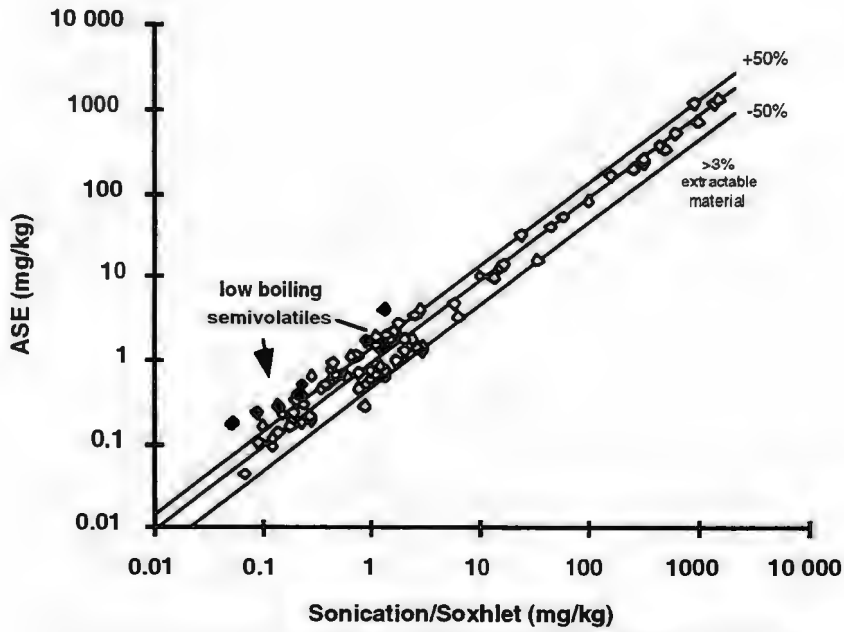

Figure 4 Comparison of Semivolatile Base/Neutral/Acid Results

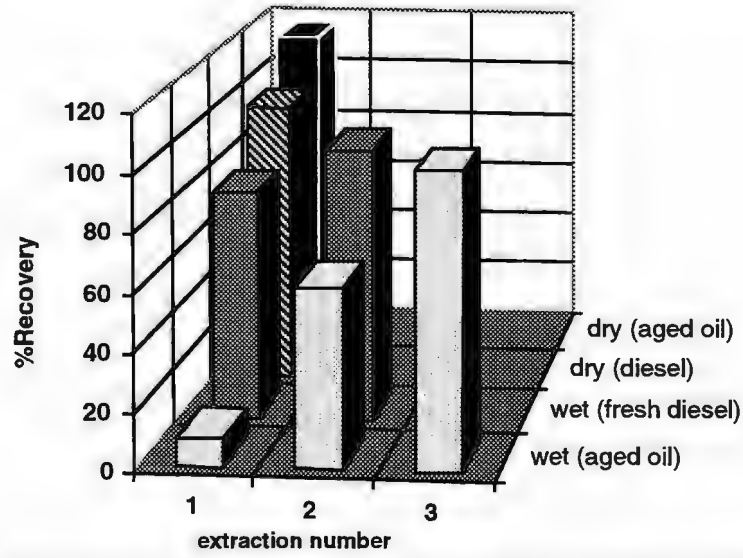

Figure 5 Recovery of Petroleum Hydrocarbons and Analysis by Infra Red

Process Evaluation

Once acceptable extraction efficiency was established for the ASE, the effects on the sample preparation process were evaluated. The evaluation covered several key areas; 1) total extraction time, 2) labor time, 3) equipment cost, 4) supplies cost and 5) side effects on other aspects of the sample analysis process.

The total extraction turn around time is about 13 minutes. This is the extraction time only. It does not include sample homogenization, vessel loading, extract concentration or clean-up. This extraction time compares well with sonication and is shorter than most implementations of supercritical fluid extraction and microwave assisted extraction. It is dramatically shorter than the traditional Soxhlet extraction and newer automated Soxhlets. Since the ASE is an automated sequential extractor, the total extraction time for a batch of samples will depend on the number of samples in the batch. For example, a batch of 10 samples plus 4 QC extractions would take about 3 hours of unattended extraction time.

The labor time component for the extraction process is small and primarily consists of sample homogenization, drying agent mixing and QC spiking. This part of the process is about the same for each of the extraction alternatives. Thus, ASE and Soxhlet labor times are about the same. Sonication has significantly higher labor cost. Note, this labor time comparison does not include extract concentration, see side effects below.

The initial cost of automated extraction equipment is often a major component of the total cost of performing the extraction. An automated ASE system costs about $45,000. This is significantly more expensive than equivalent sonication, Soxhlet or automated Soxhlet equipment. However, the ASE system is less expensive than many similarly automated SFE systems.

The supplies cost of the automated ASE system can not be estimated now, since the ASE has not been used in a long term production mode yet. The frits and seals of the extraction vessels have a finite but undetermined lifetime at present. Under ideal conditions these components could last for hundreds of extractions, but contamination from real samples and misuse by extractionists will shorten their lifetime. Other supplies such as solvent, sodium sulfate and filter paper should be less expensive (in total) since solvent volume is reduced relative to traditional techniques.

Most new sample preparation techniques will have side effects on other parts of the preparation and analysis process. Some new extraction techniques (such as the automated SFE systems) limit the amount of sample extracted to 5-10 g. This would raise non-detected analyte reporting limits unless other steps in the concentration or analysis process compensate. The ASE system does not produce this negative side effect since 30 g sample sizes are maintained. The ASE produces a positive side effect on extract concentration. Since the ASE extract volume is much smaller than sonication or Soxhlet extracts (50 mL compared to 200-300 mL), the macro-concentration is much quicker and requires smaller glassware.

CONCLUSION

ASE extraction efficiency is generally equivalent or better than the traditional sonication and Soxhlet techniques. Actual extraction time is short and about the same as sonication. Labor time is small and comparable to Soxhlet extraction. Initial equipment cost is much higher than current extraction techniques. The on-going cost of supplies can not be accurately estimated at present because some of the component lifetimes are undetermined. The ASE extraction has the positive side effect of reducing concentration time. No negative side effects have been identified at this time. If applied properly, the ASE should improve extraction turn-around time, reduce total cost and diminish the health & environmental effects of solvent usage.

ACKNOWLEDGMENTS

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Sample Preparation Using Accelerated Solvent Extraction (Method 3545, Proposed)

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Abstract

Various techniques have been promoted during the last decade to replace solvent intensive extraction techniques such as Soxhlet and sonication. These methods typically require 300 to 500 mL for each sample. However, replacement techniques have been difficult to use, have taken extensive time and labor for methods development, have been matrix dependent, or have not provided adequate recoveries. Accelerated solvent extraction (ASE) was developed to overcome these problems. ASE applies solvents at elevated temperatures and pressures compared to traditional methods. At the temperatures used in ASE, dissolution kinetics are accelerated and solvent capacity is enhanced. The result is an enhancement of the extraction conditions which allows the extraction of a wide range of environmentally important matrices in a few minutes with minimal solvent consumption. For example, a 10-g sample requires only 13 to 15 mL of solvent and the extraction is completed in twelve minutes. ASE has been compared to conventional solvent extraction of chlorinated pesticides, BNAs, organophosphorus pesticides and herbicides, in two laboratory validation studies. Based on results presented here, ASE will be included as Method 3545 (proposed) in Update III of CFR 40.

Introduction

Preparation of solid waste samples for chromatographic analysis usually requires an extraction procedure to separate the desired analytes from the matrix. Techniques such as Soxhlet which has been in use since the turn of the century are generally solvent intensive. Typically 150 to 500 mL of solvent are required for samples in the range of 10 to 30 g. Both environmental and economic concerns have led to the push to develop less solvent intensive extraction techniques. In the last decade, reduced solvent techniques including automated Soxhlet, microwave digestion and supercritical fluid extraction (SFE) have appeared. However, some of the new techniques, while ostensibly showing great promise for reducing solvent usage, have faced other difficulties in assuring general acceptance in the chemical laboratory setting. Some of the problems include difficulty in use, time required for each extraction, intensive labor requirements, difficult methods development, matrix dependence, and poor recoveries of target analytes.

Accelerated Solvent Extraction (ASE) was developed to overcome these problem areas. ASE applies solvents at elevated temperatures and pressures to achieve complete

extraction of the typical environmental matrices. As temperature increases, the various kinetic processes controlling extraction are accelerated. Temperature will also beneficially affect the solubility of most analytes. The consequence of using solvents at higher temperatures than typically used in other solvent methods is an enhancement of the extraction conditions which then allows the extraction of a wide range of environmentally important matrices in a few minutes with minimal solvent consumption. The ASE system consists of an oven chamber, a pump, a solvent source and valves to control the both liquid and gas purge flow paths. A schematic diagram of an ASE system is shown in Figure 1.

Methods

Apparatus and Materials. Extractions were performed on a pre-production accelerated solvent extraction (ASE) system (Dionex Corporation, Sunnyvale, CA) and by conventional Soxhlet and shaker extraction. All solvents were analytical grade or better quality. Spiked soils were purchased from Environmental Research Associates (ERA, Arvada, CO), and were stored at approximately 4°C until used. These soils were prepared in batch mode, and represent artificially aged samples.

Equivalency Study.
Extractions by ASE and automated Soxhlet, Soxhlet or shaker were performed in parallel. All extracts from both ASE and the conventional method were placed in the normal sample queue. No samples were re-extracted, and no extracts were re-analyzed. Seven replicate extractions by each technique of each concentration level on each matrix for the two compound classes were performed. Matrix blanks, spikes and spike duplicates (quality control samples) were included for each matrix. These spikes and blanks were obtained using clean soils from the same batches that were used for the spiked soils and were provided by ERA. The total number of extractions and analyses for both equivalency studies, including blanks and standards was over 600.

Extraction. ASE extractions were performed at a pressure of 2000 psi and a temperature of 100°C. Additional information on the operation of ASE are reported in a separate paper (1). Stainless steel extraction vessels with 10.4 mL volumes and rated for use at 5000 psi (9.4 mm x 150 mm, Keystone Scientific, Bellefonte, PA) were used. Surrogate compounds (QA/QC compounds, not target analytes) were spiked directly onto the soils immediately prior to sealing the sample vessels. Ten gram samples of spiked soil were used for all extractions. Chlorinated pesticide spiked soils were extracted with a 1:1 mixture of hexane/acetone. Organophosphorus pesticide and BNA spiked soils were extracted with a 1:1 mixture of methylene chloride/acetone, while herbicide spiked soils were extracted with a 1:2 mixture of methylene chloride/acetone with 4% (v/v) H_3PO_4/H_2O (1:1). All extracts were collected into amber, precleaned 40 mL vials purchased from I-Chem (New Castle, DE).

Quantitation. All analysis were performed by contract laboratory personnel. Average recoveries for each analyte were determined from 7 replicate extractions and analysis. For all data sets, no recoveries above 150% were included in the calculations of

average recoveries, however, any zero values were included. The accuracy and precision data from the surrogate compounds were well within established quality control limits. No method analyte was found in any reagent or method blank sample at levels above detection limits.

Results and Discussion

ASE Extractions

A schematic diagram of the accelerated solvent extraction system used in this study is presented in Figure 1. The sample is loaded into the extraction vessel and it is filled with the extraction solvent by opening the pump valve. Once filled, the cell is maintained at constant pressure by the pump. The sample and solvent are then heated by placing the cell in contact with a pre-heated metal block. While heating, thermal expansion of the solvent occurs resulting in an increase in the measured pressure. This pressure increase is relieved by periodically opening the static valve, venting small amounts of solvent into the collection vial. Following 10 minutes in this configuration, the static valve is opened to allow 7-8 mL of fresh solvent to flow through the cell. The pump valve is then closed and the purge valve is opened to allow compressed nitrogen to push the remaining solvent from the cell into the collection vial.

BNAs.

The relative recovery of ASE compared to automated Soxhlet extraction for the BNA compounds are summarized in Figure 2. The average relative recovery of ASE relative to automated Soxhlet at all spike levels and from all matrices was 99.2%. Only one compound fell below the target relative recovery value of 75%; benzo[g,h,i]perylene, whose average recovery was 66.4%.

The average relative recoveries from the three matrices were as follows: clay - 96.8%, loam - 98.7%, and sand - 102.1. The average relative recoveries at the three concentration levels were as follows: low - 101.2%, mid - 97.2 and high - 99.2%. The overall average RSD values for the pesticides were 12.8% for ASE and 13.9% for Soxhlet.

Chlorinated Pesticides.

The relative recovery of ASE compared to automated Soxhlet extraction of OCPs are summarized in Figure 3. The average relative recovery of ASE relative to automated Soxhlet at all spike levels and from all matrices was 97.3%. Again, only one compound fell below the target relative recovery value of 75%; DDT, whose average recovery was 74.9%.

The average relative recoveries from the three matrices were as follows: clay - 96.0%, loam - 99.1%, and sand - 96.8. The average relative recoveries at the three concentration levels were as follows: low - 105.1%, mid - 90.7 and high - 96.1%. The overall average RSD values for the pesticides were 8.3% for ASE and 8.7% for Soxhlet.

Herbicides.

In order to extract free acid herbicides into organic solvents, soil samples are normally acidified with hydrochloric acid prior to extraction. While this procedure was followed for the samples extracted by Method 8150A, samples extracted by ASE were acidified by

direct addition of phosphoric acid to the extraction solvent, as described in **Methods**. Recovery of the herbicides by ASE relative to the shake method are summarized in Figure 4. The average recovery, relative to the shake method, at all spike levels and from all matrices was 115.7%.

As with the other data, no matrix dependency seemed to exist with the herbicides. The average relative recoveries from the three matrices were as follows: clay - 99.8%, loam - 138.7% and sand - 108.8%. The average relative recoveries at the two concentration levels were as follows: low - 112.2% and high - 119.2%. The overall average RSD values for the herbicides was 24.5 for ASE and 31.5 for the shake method. These values seem high, and can be explained by the fact that only eight compounds were used for this study. If one compound had poor precision, as was the case with Dalapon, it would heavily influence the overall precision. If the RSD for Dalapon is excluded, the averages become 15.8 for ASE and 28.8 for the shake method.

Organophosphorus Pesticides.

The relative recovery of ASE compared to Soxhlet extraction for the OPPs are summarized in Figure 5. The average recovery of ASE relative to Soxhlet for the OPPs at all spike levels and from all matrices was 98.3%. There were cases in which target compounds were not detected in the extracts by either extraction technique (TEPP, Naled, Monocrotophos at all concentrations and Fensulfothion, Azinfos Methyl and Coumaphos at low level from clay). In these cases, data points were excluded from relative recovery calculations

The average relative recoveries from the three matrices were as follows: clay - 97.0%, loam - 100.0%, and sand - 97.0%. The average relative recoveries at the two concentration levels were as follows: low - 98.9% and high - 97.6%. The overall average RSD values for the pesticides were 9.3% for ASE and 8.4% for Soxhlet.

Conclusion

Accelerated solvent extraction (ASE) has been shown in this work to be equivalent to conventional solvent extraction of chlorinated pesticides, BNAs, organophosphorus pesticides and herbicides. The time required is less than 15 minutes per sample, and solvent usage is reduced significantly (15 mL per 10 gram sample). Compared to Method 8150A, ASE eliminates the use of hydrochloric acid and diethyl ether, and significantly reduces analyst labor time. The ability of ASE to achieve these results is most likely due to enhanced solubilization, which occurs at elevated temperatures and pressures.

The data presented in this study were used in the equivalency evaluation of accelerated solvent extraction, which is scheduled to appear as SW-846 Proposed Method 3545 in 40-CFR update III (3).

References

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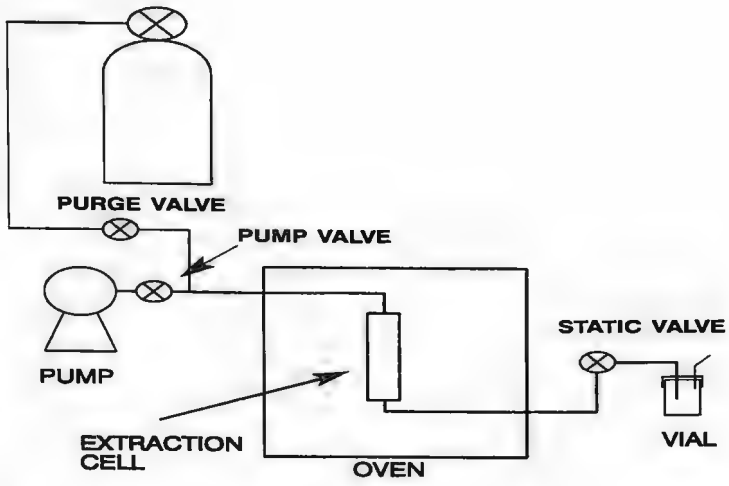

Figure 1. Schematic diagram of accelerated solvent extraction (ASE).

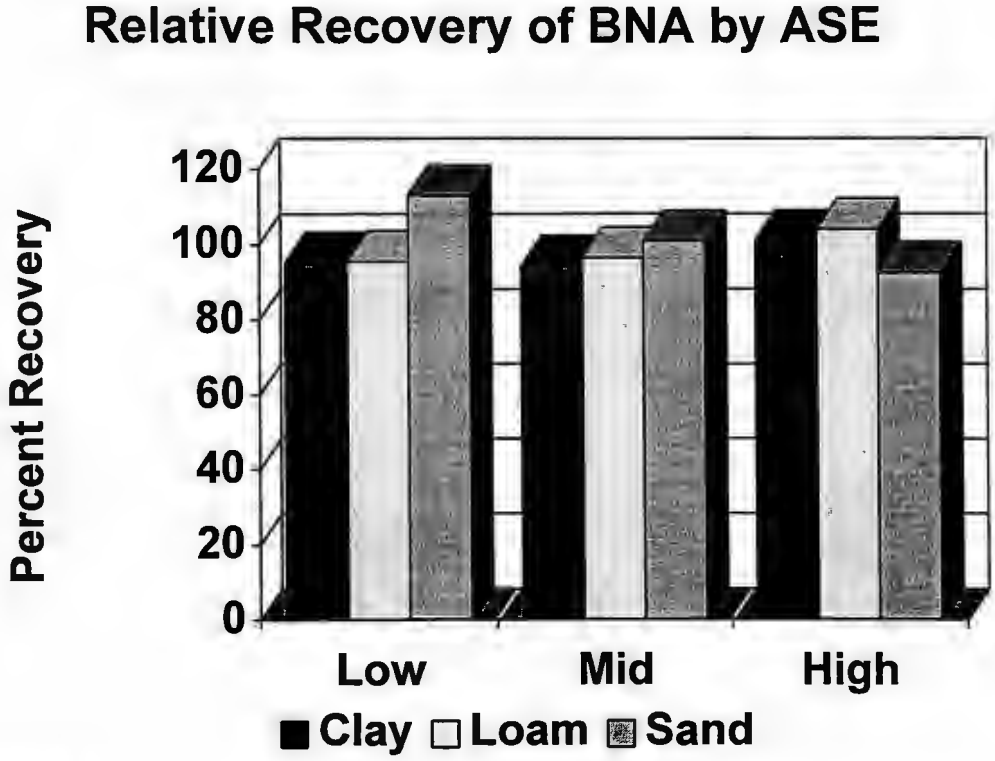

Figure 2.

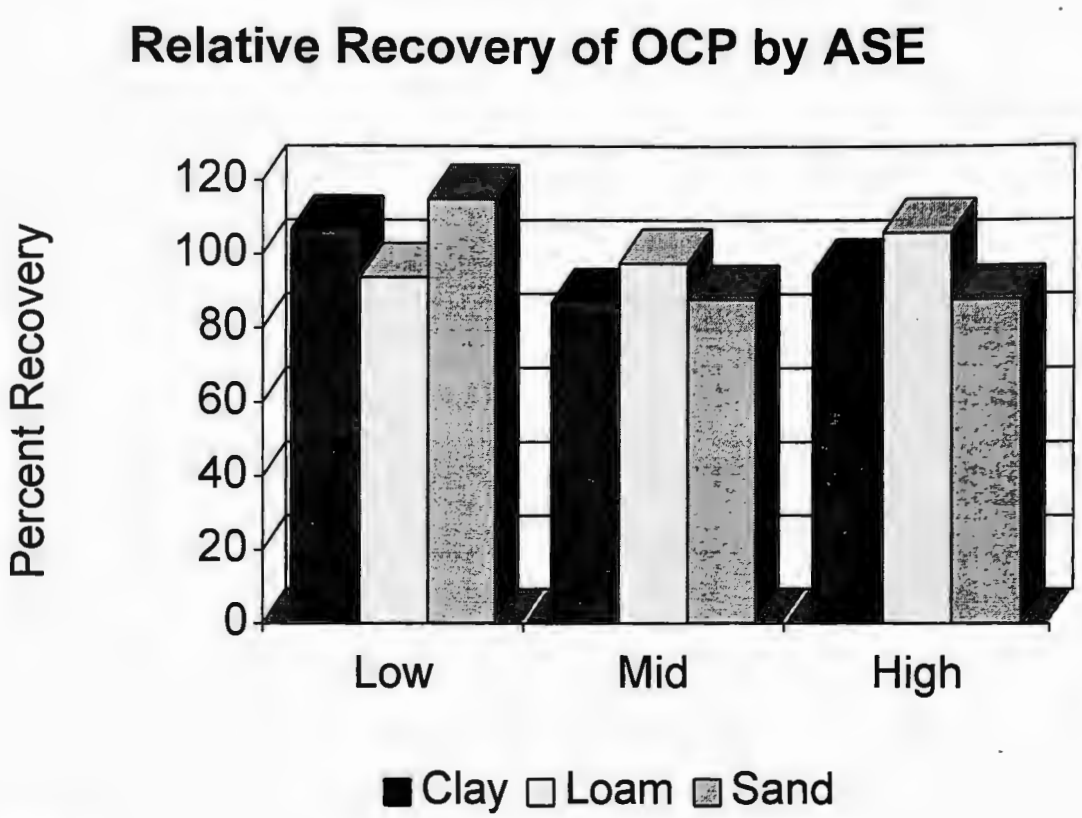

Figure 3.

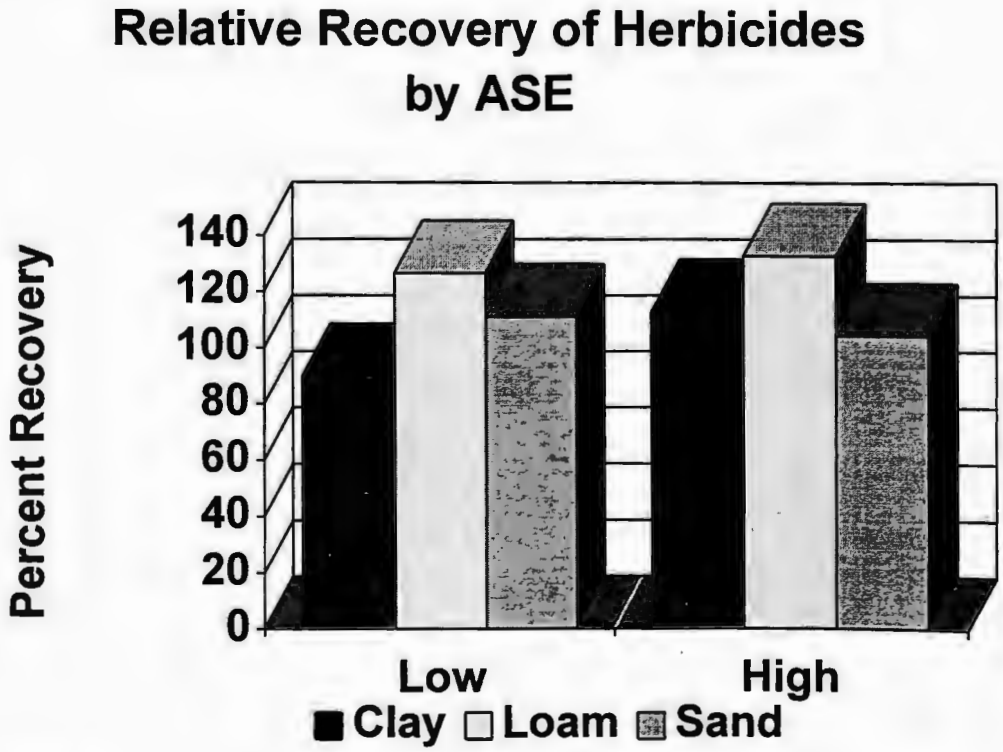

Figure 4.

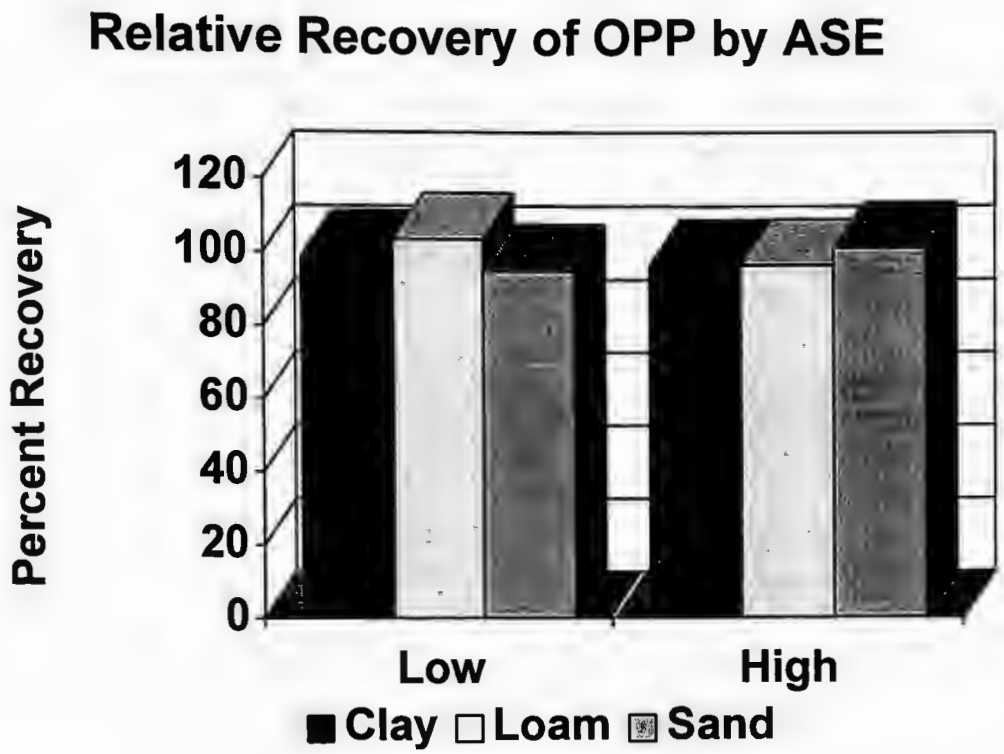
Relative Recovery of OPP by ASE
Percent Recovery
120
100
80
60
40
20
0
Low
High
Clay
Loam
Sand

Figure 5.

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EVALUATION OF THE NEW CLEAN SOLID PHASES FOR EXTRACTION OF NITROAROMATICS AND NITRAMINES FROM WATER

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ABSTRACT

Salting-out solvent extraction (SOE) is the preconcentration step currently specified in SW846 Method 8330, the reversed-phase high-performance liquid chromatography (RP-HPLC) method for nitroaromatics and nitramines in water. Previous attempts to utilize solid phase extraction (SPE) in our laboratories indicated that use of the solid phases commercially available at that time led to introduction of unacceptable interferences for some matrices. Recently, several manufacturers have introduced new cleaner solid phases. This study was conducted to evaluate their utility in providing preconcentration for low level determination of these analytes.

SOE was compared with cartridge and membrane SPE for preconcentration of nitroaromatics, nitramines and aminodinitroaromatics prior to determination by RP-HPLC. The solid phases evaluated were Porapak RDX for the cartridge method and Empore SDB-RPS for the membrane method. Thirty-three groundwater samples from the Naval Surface Warfare Center, Crane, Indiana, were analyzed using the direct analysis protocol specified in Method 8330 and the results compared with analyses conducted after preconcentration using SOE with acetonitrile, cartridge based SPE and membrane based SPE. For high concentration samples analytical results from the three preconcentration techniques were compared with results from the direct analysis protocol. The results indicated that good recovery of all target analytes was achieved by all three preconcentration methods. For low concentration samples, results from the two SPE methods were correlated with results from the SOE method. Overall, very similar data were obtained by the SOE and SPE methods, even at concentrations below 1 µg/L. Chromatograms from the three methods were examined and the large interferences observed for the SPE methods in our earlier study, using less clean material, were largely absent. A small interference was observed for both SPE methods at the retention time of RDX on the primary analysis column that translated to concentrations ranging from 0.2 to 0.6 µg/L RDX. Even though this peak was not present at the proper retention

time on the confirmation column, detection limits for RDX should be raised to 0.6 µg/L if the SPE methods are used due to this potential interference. We recommend that solid phase extraction be included with SOE as an option in SW846 Method 8330.

INTRODUCTION

One of the U.S. Defense Department's most serious environmental problems is associated with sites contaminated with residues of secondary explosives. Contamination at these sites was chiefly caused by manufacture of the explosives, loading of explosives into ordnance, and disposal of off-specification or out-of-date material. Residues from these activities contain the explosives, manufacturing impurities and environmental transformation products (1). Unlike many other organic chemicals, these compounds are quite mobile in the soil and have resulted in serious groundwater contamination (2-6). Plumes of contaminated groundwater, often miles in length, have been identified at military sites with some extending beyond installation boundaries.

A number of laboratory methods have been developed to characterize water samples potentially contaminated with secondary explosives. At present, however, the method most often used by contract laboratories conducting analyses for the Army is SW846 Method 8330 (7). This is a reversed-phase high performance liquid chromatographic (RP-HPLC) method that specifies 14 target nitroaromatic and nitramine analytes and two protocols for water analysis. When detection limits ranging between 4 and 14 µg/L are adequate for project requirements, a direct injection procedure can be used that does not require sample preconcentration prior to RP-HPLC determination. When lower detection limits are needed, a protocol including a salting-out solvent extraction (SOE) preconcentration step is specified (8,9). Winslow et al. (10,11) proposed the use of solid phase extraction (SPE) as an alternative to SOE and reported excellent recovery and detection limits that were very similar to those for SOE. Winslow's results were obtained using Porapak R, a divinylbenzene n-vinylpyrrolidone co-polymer, in the cartridge format. LeBrun et al. (12), using SPE in the membrane format, reported excellent recoveries of the analytes in Method 8330 using a membrane composed of styrene-divinylbenzene. Recently Bouvier and Oehrle (13) reported on the use of Porapak RDX for cartridge SPE preconcentration of nitroaromatics and nitramines.

Because of a number of potential advantages of SPE over SOE, we conducted a three-way comparison of SOE, cartridge-based SPE using Porapak R (SPE-C), and membrane-based SPE (SPE-M) using styrene-divinylbenzene membranes (Empore SDVB) for preconcentra-

tion of waters containing nitroaromatics and nitramines (14, 15). This evaluation included estimating detection capability and analyte recovery using fortified reagent grade water, and analyte recovery for a series of field-contaminated groundwater samples from the U.S. Naval Surface Warfare Center (NSWC), Crane, Indiana. Overall, the results can be summarized as follows:

(1) the three methods were comparable with respect to low-concentration detection capability, ranging from 0.05 to 0.30 µg/L.

(2) Recoveries generally exceeded 80%, except for HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) by membrane-SPE where recoveries were lower.

(3) Large interferences were found on about half of the groundwater samples from the NSWC using the two SPE methods, but none were found by SOE.

(4) The SPE interferences were traced to a matrix interaction of the SPE polymers with low pH groundwaters which apparently caused the release of unreacted monomers or other contaminants from the interior of the polymeric materials.

At least partly in response to the problems identified above, several manufacturers of SPE materials sought to improve the retention of SPE materials for very polar organics such as HMX and RDX, and experimented with new cleaning procedures to better remove interferences from the SPE materials. As a result, Waters Corporation released a new ultra-clean SPE material for use in cartridge SPE under the name Porapak RDX (13), and 3M Corporation developed a new surface modified styrene-divinylbenzene membrane which also had been cleaned more extensively (Empore SDB-RPS). Initial tests at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and elsewhere indicated that these materials were indeed cleaner than the original SPE materials.

OBJECTIVE

The objective of this study was to reassess SPE for preconcentration of nitroaromatic and nitramine explosives from water, using the newly released, manufacturer-cleaned SPE materials. Special attention was given to recovery of HMX and RDX, because of the low recoveries found for these analytes with membrane SPE in the initial study. The level of contamination resulting from use of these manufacturer-cleaned materials was assessed using both reagent water samples and some groundwaters from the Naval Surface Warfare Center (NSWC). These groundwaters included some of the low pH waters that had revealed the contamination problem with the initial SPE materials.

EXPERIMENTAL

Conduct of study

This work was jointly conducted by the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and CRREL, using fortified reagent grade water and actual groundwater samples from the NSWC. Groundwater samples were taken with bailers which were rinsed once with isopropyl alcohol and three times with distilled water between samples. Wells were purged with a PVC bailer to a depth midway down the well stream, allowed to recharge a minimum of 2 hours, then sampled with Teflon bailers. Samples were collected in 1-L precleaned, amber glass bottles and were stored and shipped at 4°C.

RP-HPLC analysis

All water samples were analyzed by RP-HPLC. Depending on the specific test conducted, water samples were either analyzed using the direct method specified in SW846 Method 8330 (7) or were preconcentrated using either SOE, SPE-C or SPE-M as described below (14).

Primary analysis was conducted on a 25-cm × 4.6-mm (5-µm) LC-18 column (Supelco) eluted with 1:1 methanol/water (v/v) at 1.2 mL/min. Injection volume was 50 µL introduced using a 200-µL sample loop. Concentration estimates were obtained from peak heights from a Waters 820 Maxima Chromatography Workstation. The identities of target analytes and transformation products were confirmed by analysis of the samples on a 25-cm × 4.6-mm (5-µm) LC-CN column from Supelco eluted with 1:1 methanol/water (v/v) at 1.2 mL/min (7). Quantitative results for the 2-amino and 4-amino-dinitrotoluenes (2ADNT and 4ADNT) were also taken from the LC-CN determination since better separation of these two analytes was obtained on this column. Retention times of the analytes of interest for both separations are reported elsewhere (17).

Primary analyses were conducted using a Waters Model 600 system controller, Model 610 fluid unit, Model 717 plus Auto Injector set for a 50-µL injection, a 486 UV Variable Wavelength Detector set at 245 nm, and a Maxima Chromatography Workstation. Confirmation analysis was conducted on a Waters LC Module 1 with a 486 UV Variable Wavelength Detector (245 nm), a 717 plus Auto Injector (50 µl) and a Maxima 820 Chromatography Workstation.

Salting-out solvent extraction/non-evaporative preconcentration procedure

A 251.3-g portion of reagent grade sodium chloride was added to a 1-L volumetric flask. A 770-mL sample of water was measured with a 1-L graduated cylinder and added to the flask. A stir bar was added and the contents stirred at maximum rpm until the salt was

completely dissolved. A 164-mL aliquot of acetonitrile (ACN), measured with a 250-mL graduated cylinder, was added while the solution was being stirred and stirring was continued for at least 15 minutes. If the ACN was slow in dissolving due to poor mixing, a Pasteur pipette was used to withdraw a portion of the undissolved ACN layer and reinject it into the vortex of the stirring aqueous phase. After equilibrium had been established only about 5 mL of ACN normally remained in a separate phase. The stirrer was turned off and the phases allowed to separate for 15 minutes. If no emulsion was present, the ACN phase was removed and placed in a 100-mL volumetric flask and 10 mL of fresh ACN was added to the 1-L flask. The 1-L flask was again stirred for 15 minutes, after which 15 minutes was allowed for phase separation. The ACN was removed and combined with the initial extract in the 100-mL volumetric. When emulsions were present, that portion of the sample was removed from the volumetric flask with a Pasteur pipette, placed in a 20-mL scintillation vial, and centrifuged for 5 minutes at 2000 rpm. The supernate was also pipetted into the 100-mL volumetric flask, the scintillation vial was rinsed with 5 mL of acetonitrile and the acetonitrile added to the 100-mL volumetric flask. For the first extraction the pellet that formed after centrifugation was added back to the 100-mL flask, but if it formed in the second extraction, it was discarded.

In order to reduce the volume of ACN, an 84-mL aliquot of salt water (325 g NaCl per 1000 mL of water) was then added to the 100-mL volumetric flask. The flask was placed on a vertical turntable and rotated at about 60 rpm for 15 minutes. After the phases were allowed to separate for 15 minutes, the ACN phase was carefully removed using a Pasteur pipette and placed in a 10-mL graduated cylinder. An additional 1.0-mL aliquot of ACN was then added to the 100-mL volumetric flask and the flask rotated on the turntable for 15 minutes. Again the phases were allowed to separate for 15 minutes and the resulting ACN phase was added to the 10-mL graduated cylinder. The volume of the resulting extract was measured and diluted 1:1 with reagent grade water prior to analysis.

Cartridge solid-phase extraction

Prepacked cartridges of Porapak RDX (Sep-Pak, 6 cc, 500 mg) were obtained from Waters Corporation. The cartridges were cleaned by placing them on a Visiprep Solid-Phase Extraction Manifold (Supelco) and passing 15 mL of acetonitrile through each using gravity flow. The acetonitrile was then flushed from the cartridges using 30 mL of reagent grade water. Care was taken to ensure that the cartridges were never allowed to dry after the initial cleaning.

A connector was placed on the top of each cartridge and fitted with a length of $^1/_8$-in.-diameter Teflon tubing. The other end of the

tubing was placed in a 1-L fleaker containing 500 mL of sample. The vacuum was turned on and the flow rate through each cartridge set at about 10 mL/min. If the flow rate declined significantly due to partial plugging from suspended material, it was readjusted. After the sample had been extracted, the top plug containing the fitted tubing was removed from each cartridge and 10 mL of reagent grade water was passed through the cartridge using gravity flow unless the cartridges were sufficiently plugged to require vacuum. A 5-mL aliquot of acetonitrile was used to elute retained analytes from the cartridges under gravity flow. The volume of the recovered ACN was measured and diluted 1:1 with reagent grade water.

Membrane solid-phase extraction

Empore styrene-divinyl benzene membranes (47 mm) were obtained from 3M Corporation. The membranes were designated SDB-RPS and were not commercially available at the time the study was conducted. The styrene-divinyl benzene used in these membranes had been modified to provide extra retention for polar organics such as HMX (16). These membranes were precleaned by centering on a 47-mm vacuum filter apparatus and several milliliters of acetonitrile added to swell the membrane before the reservoir was clamped in place. A 15-mL aliquot of ACN was then added and allowed to soak into the membrane for 3 minutes. The vacuum was then turned on and most (but not all) of the solvent pulled through the membrane. A 30-mL aliquot of reagent grade water was then added and the vacuum resumed. Just before the last of this water was pulled through the membrane, the vacuum was removed, the reservoir filled with a 500-mL sample, and the vacuum resumed. This sample extraction took from 5 minutes to an hour depending on the amount of suspended matter present. Once the water was eluted, air was drawn through the membrane for 1 minute to remove excess water. These extractions were conducted six at a time using an Empore extraction manifold (3M Corporation). Vials (40 mL) were placed below the outlets of the six membranes, a 5-mL aliquot of ACN was added to each reservoir, the acetonitrile was allowed to soak into the membrane for 3 minutes, and then the vacuum was applied to pull the acetonitrile through the membranes into the vials. Each resulting extract was removed with a Pasteur pipette, the volume measured in a 10-mL graduated cylinder, and the extract was diluted 1:1 with reagent grade water prior to analysis.

Preparation of analytical standards

All standards were prepared from Standard Analytical Reference Materials (SARMs) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Individual stock standards were prepared in HPLC grade acetonitrile (Baker). Combined

working standards were in acetonitrile and were diluted 1:1 with Milli Q Type I water (Millipore Corp.).

RESULTS AND DISCUSSION

Determination of retention capacity of the SDB-RPS membrane for HMX and RDX

The retention of HMX and RDX by the SDB-RPS membranes was tested by extracting a 2-L aliquot of reagent grade water that had been spiked with 100 µg/L of HMX and RDX using aqueous stock standards. Samples of the water passing through the membrane were collected every 250 mL and analyzed by RP-HPLC using the direct analysis protocol. Results indicated that no breakthrough for either analyte occurred until more than 1 L of water had been extracted (17). Thus it appears that the SDB-RPS membranes have an increased retention capacity for the very polar nitramines relative to that observed with the initial SDB membranes used in an earlier study (14,15).

Comparison of results using groundwater samples from Naval Surface Warfare Center

All 33 groundwater samples from NSWC were all analyzed by the direct RP-HPLC method (without preconcentration) and by RP-HPLC after preconcentration using salting-out solvent extraction (SOE), cartridge solid phase extraction (SPE-C), and membrane solid phase extraction (SPE-M) (17). The following target analytes were detected in these samples (the number of samples where the analytes were detected in at least one of the four analyses are given in brackets): HMX [19], RDX [22], TNB [4], DNB [5], 3,5-DNA [6], TNT [11], 2,4-DNT [2], 4ADNT [15] and 2ADNT [15]. Concentrations measured for HMX and RDX in these groundwater samples were generally much higher than for the nitroaromatics and aminonitroaromatics.

While results from the direct method are certainly not error-free, they are subject to far fewer sources of error than methods employing a preconcentration step. For that reason, we treated the results from the direct analysis as "true values" for purposes of comparison with results from the three preconcentration techniques. Table 1 summarizes results for samples where analytes were detected by the direct RP-HPLC method. Of the 33 groundwater samples analyzed, 11 had detectable HMX using direct analysis, with concentrations ranging from 25 to 325 µg/L. Likewise RDX was detected in 13 groundwaters using the direct method, with concentrations ranging from 13 to 608 µg/L; TNT in four samples with concentrations ranging from 14 to 180 µg/L; the 4ADNT and 2ADNT in five samples with concentrations ranging from 9 to 59 µg/L and 7 to 65 µg/L, respectively; and TNB in two samples at 5 and 8

Table 1. Ratio of concentrations obtained for the various preconcentration methods relative to that from the direct method.

Analyte	n	Concentration-preconc./Concentration-direct SOE	SPE-C	SPE-M
HMX	11	0.870±0.188	0.957±0.147	0.833±0.129
RDX	13	0.800±0.184	0.975±0.192	0.882±0.158
TNT	4	1.010±0.252	1.143±0.331	1.015±0.244
4ADNT	5	0.909±0.128	0.996±0.106	0.925±0.095
2ADNT	5	0.865±0.106	1.021±0.066*	0.871±0.057

* Value significantly different at the 95% confidence level.
n = the number of ratios in each mean.

µg/L, respectively. For a given analyte, the ratio of the concentration obtained for each preconcentration technique relative to that for the direct method was computed and the mean and standard deviation obtained (Table 1). Mean ratios ranged from 0.800 for RDX using the SOE method to 1.143 for TNT using the SPE-C method. Only for 2ADNT was a significant difference among methods detected (by ANOVA) at the 95% confidence level (SPE-C was different from SOE and SPE-M, which were not significantly different from each other). The results of this analysis indicate that, for relatively high concentrations, all three preconcentration techniques produced concentrations similar to that from the direct analysis method, with analyte recoveries in all cases at or above 80%. These results demonstrate a marked improvement in the recovery of HMX and RDX using the SDB-RPS membrane relative to that observed in our original study where the SDB membrane was used (14,15). This improvement is particularly striking for HMX, where recoveries improved from about 49% to 83%, and appears to be due to an improvement in retention for polar compounds resulting from sulfonation of the styrene divinylbenzene. Recovery of HMX and RDX using the Porapak RDX cartridge remains excellent at 96% and 98%, respectively.

Since the value of a preconcentration technique lies in the fact that it allows determination at concentrations below those that can be determined directly, it is important to evaluate its performance when concentrations are below the detection limits of the direct method. Since the SOE method is the procedure currently recommended in SW846 Method 8330, results for SPE-C and SPE-M were compared with those obtained for SOE for samples with analyte concentrations below the detection limits of the direct method. In Figures 1, 2 and 3 the concentrations of HMX, RDX and TNT determined using SPE-C and SPE-M are plotted against the concentrations obtained using SOE. In the absence of bias the plots should have a slope of 1.00 and an intercept of zero. Regression analyses were

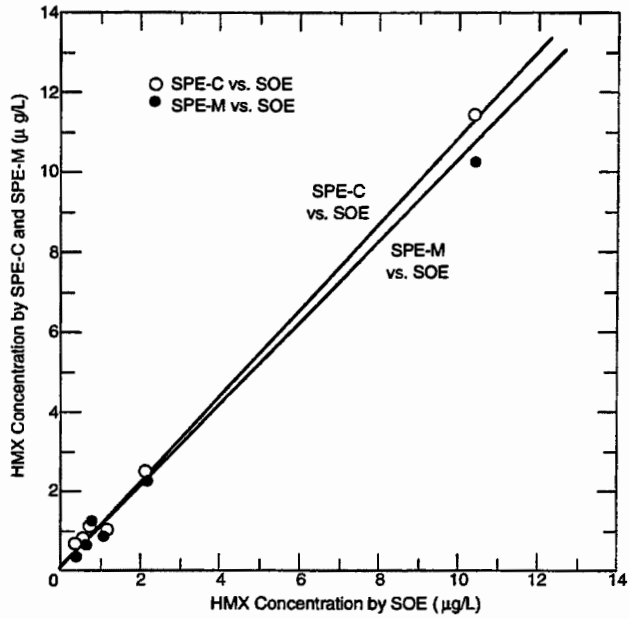

Figure 1. Plot of HMX concentrations determined for groundwater samples using SOE vs those using SPE-C and SPE-M.

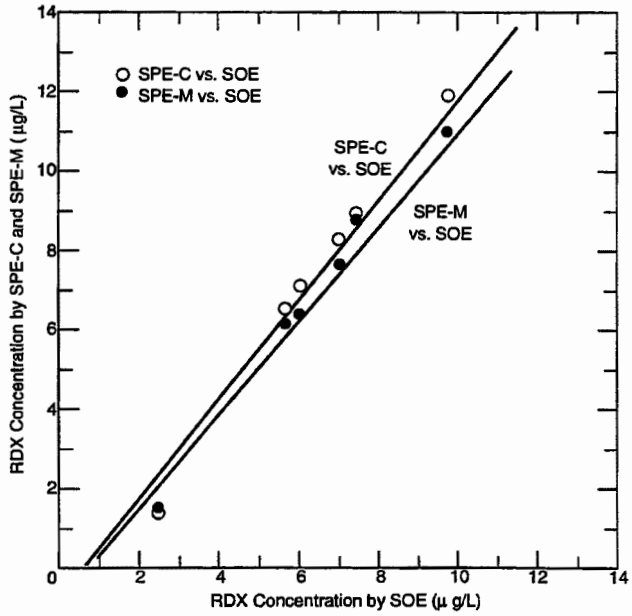

Figure 2. Plot of RDX concentrations determined for groundwater samples using SOE vs those using SPE-C and SPE-M.

conducted for the SPE-C vs SOE and SPE-M vs SOE individually for each analyte, and the resulting slopes, intercepts and correlation coefficients squared are presented in Table 2. Similarly,

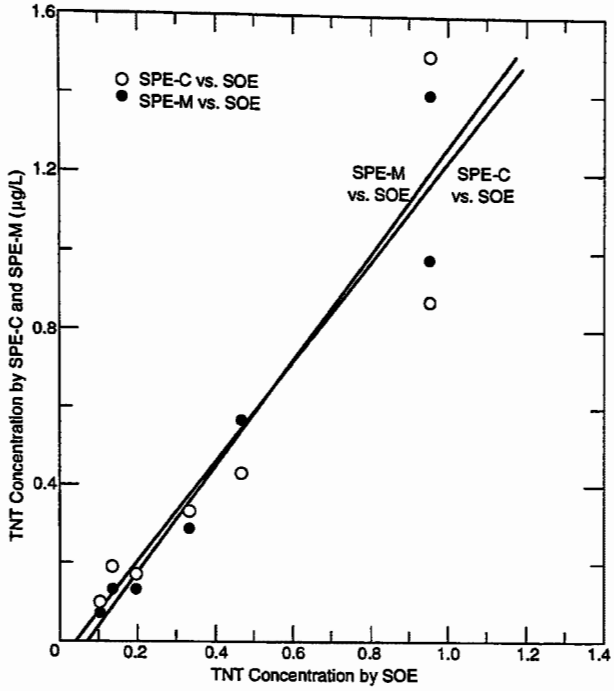

Figure 3. Plot of TNT concentrations determined for groundwater samples using SOE vs those using SPE-C and SPE-M.

Table 2. Results of regression analyses of SPE-C vs. SOE and SPE-M vs SOE for low concentration* determinations.

	SPE-C vs. SOE			SPE-M vs. SOE		
Analyte	m†	b**	r^{2}††	m	b	r^{2}
HMX	1.083	0.125	0.999	0.972	0.113	0.999
RDX	1.255	-1.044	0.987	1.160	-0.850	0.980
TNT	1.264	-0.052	0.933	1.325	-0.085	0.972
4ADNT	1.400	-0.448	0.994	1.208	-0.360	0.992
2ADNT	1.270	0.110	0.981	1.484	0.875	0.974
3,5-DNA	0.972	0.007	0.996	0.930	0.014	0.996

* Low concentration—concentrations below that detectable using the direct method.

† m - Slope.

** b - Intercept.

†† - Correlation coefficient squared.

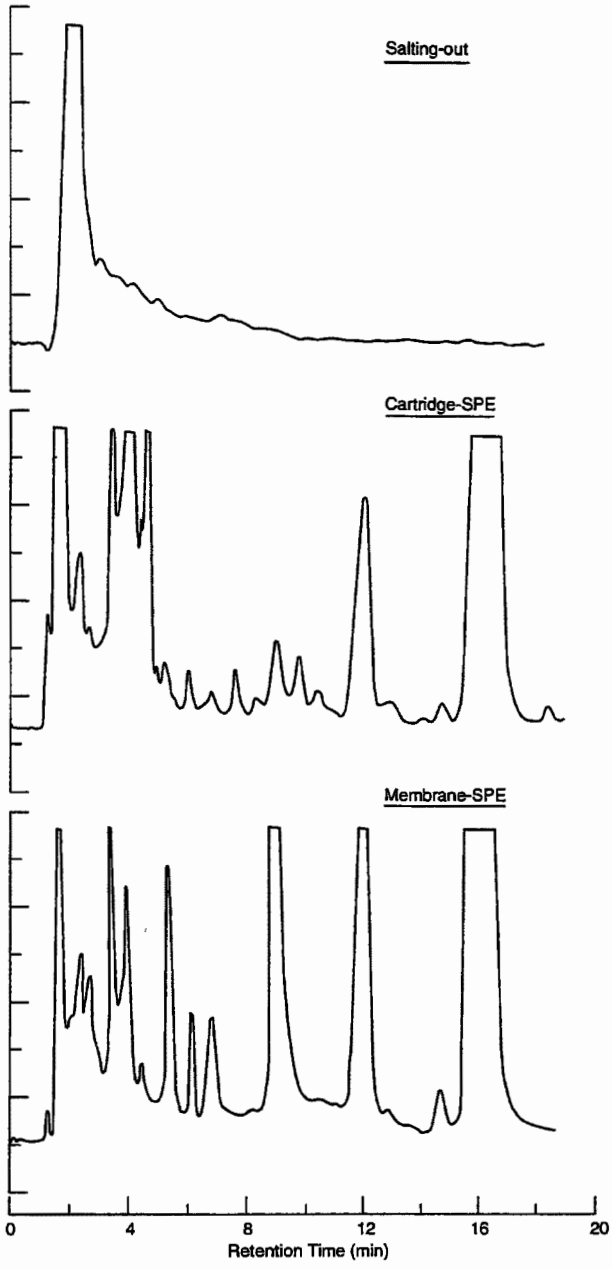

Figure 4. LC-18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C and SPE-M using initial less clean SPE materials.

regression analyses were conducted for 4ADNT, 2ADNT and 3,5-DNA (Table 2). Slopes for these 12 regression analyses range from 0.930 to 1.400, with intercepts ranging from -1.044 to +0.875. Values for the square of the correlation coefficient range between 0.933 and 0.999. The results from these regression analyses indicate that the two SPE methods are producing data which are very similar to those obtained from SOE, even at concentrations below 1 µg/L. The TNT data for concentrations below 0.5 µg/L are particularly striking in this respect (Figure 3).

Examination of chromatograms for groundwater samples

In our initial comparison of SOE, SPE-C and SPE-M, we found a series of groundwater samples that caused the solid phase materials to release high concentrations of interferences. This is illustrated for the chromatograms obtained for sample 20641 in 1992 (14) using SOE, Porapak R (SPE-C) and Empore SDB (SPE-M) (Figure 4). Chromatograms for this same sample obtained using the new, manufacturer-cleaned Porapak RDX and SDB-RPS are shown in Figure 5. Clearly there is a vast decrease in interferences released from the two solid phases. There remains, however, a small

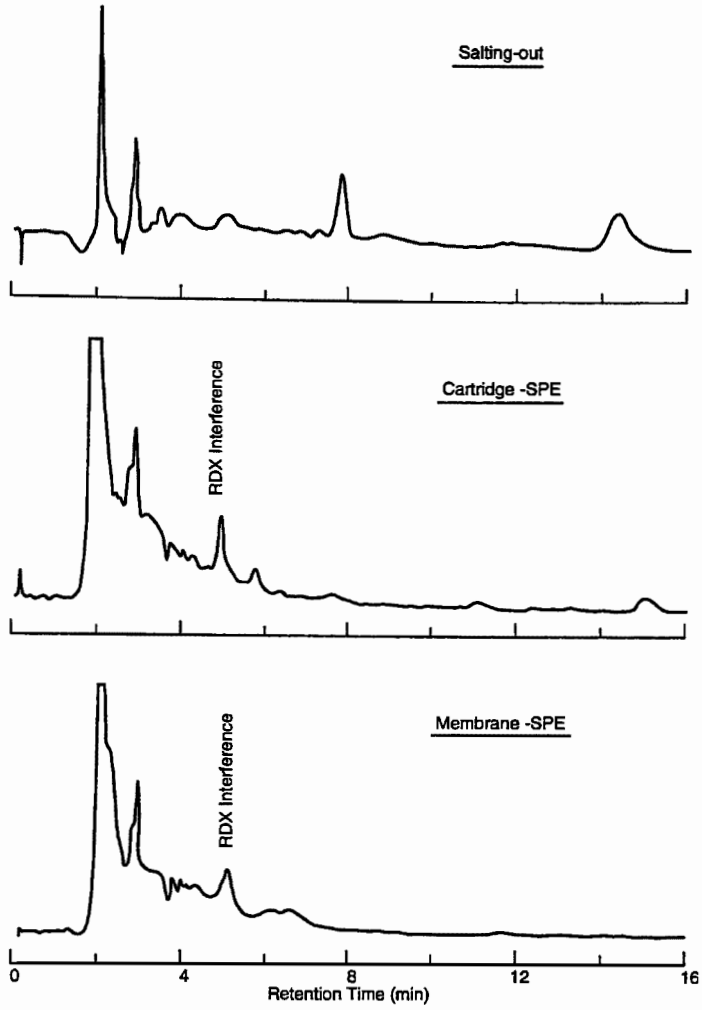

Figure 5. LC-18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C and SPE-M using new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M.

interference peak at the retention time for RDX in the two chromatograms for the SPE methods that is not observed for the SOE (Figure 5) and does not confirm as RDX using the LC-CN confirmation column (Figure 6). This peak was observed in the LC-18 chromatograms for both the SPE-C and SPE-M for the same six well waters that resulted in release of interferences in the original study. Observation of these peaks would require that a confirmation analysis be conducted, and would result in quantitative RDX estimates ranging from 0.2 to 0.6 µg/L if careful scrutiny of an LC-CN confirmation analysis had not been done. Thus when SPE pre-

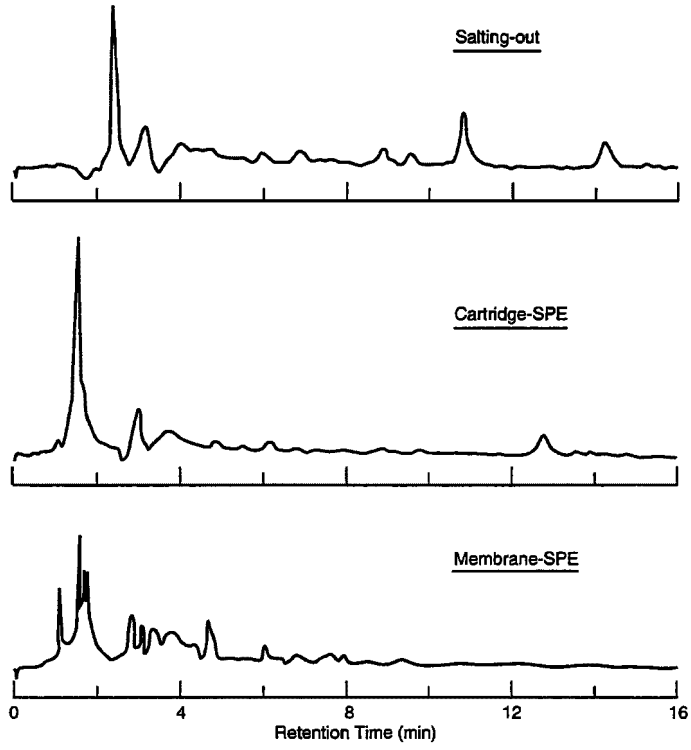

Figure 6. LC-CN RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C and SPE-M using new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M.

concentration is used, the detection limit for RDX should be raised to about 0.6 µg/L to eliminate the chance for misidentification due to this small interference peak.

CONCLUSIONS AND RECOMMENDATIONS

Solid phase extraction, in both the cartridge (SPE-C) and membrane (SPE-M) formats, was evaluated for its ability to preconcentrate nitroaromatics, nitramines and aminodinitroaromatics from water samples prior to analysis by RP-HPLC (SW846 Method 8330). A series of 33 groundwater samples from the Naval Surface Warfare Center was used for comparison. New, manufacturer-cleaned solid phase materials (Porapak RDX for SPE-C and SDB-RPS for SPE-M) were compared to salting-out solvent extraction with respect to their recovery of target analytes and their production of chromatographic interferences.

Based on these results, we recommend that solid phase extraction, in either the cartridge or membrane format, be included as an

option along with salting-out solvent extraction for the preconcentration step in SW846 Method 8330 (7). Comparison of the results of this study and earlier work (14,15) demonstrates the necessity of using carefully cleaned solid phases for this purpose or interferences will be released for certain water matrices.

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ENVIRONMENTAL SAMPLE EXTRACTION USING GLASS-FIBER EXTRACTION DISKS

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ABSTRACT

When performing environmental sample analysis, the extraction procedures are often very time consuming, expensive and possibly dangerous. A new extraction technology that would reduce those aspects would be extremely worthwhile to an environmental laboratory. Fiber membranes demonstrate that capability with respect to semi-volatile extraction methods for drinking water, wastewater, and groundwater matrices. New technologies, such as teflon based membranes, have shown improvements with clean sample matrices, but are still quite expensive, and time consuming.

The fiber membranes look promising as an alternative to current technology due to its larger pore size and depth filter capabilities. This could solve one of the biggest downfalls of SPE technology, clogging due to dirty samples. The fiber membranes would lower the amount of solvent used, as well as use less toxic solvents, increase sample capacity due to shorter extraction times and the biggest potential exists in providing a sample extract that does not have the interferences that usually accompany extracts using current liquid-liquid technology.

Experimental results were generated using the SIMDisk-GF C18, solid phase extraction disk, from Restek Corporation. The method tested was EPA Method 525.1, for semi-volatile analytes in drinking water.

INTRODUCTION

The US Environmental Protection Agency has recently adopted a streamlined tier system for promulgating new methods. This allows more rapid approval of methods that incorporate new innovative technologies. Recently, several new sample extraction methods have been approved which overcome many of the shortcomings of classical liquid-liquid techniques. Liquid-liquid extractions are time consuming, use expensive glassware, and require large amounts of solvents. Solid phase extraction has been promoted as an alternative to liquid-liquid extraction.

Solid phase extraction has been used for several years, but due to the shortcomings of the SPE tubes or cartridges for extraction of large volumes of water it has not gain acceptance for environmental applications. More recently, solid phase extraction disks have been promoted for the extraction of semi-volatile pollutants from aqueous matrices. The most popular extraction disk is a Teflon membrane that has been impregnated with a C18 bonded silica particles. These disks allow more rapid extraction of larger sample volumes while maintaining good recoveries for a wide range of non-polar and moderately polar compounds. However, clogging of these membranes from particulate matter in the sample can significantly reduce flow through the disk which greatly increases extraction time.

Restek now offers a new hydrophobic glass fiber extraction disk that is impregnated with bonded C18 silica particles. Unlike the Teflon membrane extraction disks that rely primarily on surface filtration, the glass fiber disk allows extractions to take place deep in the filter due to the thicker, more open design. This results in less clogging and faster flow rates even for samples with high particulate matter. Because of the larger pore size, SIMDisk™-GF disks run at extraction flow rates of 125-150ml per minute, compared to only 80-100ml per minute for Teflon disks with typical water samples. SIMDisk™-GF are more rigid and easier to handle than thin Teflon filter extraction disks. And, most importantly, SIMDisk™-GF costs less than Teflon disks resulting in a savings every time your lab does an extraction.

The EPA has given approval for the use of other extraction disks as long as they pass the QC criteria and are chemically the same. The only requirement to prove equivalency is to show that the recovery the compounds specified in the method are within the limits established. Since recovery data is required with any disk, whether specified in the method or not, there is really no extra work involved. The SIMDisk™-GF and the Teflon disk both contain C18 bonded silica, therefore they are considered chemically similar.

EPA Method 525.1 is used for the determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatograph/mass spectrometry. It is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C18 organic phase chemically bonded to a solid silica matrix in a cartridge or disk. [EPA methods are available from NTIS (National Technical Information Service), U.S. Department of Commerce, Springfield, VA, 22161, 703-487-4650]

PROCEDURE

SAMPLE PRETREATMENT: Allow 1 liter of deionized water to equilibrate to room temperature in a narrow-mouth amber glass bottle. Adjust sample pH to less than 2 with 6M hydrochloric acid. Add 5 ml of methanol and mix thoroughly. Spike internal standards. For QA/QC samples, spike with 2 ug of each analyte (8 ug of pentachlorophenol) and 5 ug of each internal standard.

APPARATUS ASSEMBLY: Assemble the 47mm apparatus. Place the SIMDisk-GF disk in the Diskcover-47 filter support, WRINKLED SIDE UP.

DISK PRECLEANING: Add 5 ml of methylene chloride to the top surface of the disk and immediately draw through under vacuum at 15 in. Hg (50 kPa). Continue to draw vacuum at 15 in. Hg (50 kPa) for 5 minutes to remove all solvent.

DISK CONDITIONING: Add 5 ml methanol to the top surface of the disk and immediately apply low vacuum (1-2 in. Hg, 3-7 kPa). Draw through until the top surface of the methanol is just above the disk. DO NOT ALLOW ANY AIR TO PASS THROUGH THE DISK OR TO REACH THE TOP SURFACE OF THE DISK. Immediately add 5 ml of DI water to the disk and draw through at low vacuum until the water almost reaches the top surface of the disk. NOTE: It is preferable to leave extra liquid above the disk rather than allow any air to contact the surface of the disk.

SAMPLE ADDITION: Add the sample onto the disk, adding it directly to the film of water left on the disk from the conditioning step. Adjust the vacuum to 10 in. Hg (35 kPa) for a flow rate of approximately 100 ml per minute until the entire sample has been processed.

DISK DRYING: After the sample has been processed, draw air through the disk under vacuum at approximately 15 in. Hg (50 kPa) for approximately 5 minutes.

ANALYTE ELUTION: Release system vacuum. Insert the sample collection rack and collection vessels. Reassemble the apparatus. Add 5 ml methylene chloride directly to the sample bottle and gently swirl to rinse all inner surfaces of the bottle. Allow the sample bottle to stand for 1 to 2 minutes, and transfer the methylene chloride to the disk using a glass pipet and rinsing the sides of the reservoir in the process. Draw the solvent through the disk at 5 in Hg (17 kPa). Repeat the bottle rinse and disk elution twice with fresh aliquots of methylene chloride, combining all eluates in the collection tube.

FINAL ANALYSIS: Remove water from sample eluate by passing through approximately 3 grams of anhydrous sodium sulfate. Concentrate to 1 ml, and analyze 1 ul by GC/MS.

Accuracy and Precision data from four deteminations of Method 525.1 analytes at 2ug/L
with Liquid-Solid SIMDisk-GF 47mm extraction disk and the Finnigan MAT ITS40 Ion Trap MS

Compound	Target Conc. (ug/L)	Mean (ug/L)	Std. Dev. (ug/L)	%RSD	Accuracy (% of Target)	% REC. in Method
Acenaphthalene-d10	5	-	-	-	-	-
Phenanthrene-d10	5	-	-	-	-	-
Chrysene-d12	5	-	-	-	-	-
Hexachlorocyclopentadiene	2	1.6	0.03	2.1	80	55
Dimethylphthalate	2	1.8	0.17	9.4	90	95
Acenaphthylene	2	2.0	0.06	3.1	100	95
2-Chlorobiphenyl	2	2.0	0.05	2.4	100	95
Diethylphthalate	2	2.1	0.07	3.3	105	100
Fluorene	2	2.1	0.06	3.1	105	110
2,3-Dichlorobiphenyl	2	2.0	0.07	3.2	100	115
Hexachlorobenzene	2	2.0	0.06	2.8	100	85
Simazine	2	1.9	0.19	10.2	95	105
Atrazine	2	2.1	0.16	7.5	105	110
Pentachlorophenol	8	9.7	0.79	8.2	121	97
gamma-BHC	2	2.1	0.04	2.2	105	105
Phenanthrene	2	2.2	0.04	1.9	110	120
Anthracene	2	2.0	0.09	4.6	100	85
2,4,5-Trichlorobiphenyl	2	1.9	0.04	1.9	95	85
Alachlor	2	2.1	0.04	1.7	105	-
Heptachlor	2	1.9	0.04	2.2	95	110
Di-n-butylphthalate	2	2.5	0.24	9.5	125	110
2,2',4,4'-Tetrachlorobiphenyl	2	1.9	0.02	1.2	95	75
Aldrin	2	1.6	0.20	12.7	80	80
Heptachlor epoxide	2	2.1	0.05	2.5	105	115
2,2',3',4,6-Pentachlorobiphenyl	2	1.9	0.05	2.4	95	95
gamma-Chlordane	2	1.9	0.08	4.1	95	110
Pyrene	2	2.0	0.04	2.0	100	95
alpha-Chlordane	2	1.9	0.05	2.8	95	100
trans-Nonachlor	2	1.9	0.07	3.7	95	135
2,2',4,4',5,6'-Hexachlorobiphenyl	2	1.7	0.14	8.0	85	80
Endrin	2	2.2	0.05	2.2	110	90
Butylbenzylphthalate	2	2.2	0.12	5.4	110	100
Bis(2-ethylhexyl)adipate	2	1.8	0.21	11.9	90	80
2,2',3,3',4,4',6-Heptachlorobiphenyl	2	1.8	0.04	1.9	90	70
Methoxychlor	2	2.1	0.05	2.5	105	90
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	2	1.7	0.02	1.2	85	90
Benzo(a)anthracene	2	1.9	0.02	0.9	95	90
Chrysene	2	1.9	0.02	0.9	95	110
Bis(2-Ethylhexyl)phthalate	2	2.2	0.04	2.0	110	95
Benzo(b)fluoranthrene	2	2.0	0.09	4.2	100	-
Benzo(k)fluoranthrene	2	2.0	0.08	4.2	100	105
Benzo(a)pyrene	2	2.0	0.10	5.1	100	40
Perylene-d12	5	4.7	0.34	7.3	94	100
Indeno(1,2,3-cd)pyrene	2	1.9	0.22	11.6	95	20
Dibenzo(a,h)anthracene	2	1.8	0.20	11.3	90	15
Benzo(g,h,i)perylene	2	1.8	0.18	9.9	90	35

SUMMARY

The results show that the recoveries of all compounds are well within the limits specified in the method. Recoveries ranged from 80-125%, which are well within the range of 70% to 130% specified in the method. The RSD's were also well below the 30% limit specified in the method. Even the heavier polycyclic aromatic hydrocarbons, which typically show lower recoveries, are easily recovered with the SIMDisk™-GF. Although these results prove the equivalency of the SIMDisk™-GF to other extraction disks, Restek suggests that each laboratory generate data using their extraction techniques and equipment.

When using the SIMDisk™-GF, a liter of water can be processed in about 10 minutes, compared to at least 30 minutes using Teflon disks. A package of 20 SIMDisk™-GF extraction disks costs about $35.00 less than 20 Teflon disks. Faster extraction times and lower costs equate to improved efficiency and lower costs for laboratories processing samples for EPA Method 525.1.

CAPACITY FACTORS IN HIGH-EFFICIENCY GPC CLEANUP

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ABSTRACT

High efficiency gel permeation chromatography (GPC) cleanup columns increase sample throughput and reduce hazardous waste generation by employing smaller gel particle sizes to obtain more chromatographic efficiency. They are permitted as substitutes for referenced columns in EPA methods (e.g. SW-846 Method 3640A) because the packing's chemical nature is essentially the same as columns specified in methods. Previous work[1] showed that relative analyte retention times are the same for the two column types packed in 100% methylene chloride, indicating that they are interchangeable for this application.

To some extent advantages of high efficiency columns have been obtained by sacrificing sample matrix handling capacity. In other words, commercially available high efficiency column sets pass quality control specifications provided in the method, but at any given matrix loading level the degree of cleanup obtained using the high efficiency technique may not be as great as the cleanup obtained using the traditional (low pressure) columns specified in the EPA methods. For this reason traditional GPC cleanup columns are still recommended for processing samples that are high in lipid, such as tissue extracts.

In this work degree of cleanup was studied for three column types*: Envirosep-ABC™ high efficiency columns, EnviroBeads™ low pressure column sized per Method 3640A, and a smaller version of EnviroBeads column. In addition to 100% methylene chloride eluant specified in the EPA method a non-chlorinated alternative, ethyl acetate and cyclopentane (CYP) mixture, was explored. Four types of matrix material were investigated: diesel fuel, corn oil, potting soil extract, and spinach extract.

Cleanup efficiency was rated by measuring the amount of matrix material remaining in a collected fraction when a calibrated column was loaded with various levels of matrix dissolved in mobile phase. Calibration was performed with the test mixture cited in Method 3640A. Chromatograms were obtained at more than one flow rate to determine how much flow could be increased without visually obvious loss of resolution. In all cases the traditional column provides a higher degree of cleanup than a high efficiency column set for the same matrix loading level, or the same degree of cleanup at a higher matrix loading level. The results can provide guidance for choosing a column type that is appropriate to the user's cleanup goals.

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* Envirosep-ABC is a trademark of the Phenomenex Corporation. EnviroBeads is a trademark of Laboratory Automation, Inc.

INTRODUCTION

GPC cleanup of organic extracts protects data quality and reduces analytical equipment maintenance requirements[2] by removing high molecular weight matrix coextractives. The GPC separation mechanism is primarily physical in nature, thus the cleanup is applicable to all organic analytes, including those that may be captured or destroyed by during adsorptive cleanup techniques (alumina, silica gel, Florisil® columns*).

Current EPA methodology for GPC cleanup currently cites a 25 mm x 700 mm glass barreled column packed with 70 grams of S-X3 resin beads (a styrene and divinylbenzene copolymer) in 100% DCM. Use of this column (referred to as Column ***A***) to clean up extracts for GC/MS semivolatiles analysis requires a processing time of about 50 minutes and the use of 250 mL of chlorinated solvent for each sample. Smaller particle sizes of copolymer beads provide greater chromatographic efficiency for faster sample throughput and reduced solvent consumption; however, they are usually packed in smaller columns due to cost factors. Since smaller columns overload at lower matrix coextractive levels, careful comparison of cleanup requirements to column performance factors is advisable. Two types of smaller columns were tested: 1) a low pressure column in a glass barrel (Column ***B***) and, 2) a high-efficiency column set packed in steel columns (Column ***C***).

In this study traditional columns were compared to smaller ones with presumed lower matrix handling capacity to assess completeness of cleanup for several matrix types. Table 1 compares characteristics of three column types tested. Each type was calibrated using EPA recommended solution[3]. Standard solutions of matrix material were injected on the columns and the collected fraction was analyzed for unremoved matrix material. Alternate solvent systems offer the possibility to eliminate use of chlorinated solvents[4]. Therefore, performance of columns was also compared for two mobile phase systems: 1) 100% DCM, and 2) 7:3 ethyl acetate and cyclopentane (ETA/CYP).

Table 1. Column Types Compared in This Investigation

Column Type		Weight of Packing	Bed Length	Inner Diameter
A	EnviroBeads S-X3 Select	70 grams	49 cm	2.5 cm
B	EnviroBeads S-X3 Select	21.5 grams	43 cm	1.5 cm
C	Envirosep-ABC	NA	41 cm	2.1 cm

* Florisil is a registered trademark of the Floridin Company.

EXPERIMENTAL PROCEDURE

Sample Matrices

Four matrix surrogates were examined; Mazola corn oil (biological matrix), number 2 diesel fuel from a service station (petroleum contaminated samples), potting soil extract (soils), and spinach extract (crops samples). Standard solutions of each matrix were prepared in each of the two solvent systems at several concentrations.

Column Calibration

Calibration of each column was checked first at a flow rate for which the linear velocity of mobile phase was about the same as in the traditional GPC cleanup method. This was determined by multiplying 5 mL/minute times the square of the ratio of the diameter of the column being tested to the diameter of the traditional column. Higher flow rates were also checked to determine when loss of resolution (by visual inspection of the UV chromatogram) occurs as mobile phase linear velocity is increased.

Determination of Capacity

At a given flow rate, for each of the two solvent systems, solutions of matrix material at various loading levels were injected on a column using a sample loop of 2.5 mL or 5.0 mL capacity. Dump and collect times were set for either semivolatiles (BNA) analysis or pesticides and PCBs analysis. The collected fraction was examined for unremoved matrix material using either gravimetric analysis (corn oil, potting soil extract, and spinach extract) or GC/FID analysis for matrix materials containing components that might be lost during evaporation (diesel fuel).

RESULTS

Results provided in this manuscript are for the semivolatiles (BNA) calibration only. Additional results will be presented at the conference, including column comparisons for the pesticide/PCB application.

Table 2 show amounts of unremoved matrix material for corn oil injected onto column ***B*** or column ***C*** under various conditions with either a 5.0 mL or 2.5 mL injection loop*. Similarly, Table 3 shows amounts of unremoved number 2 diesel fuel for the same pair of columns. All type ***B*** results shown are using ETA/CYP mobile phase and all type ***C*** results are using 100% DCM mobile phase. Additional data will be available for presentation at the conference.

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* There appears to be little difference in resolution whether using 2.0 mL or 2.5 mL injection. The larger size was chosen to facilitate "dirty" sample processing by avoiding viscosity effects on resolution.

Table 2. Corn Oil in the Collected Fraction of Extracts Cleaned Using Envirosep-ABC

Column Type	Injection Size	Flow Rate	Loading Level	Amount Recovered	Percent Removal
B	2.5 mL	4.0 mL/min	400 mg	14 mg	96.5 %
C	5.0 mL	5.0 mL/min	50 mg	1.3 mg	94.8 %
C			100 mg	1.1 mg	97.8 %
C			200 mg	2.5 mg	97.5 %
C			400 mg	12.8 mg	97.6 %
C		6.4 mL/min		49.6 mg	87.6 %
C		7.7 mL/min		41.8 mg	89.6 %

Table 3. Diesel Fuel in the Collected Fraction of Extracts Cleaned by GPC

Column Type	Injection Size	Flow Rate	Loading Level	Amount Recovered	Percent Removal
B	2.5 mL	4.0 mL/min	400 mg	380 mg	5.0 %
C	5.0 mL	5.0 mL/min		354 mg	11.5 %
C			200 mg	167 mg	16.5 %

DISCUSSION

Performance of GPC columns as matrix loading level is varied can be classified into two arbitrary regions (Figure 1). In the region below a "point" of matrix overloading, GPC peak shapes remain normally Gaussian, meaning that a certain percentage of the matrix material loaded is removed. That percentage depends on the amount of chromatographic resolution which the column obtains between the matrix coextractives and the largest target analyte molecules. This in turn depends on resin bed length and HETP of the column (which in turn is gel particle size and flow rate dependent). The concentration of matrix material which defines the overload point is primarily dependent on the cross section of the resin bed and permeability characteristics of the gel particle pores (which is affected by viscosity of the mobile phase and therefore temperature). Note that as the amount of matrix material injected increases toward the overload point, the fraction of injected material removed remains the same; however, the absolute amount of unremoved material is increasing linearly with the amount loaded. Thus the overload point does not define the limits of acceptable cleanup, but does serve as a reference point for comparing column types and sizes.

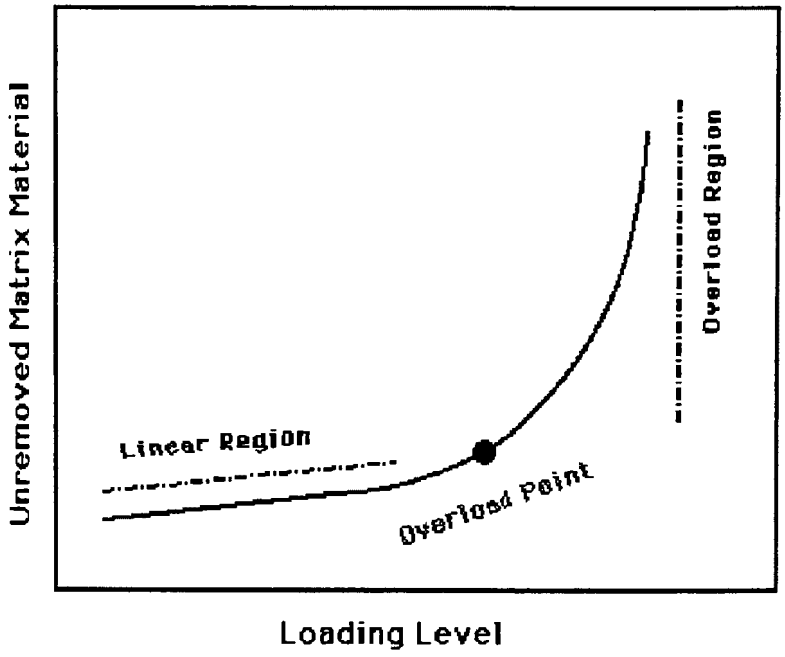

Figure 1. Two Regions of GPC Cleanup Performance

Results in Table 2 and corresponding UV chromatograms showed that at loading levels up to 200 mg with a 5.0 mL injection, column ***C*** was below the overload point. At a 400 mg loading level with corn oil, some deterioration of Gaussian shape was observed on the trailing edge of the corn oil peak, indicating column overload begins to occur near that loading level. This is consistent with previous work. At flow rates higher than the customary 5 mL/min on column type ***C*** larger amounts of oil were recovered in the collected fraction, indicating that the overload region shifts to lower loading levels when flow rate is increased past 5 mL/min

The absolute amount of corn oil in the collect fraction was 12.8 mg at the 400 mg loading level and 5.0 mL/min flow rate. That amount of oil residue is higher than the amount expected to remain in an extract that is cleaned using an EnviroBeads column per method instructions (column ***A***). This is because the larger size of the standard EnviroBeads column more than compensates for the lower chromatographic resolution of its gel particles (larger relative to Envirosep-ABC gel particles in column ***B***); therefore a larger percentage of the corn oil is removed when using column **A**. Note that column type ***B*** provided matrix removal similar to the results from column ***C*** when type ***B*** was used with ETA/CYP mobile phase at 4.0 mL/min.

The results from diesel fuel (Table 3) illustrate the difficulty in removing petroleum derived matrix contamination from samples. Waxy materials and some of the higher molecular weight aliphatic compounds are removed, but the GC/FID profile of the collected fraction appeared essentially unaltered; this is not surprising since at least one fourth of diesel fuel aliphatics have 16-carbons or less, making them too small to remove effectively when using GPC for cleanup of semivolatiles extracts. Clean up of this matrix type is expected to be much more efficient for the pesticide/PCBs application.

Column ***C*** under standard conditions removed only 16.5% of the diesel fuel when 200 mg of diesel was loaded. At 400 mg loading only 11.5% was removed. Under the same conditions column ***C*** at 4.0 mL/min in ETA/CYP was even less effective when measured at the 400 mg loading level; its collected fraction still had 95% of the diesel fuel remaining.

SUMMARY & CONCLUSIONS

1. For corn oil type matrixes, column types ***B*** and ***C*** provided similar results at loading level of a 400 mg per injection. This suggests that smaller columns can provide similar degrees of cleanup whether they are type ***B*** (large gel particle size like the traditional GPC column) or type ***C*** (smaller gel particle size in high efficiency, steel jacketed columns).

2. For type ***C*** 400 mg appears to be the beginning of the overload region for the corn oil matrix. Overload seems to occur at a lower loading level when flow rate is increased beyond 5.0 mL/min for type ***C***.

2. GPC cleanup with 100% DCM mobile phase is not efficient for removal of diesel fuel (principally aliphatic hydrocarbons) during sample clean up. Column type ***C*** appears to be more efficient than type ***B***, but at 200 mg loading level it still only removed 16.5% of the matrix. At 400 mg level it removed 11.5%. This loading level may be at or near the overload region for that matrix type.

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THE USE OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE ANALYSIS OF WASTE DRUM HEAD SPACE

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Transuranic (TRU) radioactive wastes have been retrievably stored in waste drums at Department of Energy (DOE) sites since the 1970's. Ultimately, these waste drums are destined for final disposition in the Waste Isolation Pilot Plant (WIPP). Current requirments for acceptance of waste into the WIPP dictate that a representative drum head space sample be aquired and analyzed prior to the transport and disposal of waste in the WIPP. Analysis results of the head space sample are to be used for waste characterization, verification of process knowledge, assigning Environmental Protection Agency (EPA) hazardous waste codes, determining the potential for flammability, and as input to gas generation and transport models. Because of the very large number of waste drums and the rate at which they will need to be processed, a rapid, simple and reliable analysis method for waste drum head space that can be performed "at-line" is necessary. Fourier transform infrared (FTIR) spectroscopy was selected because the analysis times are short, operation of the instrumention is simple and reliable and because it could be easily implemented "at-line". Drum head space samples are pulled directly into a cell mounted on an FTIR spectrometer and a spectrum recorded. From each infrared spectrum, 29 volatile organic compounds and the C_1-C_3 hydrocarbons are identified and quantitated. To evaluate the analytical performance of the FTIR system and methodology on real samples, ~300 gaseous samples of actual waste drum head space and the head space of other inner layers of confinement have been analyzed by the "at-line" FTIR system. Analytical results are available within 5-6 minutes of sample collection. The FTIR analysis results were compared to the results from duplicate samples that were collected in SUMMA canisters and analyzed by the standard laboratory gas chromatographic (GC) methods. The FTIR analysis results agree well with the chromatographic analyses and will meet the program required limits for accuracy and precision for the analytes of interest. To date, our results indicate that FTIR spectroscopy is a viable, cost effective alternative to the laboratory based GC methods currently specified for the analysis of TRU waste drum head space.

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A QUANTITATIVE METHOD FOR THE DETERMINATION OF TOTAL TRIHALOMETHANES IN DRINKING WATER

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Abstract

Despite the need for extensive testing for trihalomethanes (THMs) in the nation's drinking water supplies, there is as yet no simple, inexpensive, accurate procedure useful for the monitoring of total THMs. Obstacles to the development of such a procedure include the lack of a simple, reliable method for extracting THMs from water, and the inherent difficulty in normalizing the assay response of individual THMs on a weight basis. We have now developed a method which overcomes these obstacles. The test can be performed in less than 15 minutes in a laboratory setting, using ordinary laboratory equipment. The test chemistry provides quantitation of any mixture of the four trihalomethanes, on a weight basis, with an accuracy of $\pm$15% and a relative standard deviation <8%. The method MDL is <5ppb TTHMs and the RQL is <20ppb TTHMs. Cross-reactivity with most other disinfection by-products is minimal.

Introduction

Trihalomethanes form as by-products during the disinfection of water using chlorine-based oxidants. Changes in trihalomethane concentrations in finished water may reflect changes in the quality of influent raw water and indicate a need for adjustments in the treatment process. THMs are routinely measured using purge-and-trap/gas chromatographic techniques. The monetary costs involved in acquiring and maintaing the required instrumentation and the user dedication and expertise needed to assure reliable data places THM monitoring outside the scope of many municipal water treatment laboratories. As a result, considerable effort has gone into the development of simple, inexpensive, and reliable tests for the quantitative detection of THMs at concentrations typically found in drinking water. These tests are in general based on the Fujiwara reaction, in which organic halides, pyridine or a pyridine derivative, and hydroxide react to form a product with a strong UV or visible chromophore.[1] Methods have involved fluorescence detection[2,3], pentane extraction/reaction/evaporative concentration[4], and purging into solutions of pyridine and hydroxide[5]. Drawbacks to these methods have included the use of expensive equipment, difficult or lengthy procedures, matrix interferences, and poor relative recognition of THMs.

We have developed a method for the detection of THMs in drinking water samples which involves two simple procedures. First, a 100mL water sample is extracted using a proprietary, carbon-based filter cartridge. A peristaltic pump is used to filter the sample under positive pressure in a way that avoids exposing the sample to headspace. Then, the analyte is eluted from the cartridge using pyridine and analyzed using Fujiwara conditions which were developed to normalize the response of each of the THMs on a weight basis.

Analyte quantitation can be accomplished through use of a standard curve generated by the user or by running a kit standard. The method can be run in any lab equipped with a working fume hood and needs only common laboratory equipment, a spectrophotometer, and a peristaltic pump. Laboratory personnel can perform the method without training and, with little practice, can run 5-10 analyses per hour.

Experimental

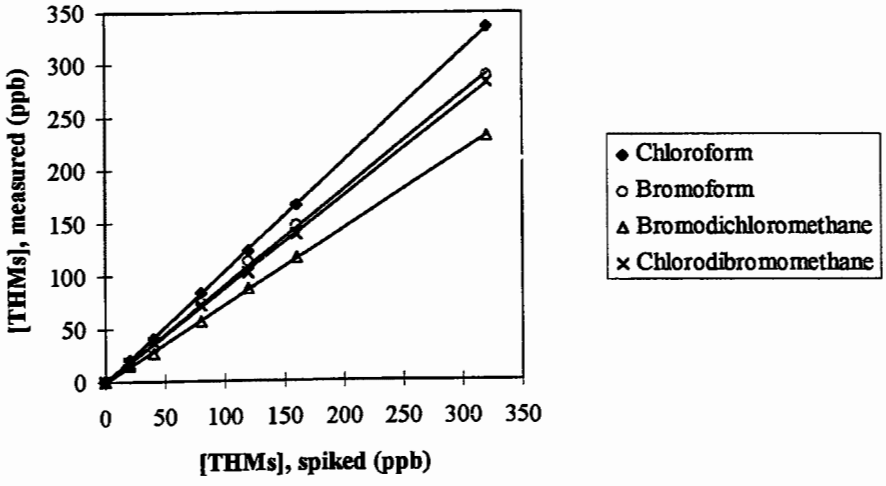
Standards and instrumentation: Trihalomethane standard solutions were prepared from neat reagents (Aldrich). Aqueous standards were prepared using water from a laboratory purifier system (MilliQ) following the procedures prescribed in EPA method 502.1. Analyses were performed using a Hach DR-2000.

Summary of the test protocol: The water sample to be analyzed is loaded into a 100mL syringe so that no headspace forms between the sample and the plunger. The volume is adjusted to 100mL, then the entire sample is pumped through the filter cartridge *via* a peristaltic pump. The cartridge is purged of excess water, then attached to a bottle-top dispenser and eluted with pyridine into a test tube. A developer reagent is added, then the solution is incubated in boiling water and cooled. The presence of THMs is indicated by a pink color which is measured at 531nm and quantitated using a kit standard.

Results and Discussion

Spike/Recovery. Figure 1 shows the results obtained from the analysis of distilled water samples spiked with individual THMs. The method exhibits excellent linearity throughout the range normally encountered in finished water samples. Relative response of the individual THMs in the method is ±15% of the mean.

Figure 1.
Spike/recovery of trihalomethanes



Precision. The method exhibits the following precision for the measurement of 20ppb spikes: (10 replicates)

Analyte	RSD
Chloroform:	5.7%
Bromodichloromethane:	3.9%
Chlorodibromomethane:	2.7%
Bromoform:	7.4%

Method sensitivity. The MDL (3SD above mean blank) is approximately 3ppb. The RQL (12SD, measured at 20ppb, above the mean blank) is approximately 12ppb.

Cross reactants. The following table illustrates the cross-reactivity of all Information Collection Rule analytes (Methods 551 and 552) and some other organochlorine analytes in the method described above.

Analyte	X-react	Analyte	X-react
Trichloroacetonintrile	59%	1,1,1-trichloroacetone	60%
Dichloroacetonitrile	0	1,1-dichloroacetone	1
Dibromoacetonitrile	1	Chloral hydrate	44
Bromochloroacetonitrile	0	Chloropicrin	0
Trichloroacetic acid	15	Trichloroethylene	31
Dichloroacetic acid	4	1,1,1-trichloroethane	0
Dibromoacetic acid	2	Carbon tetrachloride	1
Chloroacetic acid	2	Tetrachloroethylene	0
Bromoacetic acid	2		
Bromochloroacetic acid	2		

A preliminary study of ICR cross reactants present in water samples from nearby municipalities, using Method 551, indicated that they were present at concentrations of less than 10% of the TTHMs and would contribute <10% to the total signal in the test.

Conclusions:

The method described above provides a simple, rapid means of quantitating total trihalomethanes in finished drinking water. Further research will detail the correlation of the method with EPA methods (502.1).

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STABILITY STUDIES OF SELECTED ANALYTICAL STANDARDS FOR THE EXPERIMENTAL DETERMINATION OF EXPIRATION DATES

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ABSTRACT

The accuracy of analytical data in environmental analysis is dependent on the accuracy of analytical standards used in the analysis. Shelf life and stability are important considerations when making and using standards. Usually expiration dates for standards are arbitrarily set for EPA analytical methods. Valid expiration dates can only be established by stability studies over time. A protocol for experimental determination of expiration dates has been established and applied to some specific EPA method standards. Stock and working-level standard solutions have been prepared for a number of EPA methods including Method 8080 for Pesticides and PCB analysis. While some commercial sources of standards supply stability data on high-concentration stock solutions, there is very limited data on lower concentration working-level standards. Now that standards at working levels are commercially available, shelf-life studies of these mixtures are critical. A general discussion of our stability testing program, the importance of experimentally determined expiration dates, and initial results for some of our stability studies will be presented.

INTRODUCTION

Accurate determination of pollutants in the environment is reliant upon a number of factors including field sampling, laboratory sample preparation, and methods for analysis and quantitation of target analytes. Methods for many of these aspects of environmental analysis are well established and documented. The United States Environmental Protection Agency (USEPA) has published methods in documents such as the SW-846 series and the Contract Laboratory Program (CLP) Statements of Work (SOW). These types of documents describe sampling techniques, methods for preparing samples for analysis, and analytical parameters such as instrumentation and quantitation guidelines.

Analytical methods will usually include sections describing standard solutions needed for the analysis. A number of standards such as solutions for initial instrument calibration, calibration checks, internal and surrogate standards, matrix standards, and quality control standards are required for any given method. The description of standards may also include preparation methods and set guidelines for storage and shelf life of each solution.

Since the time that many of the methods were written, the commercial availability of standards has increased dramatically. There are many suppliers that specialize exclusively in providing standards to the analytical testing community. Examples of standards commercially

available include high purity neat materials, single and multicomponent solutions. Solution standards prepared at high concentrations are typically known as stock standards. These are diluted to levels at which the analytes are in a concentration range appropriate for the analytical method. The diluted solutions are known as working-level standards. Many stock solutions for specific EPA methods are commercially available. The availability of standards has removed some of the burden of preparing solutions from the analytical laboratory.

Preparation of standards on a commercial scale is often quite different than preparing standards in the analytical laboratory. Usually, the batch size is much larger on commercial scale and often solutions are packaged in flame-sealed ampules. Laboratories typically prepare smaller amounts and either store solutions in screw-cap vials, bottles, or in volumetric flasks. As analytical methods were written and guidelines were set for preparing and storing standard solutions, the focus was toward individual laboratory preparations. A solution stored in a sealed ampule may have a longer shelf life than the same standard stored in a vial or flask. Arbitrary storage conditions and expiration dates were set in the methods with limited or no experimental basis. For example, the guidelines in SW-846 Method 8081 suggest replacing stock standards after six months and replacing working-level calibration standards after two months. The most appropriate way to determine expiration dates is to prepare and store standards and study them over time to determine changes in analyte composition and concentration.

Another aspect of great concern to the testing laboratory is the traceability and documentation associated with analytical standards. Traceability of analytical reference materials has been discussed recently.[1,2] Often when laboratories are audited by government or private auditors, they are asked to provide documentation and traceability data for standards that they have used in their processes. Using standards that have exceeded the expiration date may cause data on analysis performed with the standards to be invalid. Shelf-life data is part of the traceability of the standard and should be provided by commercial suppliers of standards.

Until recently, most commercial suppliers of standards have only offered neat reference materials and stock standard solutions. Laboratories then dilute the stocks to working levels. An increasing number of working-level standards are now being prepared commercially.[3] While some data is available on stability of stock standards, the amount of data on stability of working-level solutions is very limited. Since this data is critical to laboratories using these solutions, a study was undertaken to experimentally determine shelf life of selected solutions and to establish reasonable expiration dates.

STANDARD PREPARATION

All neat materials used for standards preparation were either synthesized, purified or procured by Radian Corporation Specialty Chemicals Group.

Each material was verified for identity using a combination of methods including GC-MS, NMR, FT-IR, Melting Point (MP) or Boiling Point (BP), and Elemental Analysis. Purity assays for all materials were performed using two or more methods including GC-FID, HPLC, DSC, MP, TLC, and Elemental Analysis.

Stock solutions were prepared using the following procedure: Analytical balances were calibrated using NIST traceable weights. Neat materials for each stock standard were accurately weighed into vials and then quantitatively transferred to volumetric flasks. This procedure was performed in triplicate by three different Chemists or Technicians. The three preparations were compared to each other to ensure precision of preparation. The three preparations were then combined to form the master stock solution. Working-level standards were prepared by volumetric dilutions of the appropriate stock standards.

Ampules to be used in the aliquoting process were rinsed with deionized water, oven dried, and silanized. The ampules were then filled with appropriate amounts of working standard and flame sealed. Random ampules were removed during the early, middle, and late portions of the ampuling process and used for batch homogeneity testing. All standards were stored in a refrigerator at approximately 4°C and protected from light.

Working-level calibration standards were prepared in this manner for USEPA Methods 8080/8081. This method is applicable for the determination of Chlorinated Pesticides and Polychlorinated Biphenyls (PCBs) using Gas Chromatography (GC) with an Electron Capture Detector (ECD). A total of nine sets of calibration standards were prepared (see Tables 1-9). Each set of standards consisted of six or seven concentration levels that would allow for generating a 6 or 7-point calibration curve for each target analyte. Since most laboratories typically generate 5-point curves, the standards were designed so that a combination of 5 of the 6 or 7 levels could be used to generate a higher range or a lower range 5-point curve.

METHOD OF ANALYSIS

All analyses were performed using a Hewlett Packard 5890 Gas Chromatograph equipped with a split/splitless injector, autosampler, and ECD. The GC column used for analyses was a DB-5, 30m X 0.53mm ID, 1.5 μm film thickness column (J&W Scientific). Chromatographic conditions were as follows:

Injector Temperature	250°C
Detector Temperature	290°C
Initial Oven Temperature	150°C (0.5 min. hold)
Ramp Rate	5°C/min.
Final Oven Temperature	270°C (5.5 min. hold)

Calibration standards were analyzed and correlation coefficients were calculated for each analyte in each set. The random ampules removed during the aliquoting process were analyzed for homogeneity of all

analytes. As an additional check for accuracy of concentrations, second source standards were used for comparison. Second source standards were obtained as stock solutions and diluted to working levels that corresponded to the mid-point concentrations of each set of calibration solutions. Responses of second source solutions were directly compared to responses of appropriate mid-point solutions.

METHOD FOR STABILITY TESTING

Stability testing was performed by comparing existing solutions to freshly prepared solutions. For each set of calibration standards, a new stock solution was prepared from neat materials. Each stock solution was then diluted to a working level that resulted in concentrations at mid-points of the calibration curves. Each calibration curve was re-analyzed and correlation coefficients were calculated. The new mid-point solutions were analyzed and analyte responses were compared to responses of corresponding existing mid-point solutions.

RESULTS AND DISCUSSION

There are many factors that may affect the stability of compounds in solution. Some considerations include reactivity of an analyte with: 1) the solvent, 2) other analytes in the same solution (cross reactivity), 3) light, and 4) oxygen. Another factor to consider is storage temperature.

The most common way to detect instability of analytes in solution is to monitor change in analyte concentration over time. One cause of concentration change is the evaporation of solvent which will result in high analyte concentrations. This can occur if standards are stored in screw-cap bottles or in volumetric flasks. One way to prevent loss of solvents and to extend the shelf life of solutions is to use flame-sealed ampules for storage. Another cause for changes in concentration is the ability of some analytes to stick to glass surfaces. This may cause analyte concentration to appear low because some of the analyte is adsorbed to the glass. This effect can be very pronounced for standards at working levels because analyte concentrations are generally very low. Any small loss of analyte to the glass surface may greatly affect the concentration. The use of silanized glass ampules may help reduce this phenomenon because the silanization procedure will reduce active sites on the glass surface.

USEPA methods 8080/8081, as stated above, are appropriate for the analysis of selected Chlorinated Pesticides and PCBs. Some of the Chlorinated Pesticides in the analyte list have been reported to degrade under thermal or photochemical conditions. For example Endrin is known to decompose to Endrin Aldehyde and Endrin Ketone.[4] It has also been reported that Dieldrin will photochemically decompose.[5] Although these materials are expected to be stable in hydrocarbon solvents such as isooctane, the potential for degradation either thermally or photochemically was taken into consideration.

Analysis of PCBs by Methods 8080/8081 is done by classifying PCBs under the commercial term of Aroclors. Aroclors are mixtures of PCBs that fall into a specific boiling point range that is dependent on the degree of chlorination. PCBs are thought to be very stable and degradation is not expected to occur in hydrocarbon solution.

The duration of the stability testing study for the nine calibration mixes was two years. The initial mixes were prepared and verified as described above. The original correlation coefficients for all calibration curves were 0.997 or greater. Comparison of original mid-point solutions to second source standards indicated percent differences for pesticides to be less than 10% and for PCBs to be less than 15%.

After two years, new standards were prepared from neat materials and comparison studies were performed. The first analysis of the stability study was to re-verify each original calibration curve for linearity. Changes in any specific analyte concentration at any of the calibration levels should be indicated by non-linearity. This analysis, however, would not give any indication of overall changes in concentration due to solvent evaporation. For this reason, it is critical to prepare new solutions from neat materials to verify analyte concentrations. Diluting the new stock solution to concentrations that are comparable to existing levels allows for a direct comparison of old and new solutions at the same prepared concentration.

Results from curve linearity analysis and mid-point comparisons of old and new solutions for each set of standards are summarized in Tables 10-18. All correlation coeffecients were 0.997 or better. The correlations are not significantly different than initial linearity data on the solutions indicating significant changes in analyte concentration at any specific concentration level did not occur.

The point to point comparisons of existing solutions to new solutions also did not reveal significant differences in analyte concentration. A change in analyte response of greater than ±15% was considered to be significant. Only four analytes out of 42 analytes studied were greater than 10% with the largest difference at 14.2%. These results indicate that analytes at the mid-point levels were stable over the two year time period.

Methods 8080/8081 discuss generation of a multi-point calibration curve to initially calibrate instruments. It is also suggested to inject a single mid-concentration standard after each group of 20 samples as a calibration check. The variance of analyte responses of the single point check to average responses of the multicalibration should be less than 30%. A variance of greater than 30% indicates that multipoint recalibration is necessary. Laboratories will often use separately prepared solutions as calibration check standards.

Additional calculations were performed on the data from the stability analysis to illustrate consistency of the existing calibration solutions

with separately prepared check standards. Comparison of the curve responses to the freshly prepared mid-point standard responses yielded variances of less than 15%. This indicates that a multipoint calibration of the existing two year old standards would still yield acceptable data.

SUMMARY

The approach for stability analysis of working-level calibration standards for USEPA Methods 8080/8081 was two-fold. Linearity over the full range of each set of solutions needed to be initially verified and then re-evaluated after long-term storage. Additionally, concentrations of analytes needed to be confirmed by comparison to new gravimetrically prepared solutions.

Results from both aspects of the study met the established criteria. No significant changes were observed in the existing solutions. Based on this data it can be concluded that working level calibration standards for Methods 8080/8081 prepared in isooctane, stored in flame-sealed silanized amber ampules at 4°C are stable for at least two years.

These results have established experimentally determined expiration dates for each set of standard solutions included in the study. The study will continue and another set of analyses will be performed at the end of three years that may further extend the shelf life of these standards. Based on data from the above studies, no significant changes in these solutions are anticipated.

Similar studies are currently in progress that include stability testing on working-level calibration standards for Method 8240 (volatile organics analysis) and Method 8270 (semivolitale organics analysis).

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TABLE 1. PESTICIDE CALIBRATION MIX A

Analyte	Concentration (ng/mL) in Isooctane						
	C1	C2	C3	C4	C5	C6	C7
gamma-BHC	1	2.5	5	10	25	50	100
Heptachlor	2	5	10	20	50	100	200
Aldrin	2	5	10	20	50	100	200
Heptachlor-2,3-exo-epoxide	2	5	10	20	50	100	200
Endosulfan I	2	5	10	20	50	100	200
Dieldrin	2	5	10	20	50	100	200
Endosulfan II	4	10	20	40	100	200	400
p,p'-DDT	4	10	20	40	100	200	400
Endrin Aldehyde	4	10	20	40	100	200	400
Methoxychlor	16	40	80	160	400	800	160
Decachlorobiphenyl	4	10	20	40	100	200	400
Tetrachloro-m-xylene	4	10	20	40	100	200	400

TABLE 2. PESTICIDE CALIBRATION MIX B

Analyte	Concentration (ng/mL) in Isooctane						
	C1	C2	C3	C4	C5	C6	C7
(±)-alpha-BHC	1	2.5	5	10	25	50	100
beta-BHC	4	10	20	40	100	200	400
delta-BHC	2	5	10	20	50	100	200
cis-Chlordane (alpha)	2	5	10	20	50	100	200
trans-Chlordane (gamma)	2	5	10	20	50	100	200
p,p'-DDD	4	10	20	40	100	200	400
p,p'-DDE	2	5	10	20	50	100	200
Endosulfan Sulfate	4	10	20	40	100	200	400
Endrin	4	10	20	40	100	200	400
Endrin Ketone	4	10	20	40	100	200	400
Decachlorobiphenyl	4	10	20	40	100	200	400
Tetrachloro-m-xylene	4	10	20	40	100	200	400

TABLE 3. PCB CALIBRATION MIX A

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Aroclor® 1016	50	100	250	500	750	1000
Aroclor® 1260	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 4. PCB CALIBRATION MIX B

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Aroclor® 1221	50	100	250	500	750	1000
Aroclor® 1254	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 5. PCB CALIBRATION MIX C

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Aroclor® 1232	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 6. PCB CALIBRATION MIX D

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Aroclor® 1242	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 7. PCB CALIBRATION MIX E

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Aroclor® 1248	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 8. CHLORDANE CALIBRATION MIX

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Chlordane (tech.)	50	100	250	500	750	1000
Decachlorobiphenyl	10	20	50	100	150	200
Tetrachloro-m-xylene	10	20	50	100	150	200

TABLE 9. TOXAPHENE CALIBRATION MIX

Analyte	Concentration (ng/mL) in Isooctane					
	C1	C2	C3	C4	C5	C6
Toxaphene	50	100	250	500	750	1000
Decachlorobiphenyl	2	4	10	20	30	40
Tetrachloro-m-xylene	2	4	10	20	30	40

TABLE 10. PESTICIDE CALIBRATION MIX A

Analyte	Correlation Coefficient (C1-C7)	Comparison of New Std. (C4) to Existing Std. (C4)	
		Theoret. Conc. (ng/mL)	% Difference
gamma-BHC	0.9991	10	-0.26
Heptachlor	0.9984	20	-10.71
Aldrin	0.9999	20	0.49
Heptachlor-2,3-exo-epoxide	0.9999	20	0.18
Endosulfan I	0.9999	20	1.27
Dieldrin	0.9999	20	2.22
Endosulfan II	0.9997	40	14.21
p,p'-DDT	0.9984	40	-12.32
Endrin Aldehyde	0.9997	40	1.39
Methoxychlor	0.9994	160	-7.41
Decachlorobiphenyl	0.9979	40	-2.38
Tetrachloro-m-xylene	0.9991	40	2.55

TABLE 11. PESTICIDE CALIBRATION MIX B

Analyte	Correlation Coefficient (C1-C7)	Comparison of New Std. (C4) to Existing Std. (C4)	
		Theoret. Conc. (ng/mL)	% Difference
(±)-alpha-BHC	0.9985	10	0.67
beta-BHC	0.9998	40	11.59
delta-BHC	0.9995	20	1.91
cis-Chlordane (alpha)	0.9999	20	1.08
trans-Chlordane (gamma)	0.9997	20	-1.33
p,p'-DDD	0.9998	40	-2.65
p,p'-DDE	0.9998	20	4.00
Endosulfan Sulfate	0.9999	40	-2.71
Endrin	0.9997	40	-6.06
Endrin Ketone	0.9999	40	-0.61
Decachlorobiphenyl	0.9990	40	-2.78
Tetrachloro-m-xylene	0.9998	40	1.99

TABLE 12. PCB CALIBRATION MIX A

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Difference
Aroclor® 1016/1260	0.9997	250	0.71
Decachlorobiphenyl	0.9992	50	-6.51
Tetrachloro-m-xylene	0.9988	50	-1.95

TABLE 13. PCB CALIBRATION MIX B

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Diff.
Aroclor® 1221/1254	0.9996	250	-1.33
Decachlorobiphenyl	0.9990	50	-5.85
Tetrachloro-m-xylene	0.9997	50	-0.39

TABLE 14. PCB CALIBRATION MIX C

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Difference
Aroclor® 1232	0.9998	250	3.94
Decachlorobiphenyl	0.9988	50	-5.14
Tetrachloro-m-xylene	0.9998	50	0.45

TABLE 15. PCB CALIBRATION MIX D

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Difference
Aroclor® 1242	0.9997	250	4.01
Decachlorobiphenyl	0.9991	50	-3.33
Tetrachloro-m-xylene	0.9997	50	2.28

TABLE 16. PCB CALIBRATION MIX E

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Difference
Aroclor® 1248	0.9998	250	-0.73
Decachlorobiphenyl	0.9990	50	-3.76
Tetrachloro-m-xylene	0.9998	50	-1.49

TABLE 17. CHLORDANE CALIBRATION MIX

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C3) to Existing Std. (C3)	
		Theoret. Conc. (ng/mL)	% Difference
Chlordane (tech.)	0.9999	250	9.99
Decachlorobiphenyl	0.9994	50	-2.64
Tetrachloro-m-xylene	0.9998	50	2.77

TABLE 18. TOXAPHENE CALIBRATION MIX

Analyte	Correlation Coefficient (C1-C6)	Comparison of New Std. (C4) to Existing Std. (C4)	
		Theoret. Conc. (ng/mL)	% Difference
Toxaphene	0.9971	500	-9.91
Decachlorobiphenyl	0.9994	20	-1.98
Tetrachloro-m-xylene	0.9981	20	3.47

DETERMINING VOLATILE ORGANIC COMPOUND CONCENTRATION STABILITY IN SOIL

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ABSTRACT

The pre-analysis concentration stability of volatile organic compounds (VOCs) in soil matrices were evaluated independent of volatilization losses. Soil subsamples were fortified with benzene, toluene, ethyl benzene, p-xylene, o-xylene, trans-1,2-dichloroethylene, trichloroethylene and perchloroethylene, sealed inside glass ampoules, and handled in a manner consistent with the EPA's SW-846 Method 8240. Experiments have repeatedly shown that chlorinated-hydrocarbon concentrations remain fairly constant, while aromatic hydrocarbons often experience a complete (>99%) loss when soils are held at 22°C for several days. While refrigeration at 4°C reduces the rate of biodegradation, more than 50% of some of the hydrocarbons are lost when soils are held for 14 days. Chemical preservation by soil acidification with $NaHSO_4$ mitigates the loss of these aromatic hydrocarbons for periods beyond 14 days when held at 22°C.

INTRODUCTION

Despite the large number of soil subsamples analyzed for volatile organic compounds (VOCs) each year, there exists little information on the stability of these compounds in the absence of volatilization losses (1). The routine acceptance of refrigerated storage (4°C) up to 14 days after subsamples have been transferred to airtight vessels (2) continues, even though it is well recognized that soils remain biologically active under these conditions. Several investigators have observed significant reductions in VOC concentrations during storage; however, the experimental approaches used were incapable of distinguishing between volatilization and biodegradation losses (3-5). By eliminating volatilization losses by encapsulating subsamples in glass ampoules and then transferring them to volatile organic analysis (VOA) vials, we can isolate the effect of biodegradation and evaluate methods of chemical preservation (1, 6, 7).

Our initial experiments used a vapor-fortification procedure to spike soils. Although this method has many useful applications (8-10), the number of subsamples that can be made from a single batch of soil is often limited (< 25), treatment takes several days and requires that the soil be desiccated. Here, a much

quicker procedure is described. It uses a spiked aqueous solution to introduce benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), para- and ortho-xylene (p-Xyl, o-Xyl), trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), and perchloroethylene (PCE) to 48 replicate soil subsamples held in small glass ampoules. After treatment, the ampoules are sealed, creating airtight vessels that can be stored and/or transferred intact to VOA vials. For the latter, once the VOA vial has been capped the ampoule can be broken by hand shaking to release the treated soil. Ampoules and/or VOA vials can be stored according to protocols for low- (< 1 µg VOC/g) and high- (> 1 µg VOC/g) level purge-and-trap gas chromatography mass spectrometry (PT/GC/MS), aqueous extraction headspace gas chromatography (HS/GC), or any other method of analysis, without exposing the sample to the atmosphere. Here, a protocol is tested that is consistent with soil samples retained in vapor-tight glass bottles awaiting subsampling [although this practice is not recommended by the author (11)], or in VOA vials awaiting low-level PT/GC/MS analysis (2). Samples were chemically preserved with $NaHSO_4$ because it is one of the more practical biodegradation inhibitors (12).

SOIL SUBSAMPLE PREPARATION AND TREATMENT

The silty-sand topsoil used in this study was obtained locally just prior to the experiment, from between 5 and 10 cm below the ground surface. It was air-dried for 24 hr, passed through a 30-mesh sieve and thoroughly mixed. The moisture content was 4.3% and the organic carbon content was 0.89%.

Subsamples of 1.00 ± 0.01 g were transferred to 2-mL glass ampoules (Wheaton, actual vol. ≈3.1 mL) some of which contained 0.25 g of $NaHSO_4$ (see Figure 1). In this experiment, 21 ampoules contained both $NaHSO_4$ and soil, and 27 contained just soil.

The fortification solution was prepared by adding microliter volumes (3.1-5.8 µL) of Ben, Tol, E-Ben, p-Xyl, o-Xyl, TDCE, TCE, and PCE to a 100-mL volumetric flask containing about 102 mL of groundwater. Each analyte would have an aqueous concentration of approximately 50 mg/L if dissolution was complete. However, this is unlikely, based on their solubilities. After adding the analytes the solution was shaken, a stirring bar introduced, and the flask topped off with groundwater, leaving less than 0.5 mL of headspace after inserting the glass stopper. This solution was stirred for at least 24 hr and allowed to sit undisturbed for 1 hr prior to removing aliquots.

Each soil subsample was spiked with a 200-µL aliquot of this aqueous solution using a 500-µL glass syringe (Hamilton). To avoid undissolved low density analytes that would accumulate at

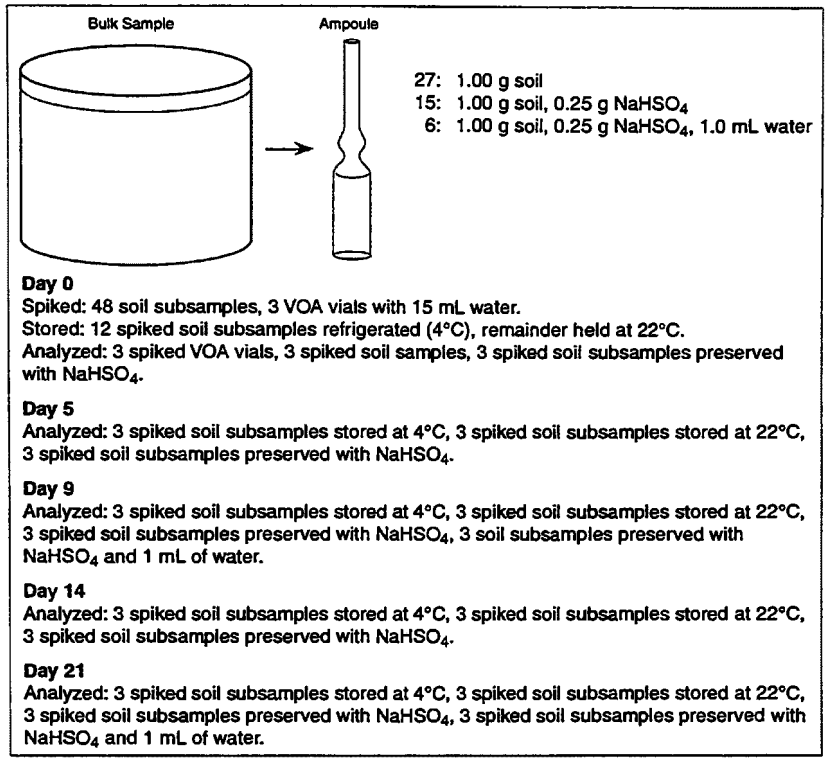

Figure 1. Flow diagram of subsample preparation and analysis.

the surface, aliquots were taken from well below the water-air interface, and the stainless steel needle was wiped prior to inserting into the ampoule's neck. Before transferring a spike, each ampoule was placed in a metal clamp so it be could heat-sealed with a propane torch immediately after spiking. To enhance mixing, 1 mL of Type 1 water (Milli Q, Millipore Corp.) was introduced with a pipette to 6 of the ampoules containing both treated soil and $NaHSO_4$ (see Figure 1). It took approximately 1 hour to spike and seal the 48 soil subsamples, after which each one was hand shaken, mixing its contents. In addition to preparing the soil subsamples, a 200-µL aliquot of the spiking solution was placed in each of three autosampler headspace vials (22 mL, Tekmar) containing 15 mL of Type 1 water, which were immediately capped with crimp-top caps and Teflon-faced butyl rubber septa (Wheaton). One of these samples was prepared at the beginning, middle and end of the soil subsample fortification process to estimate the spiking solution concentration and homogeneity.

The first, middle, and last soil subsamples prepared with and without $NaHSO_4$ were selected for analysis on Day 0 (day of treatment). Also on Day 0, twelve sealed ampoules containing only for-

tified soil were selected at random and placed in a refrigerator (4°C) for storage. All other subsamples remained at room temperature (22°C). Triplicates from these three subsample sets (22°C preserved and unpreserved, 4°C unpreserved) were selected at random and analyzed after 5, 9, 14, and 21 days of storage. The six subsamples preserved with $NaHSO_4$ and made into a slurry by adding 1 mL of water were split into two batches, and analyzed after holding periods of 9 and 21 days (see Figure 1).

ANALYSIS

All samples were analyzed with a HS autosampler (Tekmar 7000) coupled to a GC (SRI model 8610-0058) equipped with a 15-m DB1 0.53 capillary column. Subsamples in ampoules were prepared for analysis by placing them in autosampler vials (22 mL) that contained 14 mL of Type 1 water, or 13 mL for the six ampoules that already contained 1 mL. After sealing with a crimp-top cap, each vial was vigorously hand shaken, causing the ampoule to break and allowing the treated soil to be completely dispersed. Headspace equilibration was obtained by two minutes of manual shaking followed by holding at 25°C for 20 min. A 1-mL headspace sample was drawn through a heated needle and transfer line to the GC for separation and flame ionization detection (FID). The GC temperature sequence started with the sample injection, stayed at 40°C for 1 min, then increased to 100°C in 6 min, and held at 100°C for an additional 3.5 min. Sample analyte concentrations were established relative to aqueous headspace standards prepared by adding small (<10 µL) quantities of a methanol stock solution to autosampler vials containing 15 mL of Type 1 water (8).

RESULTS AND DISCUSSION

Results for the spiking solution and the treated soil subsamples appear in Tables 1, 2, and 3. The means and standard deviations of the analyte mass obtained for the three aqueous aliquots (Table 1) and those of the treated soils analyzed on Day 0 (Tables 2 and 3) demonstrate that the treatment procedure was precise. The small (≤ 15%) concentration decrease from the spiking solution to the unpreserved spiked soil samples is consistent with observed analyte-organic carbon partition phenomena (13); the changes for the preserved spiked samples is a result of both partitioning and salting out (14).

Table 1. Means and standard deviations of analyte concentrations (µg/vial) of the spiking solution in the autosampler vials (triplicate analyses).

Analyte	Treatment aliquot (µg)
Ben	7.0 ± 0.3
Tol	8.5 ± 0.2
E-Ben	7.8 ± 0.1
p-Xyl	8.2 ± 0.1
o-Xyl	8.2 ± 0.1
TDCE	10 ± 0.3
TCE	13 ± 0.3
PCE	9.6 ± 0.3

Table 2. Means and standard deviations of analyte concentrations (µg/g) in unpreserved subsamples stored at 22 and 4°C (triplicate analyses).

Analyte	Analysis day 0*	5	9	14	21
			A. 22°C		
Ben	6.6 ± 0.1	ND†	ND	ND	ND
Tol	8.0 ± 0.0	ND	ND	ND	ND
E-Ben	7.0 ± 0.3	ND	ND	ND	ND
p-Xyl	7.1 ± 0.3	0.2 ± 0.03	ND	ND	ND
o-Xyl	7.3 ± 0.6	5.5 ± 0.3	ND	ND	ND
TDCE	9.5 ± 0.3	9.7 ± 0.0	9.3 ± 0.1	8.7 ± 0.1	9.3 ± 0.3
TCE	12 ± 0.3	11 ± 0.2	11 ± 0.6	9.6 ± 0.1	10 ± 0.2
PCE	8.2 ± 0.2	7.2 ± 0.4	6.9 ± 0.6	6.3 ± 0.1	6.8 ± 0.1
			B. 4°C		
Ben	6.6 ± 0.1	6.5 ± 0.2	5.7 ± 0.9	1.2 ± 1.4	ND
Tol	8.0 ± 0.0	7.6 ± 0.1	7.6 ± 0.2	7.1 ± 0.5	4.4 ± 0.4
E-Ben	7.0 ± 0.3	6.4 ± 0.1	6.3 ± 0.1	6.1 ± 0.2	5.7 ± 0.2
p-Xyl	7.1 ± 0.3	6.5 ± 0.1	6.2 ± 0.2	6.0 ± 0.3	4.6 ± 0.4
o-Xyl	7.3 ± 0.6	6.7 ± 0.1	6.6 ± 0.2	6.5 ± 0.2	6.6 ± 0.2
TDCE	9.5 ± 0.3	9.4 ± 0.3	9.6 ± 0.2	10 ± 0.4	9.4 ± 0.4
TCE	12 ± 0.3	12 ± 0.2	12 ± 0.1	12 ± 0.4	11 ± 0.4
PCE	8.2 ± 0.2	7.5 ± 0.1	7.5 ± 0.2	8.0 ± 0.3	7.4 ± 0.2

* Same subset used for Day 0 values for both storage conditions.
† Not detected: less than 0.02 µg VOC/g.

Table 3. Means and standard deviations of analyte concentrations (µg/g) in preserved soil subsamples stored at 22°C (triplicate analyses).

Analyte	Analysis day 0*	5	9	14	21
			A. Soil subsamples preserved with $NaSO_4$		
Ben	7.5 ± 0.2	7.4 ± 0.1	7.4 ± 0.2	6.5 ± 0.1	7.3 ± 0.2
Tol	9.1 ± 0.2	8.6 ± 0.3	8.6 ± 0.3	7.4 ± 0.1	8.5 ± 0.3
E-Ben	7.7 ± 0.4	6.9 ± 0.3	6.9 ± 0.2	5.9 ± 0.2	6.7 ± 0.5
p-Xyl	7.7 ± 0.2	7.0 ± 0.2	6.9 ± 0.2	6.1 ± 0.2	6.6 ± 0.5
o-Xyl	7.9 ± 0.2	7.1 ± 0.4	7.2 ± 0.3	6.2 ± 0.2	6.9 ± 0.4
TDCE	11 ± 0.4	11 ± 0.2	10 ± 0.2	9.5 ± 0.2	10 ± 0.3
TCE	14 ± 0.4	13 ± 0.4	13 ± 1.0	11 ± 0.1	13 ± 0.6
PCE	8.7 ± 0.5	8.0 ± 0.3	7.8 ± 0.2	7.3 ± 0.1	7.6 ± 0.2
			B. Soil subsample slurries preserved with $NaHSO_4$		
Ben	7.5 ± 0.2		7.3 ± 0.4		7.3 ± 0.2
Tol	9.1 ± 0.2		8.1 ± 0.3		8.4 ± 0.2
E-Ben	7.7 ± 0.4		6.3 ± 0.3		6.5 ± 0.2
p-Xyl	7.7 ± 0.2		6.2 ± 0.4		6.5 ± 0.3
o-Xyl	7.9 ± 0.2		6.5 ± 0.3		6.7 ± 0.2
TDCE	11 ± 0.4		10 ± 0.4		10 ± 0.6
TCE	14 ± 0.4		13 ± 0.6		13 ± 0.2
PCE	8.7 ± 0.5		7.3 ± 0.4		7.6 ± 0.1

* Same subset used for Day 0 values for both storage conditions.

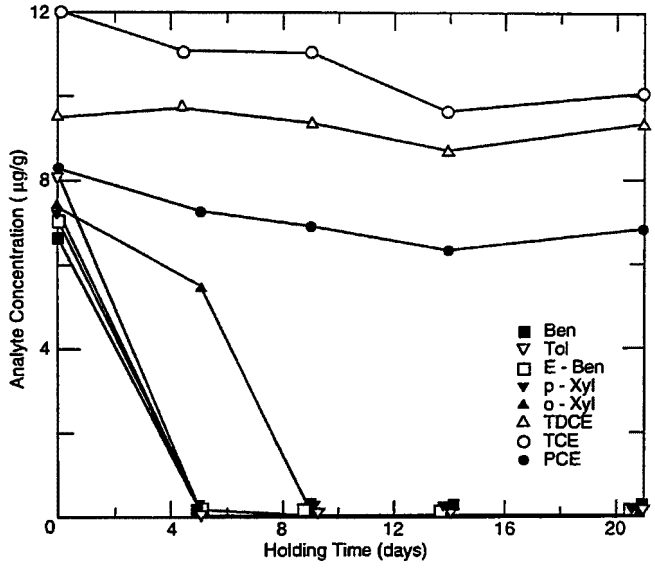

Figure 2. Mean concentrations (µg/g) of VOCs in soil subsamples stored in ampoules up to 21 days at 22°C.

As previously observed when storing samples in sealed glass ampoules or capped VOA vials, the chlorinated compounds showed little (≤ 23%) change in concentration, confirming that vapor losses were controlled (1, 6, 7). Except for the six subsamples made into slurries, only soil (moisture content 24%) and 2.5 mL of air existed during storage in the 2-mL glass ampoules. This moisture and oxygen content is sufficient for complete microbial degradation of the spiked VOCs (15). Indeed, the soil subsamples held at room temperature (22°C), showed a complete (> 99%) loss of the aromatic hydrocarbons within 9 days (Figure 2). These degradation rates are consistent with those observed in aqueous systems, showing half-lives on the order of days for these aromatic hydrocarbons, and weeks to months for the chlorinated compounds (16). Refrigeration (4°C) slowed the degradation, but after 14 days Ben was substantially (> 50%) reduced in concentration relative to Day 0 (Figure 3). In contrast, the subsamples preserved with $NaHSO_4$ showed only small (≤ 23%) concentration changes relative to Day 0 for all of the test analytes over a 21-day room-temperature storage period (Figure 4). Similarly, immersion in MeOH has been shown to be an effective means of preserving VOC concentrations (1). These findings and others (1, 7) suggest that refrigeration is not sufficient to eliminate microbial degradation of VOCs.

Even though these experiments used laboratory-fortified samples, field samples should behave similarly because the chemical pre-

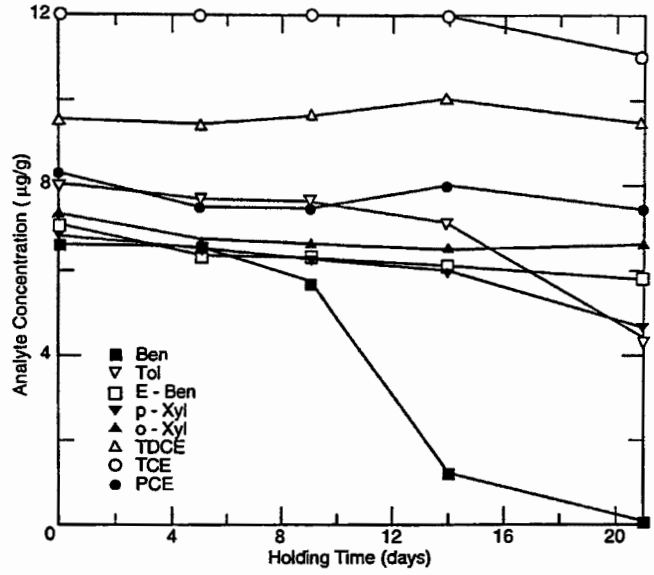

Figure 3. Mean concentrations (µg/g) of VOCs in soil subsamples stored in ampoules up to 21 days at 4°C.

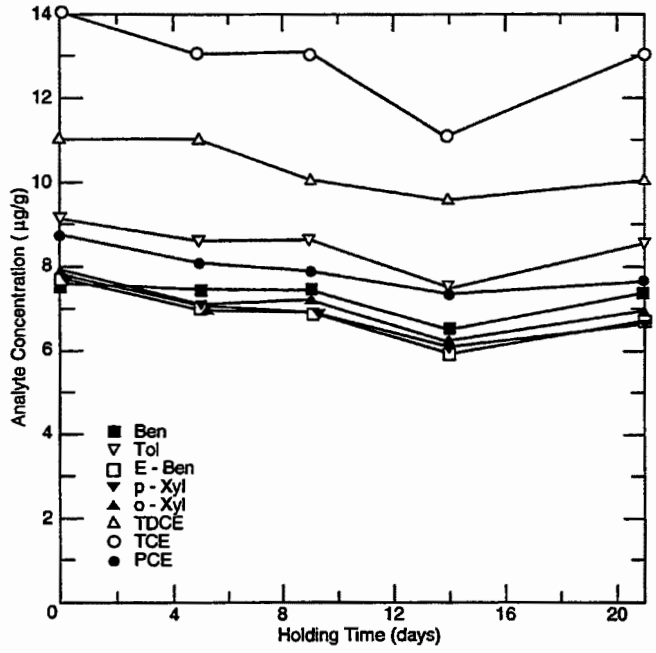

Figure 4. Mean concentrations (µg/g) of VOCs in soil subsamples preserved with $NaHSO_4$ and stored in ampoules up to 21 days at 22°C.

servative inhibited the activity of the indigenous soil microbes. There are, however, some precautions that need to be addressed. Analyte transformations due to acidification have been found to affect the stability of styrene, but not that of the other 23 VOCs tested to date [Appendix (17)]. In addition, it is probably important to obtain pH 2 or lower throughout the sample to inhibit microbial degradation, perhaps requiring an aqueous slurry. In the experiment presented here, slurries were not necessary; the final analyte concentrations in the slurries were not significantly different from those in the other chemically-preserved samples (Table 3). Until more information is available it is recommended that soils be evaluated on a case-by-case basis, and furthermore, that preservation methods other than acidification (e.g., mercuric chloride or sodium azide) be used when a soil contains carbonates.

By using chemical preservation and sample collection and handling protocols that minimize volatilization losses during storage and analysis, environmentally representative analyte concentrations are more apt to remain stable for 14 days, and perhaps longer (11). Small (5-15%) VOC losses are expected even with acidification since the Teflon septum cap liner is somewhat transparent to VOCs (17, 18). Losses through Teflon-lined caps, however, do not appear to be a problem when soil samples are immersed in MeOH (1, 7). Another advantage of chemical preservation is that refrigeration is not as critical.

SUMMARY

Confinement of subsamples in vapor-tight vessels throughout handling and analysis is critical to the accurate assessment of both biological degradation and chemical preservation of VOCs in soil. Using such storage protocols allows investigators to determine if measures other than refrigeration are necessary or effective in maintaining stable VOC concentrations over the holding times permitted by regulations. For the surface soils used in studies at this laboratory (1, 7) chemical preservation by acidification with $NaHSO_4$ (except for soil containing styrene) succeeded in maintaining stable concentrations of aromatic hydrocarbons for periods of 21 days, while refrigeration at 4°C usually failed.

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Appendix: Volatile organic compounds studied in holding-time and chemical preservation experiments.

Benzene
Bromodichloromethane
n-Butyl benzene
Carbon tetrachloride
Chlorobenzene
Chloroform
1,3-Dichlorobenzene
1,1-Dichloroethane
1,2-Dichloroethane
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
Ethylbenzene
Isopropylbenzene
Methylene chloride
n-Propylbenzene
Styrene
Tetrachloroethene
Toluene
1,1,2-Trichloroethane
Trichloroethene
o-Xylene
m-Xylene
p-Xylene

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Photolysis of Laboratory Dioxins/Furans Waste

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Abstract

The photolysis of polychlorinated dioxins and furans in an environmentally benign solvent of propylene glycol, was demonstrated to be an efficient process.

Introduction

The problem with the disposal of the dioxins/furans wastes in the laboratories is troublesome due to no legal disposal way stated in RCRA and denial of this kind of waste from most waste companies. The EPA 1613 method indicates that the dioxins/furans can be decomposed by photolyzing dioxins/furans in methanol or ethanol for two to three days. However, both methanol and ethanol are highly volatile and, therefore, very flammable. In addition, methanol is toxic and ethanol is a controlled substance. We would like to find a solvent which is economical, non-toxic, less volatile, and, in the mean time, efficient in the solvation and decomposition of dioxins/furans in photolysis.

Propylene glycol is selected for this purpose since it is harmless (can even be taken internally), high boiling (bp_{760} 188.2°), and also miscible with water and can dissolve most of organic compounds.

Experimental

A 90 mL of propylene glycol (PG) in a 140mL beaker was spiked with a

300 uL of dioxins/furans at the concentrations shown in Table 1. The solution was magnetically stirred through out the entire experiment. The beaker was wrapped with aluminum foil on the outside and bottom to prevent UV from emitting beyond the beaker. The UV light was then turned on and sampling performed at 0 min, 5 min, 15 min, 35 min, 75 min, 3.25 hr, 9.25 hr, 24 hr, and 50 hr from the start of the experiment. Two separate aliquots of the solution was sampled at zero time and only one aliquot at all other sampling times. During sampling, a 3 mL aliquot of the solution was quantitatively transferred to a vial containing 6 mL of water. After thoroughly mixing, a 10 mL hexane was added to the PG-water mixture. A 20 uL of an internal standard mixture (Table 2) was spiked into the hexane layer. The mixture was shaken vigorously for 30 seconds. The top layer was transferred to another vial. The PG-water mixture was again extracted with another aliquot of hexane (10 mL). Both of the hexane extracts were then combined and blown down to 6 mL. A 2 mL of reagent water was added to the vial containing hexane extract and the mixture shaken for 20 seconds. The hexane extract was then quantitatively transferred to another vial. Two mL of hexane was used to rinse out the residue left in the original vial. The hexane extract was blown down to dryness. The wall of the vial was rinsed with a 1 mL methylene chloride, which also blow down to dryness. The extract was quantitatively transferred to an injection vial with two aliquots of 200 uL methylene chloride. The methylene chloride solution in the injection vial was blown down to dryness. The wall of the injection vial is then rinsed with a 50 uL methylene chloride, which was again blown down to dryness. Finally, 20 uL of a recovery standard mixture (Table 2) was added to the vial and mixed well before the gas chromatograph/mass spectrometer analysis.

Result and Discussion

The concentrations of each congener at different sampling intervals were shown in Tables 3. This result indicated that only approximate 1.3% of OCDD and OCDF left after 195 minutes of UV photolysis of total PCDD/PCDF in propylene glycol. All the other PCDD/PCDF, including TCDD/TCDF,

PeCDD/PeCDF, HxCDD/HxCDF and HpCDD/HpCDF were decomposed. Within 50 hours of UV photolysis, all the rest of OCDD/OCDF was decomposed. As shown in Table 4, the photolysis within first five minutes causes significant decomposition of both OCDD and OCDF. In this initial interval, the number of isomers and total concentration increased for tetra- through hexa-PCDDs. However, total concentration for tetra- through hepta-PCDFs decreases in the first five minutes of photodegradation and only the number of isomers of TCDF increases. In general, PCDF is photodegraded much faster than the corresponding PCDD except OCDD. Both OCDD and OCDF have approximately the same rate in photodegradation. Two compounds, 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD, which were not spiked to the solution and not found in the two solutions sampled at zero time, were found in the solution sampled 5 minutes from the beginning of photodegradation, at 0.107 ng/mL and 0.60 ng/mL, respectively. These were photodegradation products of HpCDD or most likely OCDD.

The table 4 showed the same results as in Table 3, but expressed in TEF (2,3,7,8-TCDD toxicity equivalent factor). This table showed that TEF was decreased to less than 10% of the original TEF in 35 minutes, and to about 3% in 75 minutes.

Conclusion

Photodegradation by UV light in propylene glycol is an effective way of destroying dioxins/furans. Better photolysis conditions are being sought to speed up the process. The mechanism of PCDD/PCDF photolysis are being studied by using OCDD (or OCDF) as the only substrate. Comparision between using UV light and sunlight in PCDD/PCDF photolysis are also being studied.

Table 1
Concentration of Spiked Solution

Analytes	Concentration (ng/uL)
2378-TCDD	2.5
2,3,7,8-TCDF	2.5
1,2,3,7,8-PeCDD	6.25
1,2,3,7,8-PeCDF	6.25
1,2,3,6,7,8-HxCDD	6.25
1,2,3,6,7,8-HxCDF	6.25
1,2,3,4,6,7,8-HpCDD	6.25
1,2,3,4,6,7,8-HpCDF	6.25
OCDD	12.5
OCDF	12.5

Table 2
Internal and Recovery Standard Solution

Compound	Standard	Concentration (ng/uL)
$^{13}C_{12}$-1,2,3,4-TCDD	Recovery	0.56
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	Recovery	0.48
$^{13}C_{12}$-2,3,7,8-TCDD	Internal	0.56
$^{13}C_{12}$-2,3,7,8-TCDF	Internal	0.46
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	Internal	0.54
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	Internal	0.52
$^{13}C_{12}$-OCDD	Internal	0.98

Table 3
Concentration of PCDD/PCDF in ng/mL (ppb) of Propylene Glycol

	Minutes into experiment										
	0	0	0 average	5	15	35	75	195	555	1440	3000
2,3,7,8-TCDD	5.17	5.33	**5.25**	3.55	1.39	.453	.373	0	0	0	0
1,2,3,7,8-PeCDD	21.3	19.4	**20.4**	15.2	7.51	2.5	.387	0	0	0	0
1,2,3,6,7,8-HxCDD	4.27	4.27	**4.27**	2.71	.573	.067	0	0	0	0	0
1,2,3,4,6,7,8-HpCDD	11.4	12.0	**11.7**	4.58	.707	0.247	.113	0	0	0	0
OCDD	21.1	23.3	**22.2**	4.19	1.09	0.62	.273	.287	.153	.073	0
2,3,7,8-TCDF	5.31	5.68	**5.50**	1.05	.147	.067	0	0	0	0	0
1,2,3,7,8-PeCDF	18.2	17.3	**17.8**	1.59	0.22	0.14	0	0	0	0	0
1,2,3,6,7,8-HxCDF	9.8	10.1	**9.95**	.733	.173	.107	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	10.5	10.7	**10.6**	.947	.267	0.16	0	0	0	0	0
OCDF	19.5	21.2	**20.4**	3.14	0.96	0.58	.273	.273	.127	0	0
IS % Recovery											
$^{13}C_{12}$-2,3,7,8-TCDD	50	58	**54**	50	42	56	75	80	85	91	81
$^{13}C_{12}$-2,3,7,8-TCDF	47	56	**52**	52	47	62	80	87	91	107	114
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	96	96	**96**	90	83	90	94	86	90	95	107
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	97	100	**99**	88	85	87	94	83	87	94	113
$^{13}C_{12}$-OCDD	98	97	**98**	84	88	80	86	70	75	95	112

Note 1: concentration below 0.067 ng/mL (instrument detection limit) is reported as 0.

Note 2: 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD, which were not spiked to the solution and not found in the solution sampled at zero time, are found in B at 0.107 ng/mL and 0.60 ng/mL, respectively

Table 4

Concentration (ng/mL in PG) of Total PCDD/PCDF with Isomer Number in Parentheses ("Total" includes 2,3,7,8-substituted isomers)

TOTAL PCDD/PCDF	Minutes Into Experiment							
	0 min	0 min	0 min (Average)	5 min	15 min	35 min	75 min	195 min
Total TCDD (22)*	5.17 (1)	5.33 (1)	5.25 (1)	5.37 (4)	9.21 (7)	8.34 (9)	2.71 (9)	0 (0)
Total PeCDD (14)*	21.8 (1)	19.4 (1)	20.6 (1)	24.3 (7)	13.5 (6)	3.36 (6)	0.389 (1)	0 (0)
Total HxCDD (10)*	4.27 (1)	4.27 (1)	4.27 (1)	16.3 (8)	2.39 (5)	0 (0)	0 (0)	0 (0)
Total HpCDD (2)*	11.4 (1)	12.0 (1)	11.7 (1)	9.21 (2)	1.03 (2)	0.247 (1)	0.113 (1)	0 (0)
OCDD (1)*	21.1 (1)	23.3 (1)	22.2 (1)	4.19 (1)	1.09 (1)	0.62 (1)	0.27 (1)	0.29 (1)
Total TCDF (38)*	5.31 (1)	5.68 (1)	5.50 (1)	1.76 (4)	0.147 (1)	0.067 (1)	0 (0)	0 (0)
Total PeCDF (28)*	18.2 (1)	17.3 (1)	17.8 (1)	1.59 (1)	0.22 (1)	0.14 (1)	0 (0)	0 (0)
Total HxCDF (16)*	9.81 (1)	10.1 (1)	9.96 (1)	0.733 (1)	0.173 (1)	0.107 (1)	0 (0)	0 (0)
Total HpCDF (4)*	10.5 (1)	10.8 (1)	10.7 (1)	0.947 (1)	0.267 (1)	0.16 (1)	0 (0)	0 (0)
OCDF (1)*	19.5 (1)	21.2 (1)	20.4 (1)	3.14 (1)	0.96 (1)	0.58 (1)	0.27 (1)	0.27 (1)

* Maximum number of isomers possible.

Table 5

Concentration (ng/mL in PG) Expressed as 2,3,7,8-TCDD Equivalent Factors (TEFs*)

Minutes into Experiment	0 min	0 min	0 min (Average)	5 min	15 min	35 min	75 min	195 min
TEF (ng/mL)	18.9	18.2	18.6	11.8	5.25	1.73	0.57	0

* Only the 2,3,7,8-chlorinated PCDDs/PCDFs are assigned with toxicity equivalence factors (TEF) in this table.

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THE EFFECTIVENESS OF METHYLENE CHLORIDE STABILIZERS IN AN ENVIRONMENTAL LABORATORY RECYCLING PROGRAM

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ABSTRACT

As solvent purchasing and waste disposal costs rise and EPA regulations governing stack emissions tighten, more labs are turning to solvent recycling. Methylene Chloride is especially suitable for in-house recycling by the environmental labs that generate large quantities of this solvent. When recycling, though, one must be aware of the preservative used by the manufacturer. Some preservatives are lost to the aqueous phase during a water sample extraction, leaving the solvent open to degradation. Other preservatives react during the recycling to form oxidation products which may interfere with the sample analysis. The initial use of the proper preservative in the virgin methylene chloride and the use of a nitrogen blanket during the distillation process by this laboratory has resulted in the consistent generation of solvent clean enough for BNA extractions. The distillate which is concentrated 300:1 and analyzed by GC/MS, is free of oxidation products, and does not degrade in either the long or short terms.

INTRODUCTION

As solvent purchasing and waste disposal costs rise and environmental emission standards tighten, the recycling of waste solvents is becoming a more attractive option for many environmental analytical labs. Recycling allows them reduce their costs while conforming with environmental regulations. Methylene chloride in particular is a viable candidate for a solvent recycling program because it is used in large quantities, is easy to recover, presents no particular storage problems, and can be sufficiently cleaned up by distillation. It is, however, susceptible to degradation leading to the presence of such impurities as phosgene, hydrochloric acid, chloroform and 1,1,2,2-tetrachloroethane. Manufactures add preservatives to reduce degradation of the solvent. These preservatives normally do not interfere with the analysis of samples extracted using the preserved solvent. When recycling, though, one must be aware of the preservative used. Some preservatives can be lost to the aqueous phase during water sample extraction, leaving the solvent open to degradation. Other preservatives may react during the recycling process to form products which interfere with the sample analysis. In this study we found that if we extracted samples using methylene chloride which contained the proper preservative, and if we distilled under a nitrogen blanket,

we could collect the solvent after sample concentration and successfully distill it to produce solvent consistently clean enough to be reused for BNA extractions.

EXPERIMENTAL

Materials

ABC Integrity 2000 spinning band distillation unit
4 Liter amber glass solvent jugs
Buchner funnel
boiling chips
Nitrogen gas
aluminum foil
Kuderna-Danish evaporator-concentrator with Snyder column
Organomation S-Evap unit
Hewlett-Packard 5890 Gas Chromatograph & 5970 Mass Spectrometer
Alltech EPC 1000

Methods

In the first part of this experiment (referred to below as normal conditions) we tested four different preservatives of methylene chloride for their suitability for use in a recycling program. The four preservatives we tested were 1)methanol, 2)cyclohexene, 3)amylene, and 4)amylene and methanol. In each case, we used the methylene chloride to extract water samples according to the semivolatile extraction method 3510. We added total of 300 ml of solvent to each sample, shook it out, and concentrated it using a K-D apparatus with Snyder column over a steam bath. The solvent vapors were condensed and collected using an Organomation S-Evap. The waste solvent was stored in amber glass jugs until 20 liters of solvent had been collected. This waste solvent was then poured into the ABC spinning band unit and glass boiling chips added. Each distillation run was conducted using the following parameters:

shut down temperature = 44
motor speed = 2
motor on temp = 30 C

	First Cut	Second Cut
open cut	30 C	40 C
close cut	39 C	41 C
equilibrium hours	0	0
equilibrium minutes	45	45
reflux ratio	2:1	4:1
mantle rate	30	30

The distillate from each run was collected in a 20 Liter glass bottle. When the run was complete, 300 mL of the distillate was concentrated to 1.0 mL in a Kuderna-Danish with a Snyder column, and analyzed by GC/MS on a 30 meter J&W DB-5.625 .25mm i.d. column with a 1 micron film thickness. The gas chromatograph was operated in splitless injection mode. The GC temperature program used was:

injector temp	= 275 C
detector temp	= 300 C
initial oven temp	= 45 C
initial time	= 3 min
temp ramp	= 8 C/min
final oven temp	= 300 C

In the second part of the experiment, three of the above methylene chloride preservatives were tested for their suitability in a recycling program that used a nitrogen blanket over the still to remove all air from the system and used aluminum foil over the distillate collection bottle to keep light out. The methylene chloride preserved with methanol only was not tested in this part because it was found to be inappropriate for semivolatile extractions for reasons discussed below. The nitrogen blanket was accomplished by running copper tubing from a nitrogen tank to a teflon tee; one leg of the tee was connected by teflon tubing to the distilling head, and the other leg was connected by teflon tubing to a 100 mL round bottom three neck flask which contained a reservoir of oil. The middle neck of the flask was plugged and the third neck was vented to the atmosphere. The nitrogen pressure was adjusted so that the nitrogen slowly bubbled through the oil. This low pressure was enough to keep air out of the system, but not so high that it would affect the distillation. Before the distillation run was started, nitrogen was flushed through the boiling pot and the distillate collection bottle to force out any air. The distillate collection bottle was then completely covered with aluminum foil to keep out all light. Since the boiling pot was covered with an insulative blanket and the distillation column was silvered on the inside, the solvent's contact with light was minimal.

As in the first part of the experiment, the methylene chloride was used in a water extraction, collected on an S-evap, stored in amber jugs, poured into the still in 20 Liter batches, and distilled using the same parameters as before. The distillate was concentrated 300:1 and analyzed by GC/MS.

RESULTS AND DISCUSSION

When distilled under normal conditions, peaks were found which interfered with GC/MS analysis in the methylene chloride preserved with each of the four preservative which were

examined. The methylene chloride preserved with methanol was determined to be unacceptable because most of the methanol partitioned from the solvent into the water during the extraction, leaving the solvent unprotected. Figure 1 is the chromatogram produced by GC/MS analysis. The largest peak in the chromatogram, at 8.23 minutes, is tetrachloroethane, a common impurity in degraded methylene chloride. This indicates that the solvent is unprotected and breaking down. Another problem is the absence of the last internal standard, Perylene-d12. Methylene chloride degradation products have been implicated in the quenching of polyaromatic hydrocarbons used as semivolatile internal standards. We observed similar results in the actual samples which had been extracted using this solvent in a continuous liquid/liquid extraction . For these reasons, we determined that the methanol preserved solvent was inappropriate for semivolatile extractions, and did not test it any further.

When distilled under normal conditions methylene chloride which had been preserved with cyclohexene exhibited two main peaks which elute at 10.51 and 11.44 minutes in the chromatogram in figure 2. A library search of the first peak suggested 2-chlorocyclohexanol. GC/MS analysis of a solution made from the purchased neat compound produced the same two peaks at the same retention times, confirming the identity of the contaminant as 2-chlorocyclohexanol.

When distilled under normal conditions, the methylene chloride preserved with amylene exhibited a cluster of early eluting peaks (figure 3). We have not been able to positively identify these peaks, but based on the mass spectra we believe that the two largest peaks could be a result of acid induced polymerization of the amylene preservative.

When distilled under normal conditions, the methylene chloride preserved with amylene and methanol exhibited the same cluster of early eluting peaks seen in the solvent preserved with amylene alone (figure 4). The size of the peaks, though only about 10% of those seen in the solvent preserved with amylene alone, were still too large to pass our criteria for solvent to be used in BNA extractions. None of the peaks observed in the solvent preserved with methanol alone were observed in the solvent preserved with amylene and methanol, and no quenching of the last internal standard was exhibited.

When distilled under a nitrogen blanket and with aluminum foil over the collection bottle, methylene chloride preserved with each of the three preservatives tested: cyclohexene, amylene, and methanol and amylene, was free of any peaks which would significantly interfere with an 8270 GC/MS analysis. Figure 5 is a samples of methylene chloride preserved with cyclohexene which has been successfully cleaned up. The criteria we used was that no peak could be greater than 3% of the closest internal standard. This modification to the still

has also allowed us to clean up waste from the Gel Permeation Chromatograph without drying, filtering, neutralizing, or predistilling the waste before pouring it into the spinning band distillation unit (figures 6 & 7).

CONCLUSION

Setting up a successful methylene chloride recycling program in an environmental analytical laboratory can have positive environmental and economic rewards, but some thought must be given to the type of preservative which is present in the methylene chloride when it is purchased. We found in this study that methanol alone is not an acceptable preservative. The other three preservatives that we tested under normal distillation procedures all produced peaks which interfered with an 8270 semivolatile analysis by GC/MS. By placing the distillation unit under a blanket of nitrogen to exclude air from the system and by wrapping the distillate collection bottle with aluminum foil to keep out light, we were able to consistently distill methylene chloride waste and recover solvent which was pure enough to reuse for BNA sample extractions.

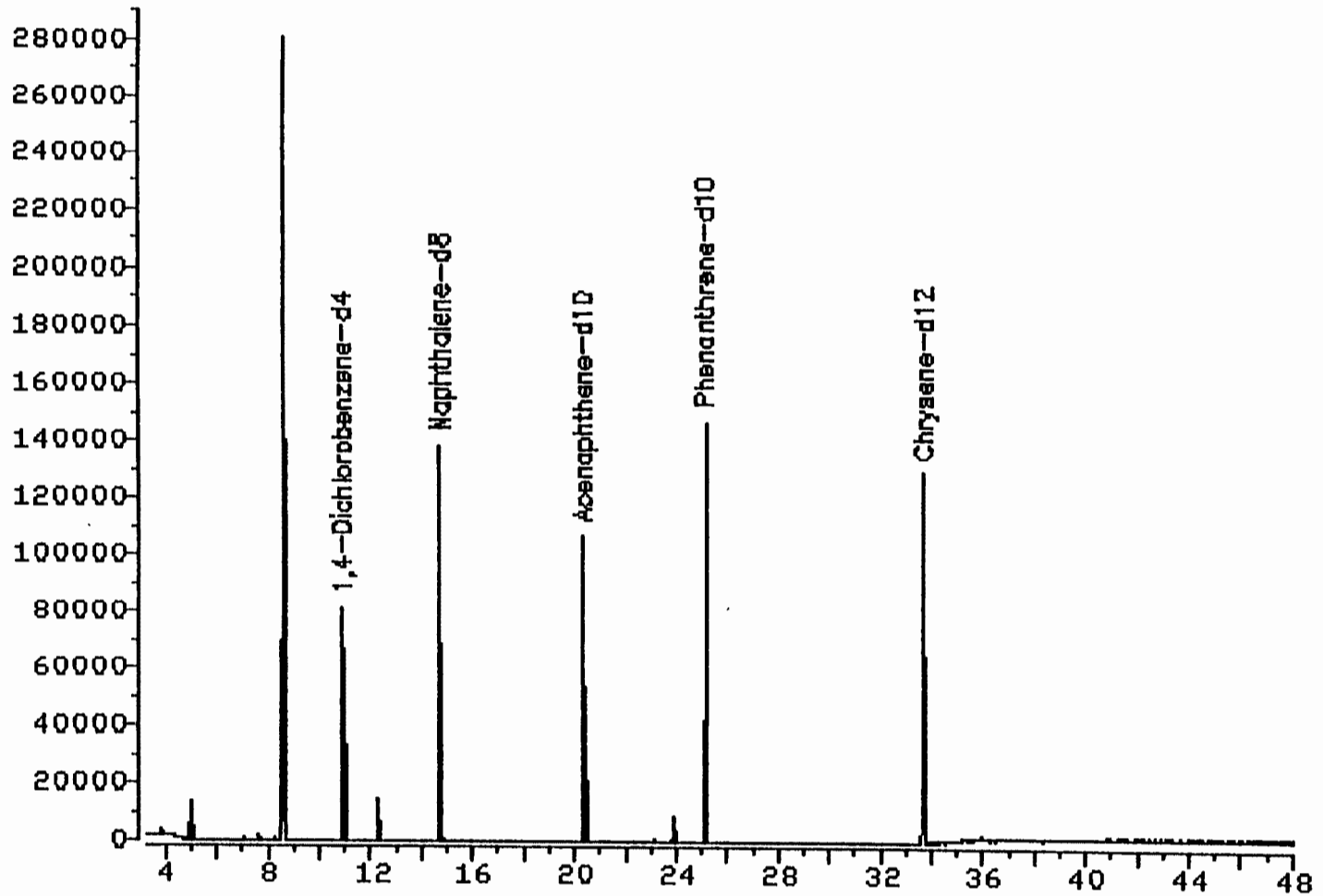

Figure 1. Total Ion Chromatogram of methylene chloride preserved with methanol which has been distilled under normal conditions and concentrated 300:1. Internal standards are at 40ng/ul.

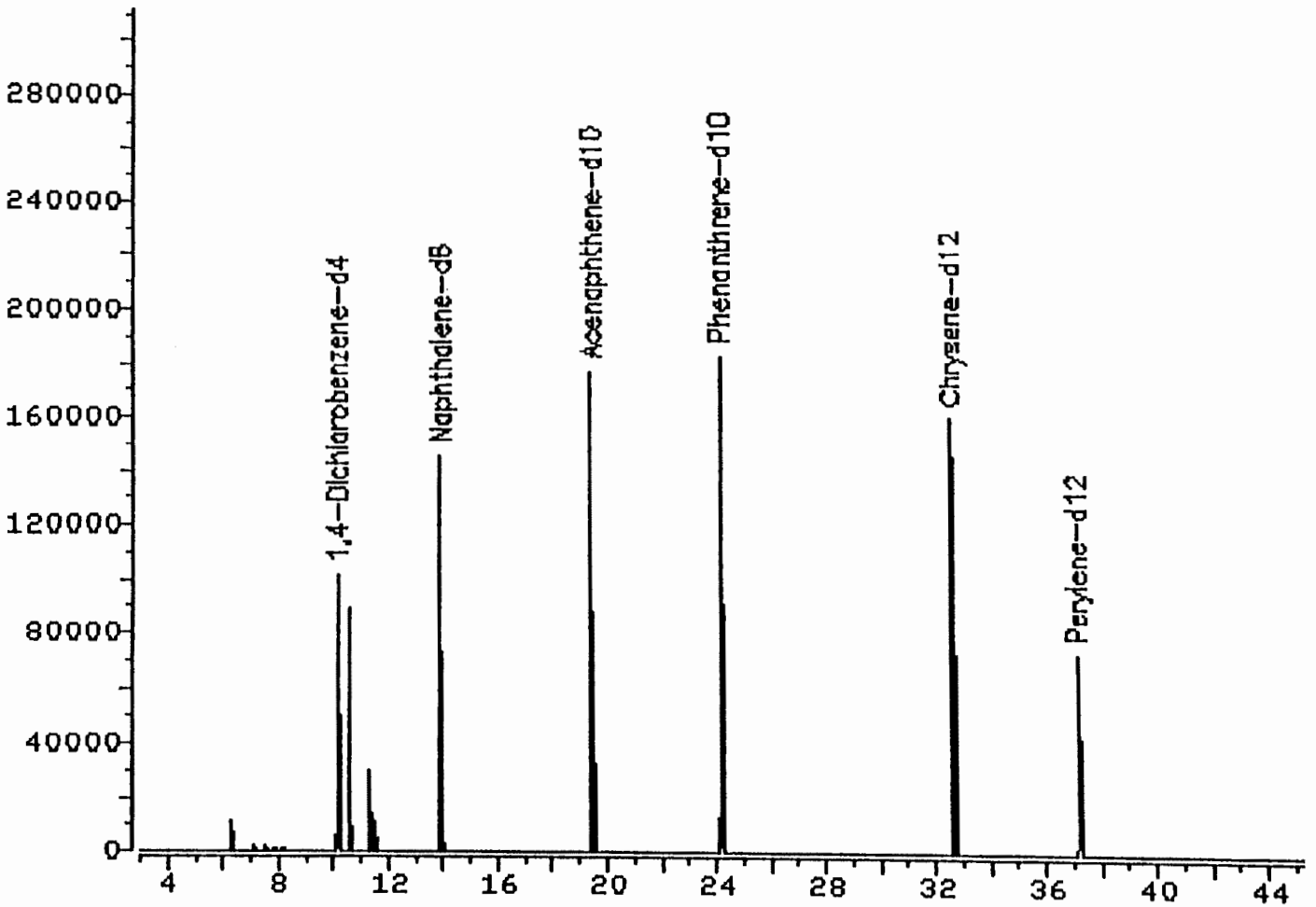

Figure 2. Total Ion Chromatogram of methylene chloride preserved with cyclohexene which has been distilled under normal conditions and concentrated 300:1. Internal standards are at 40ng/ul.

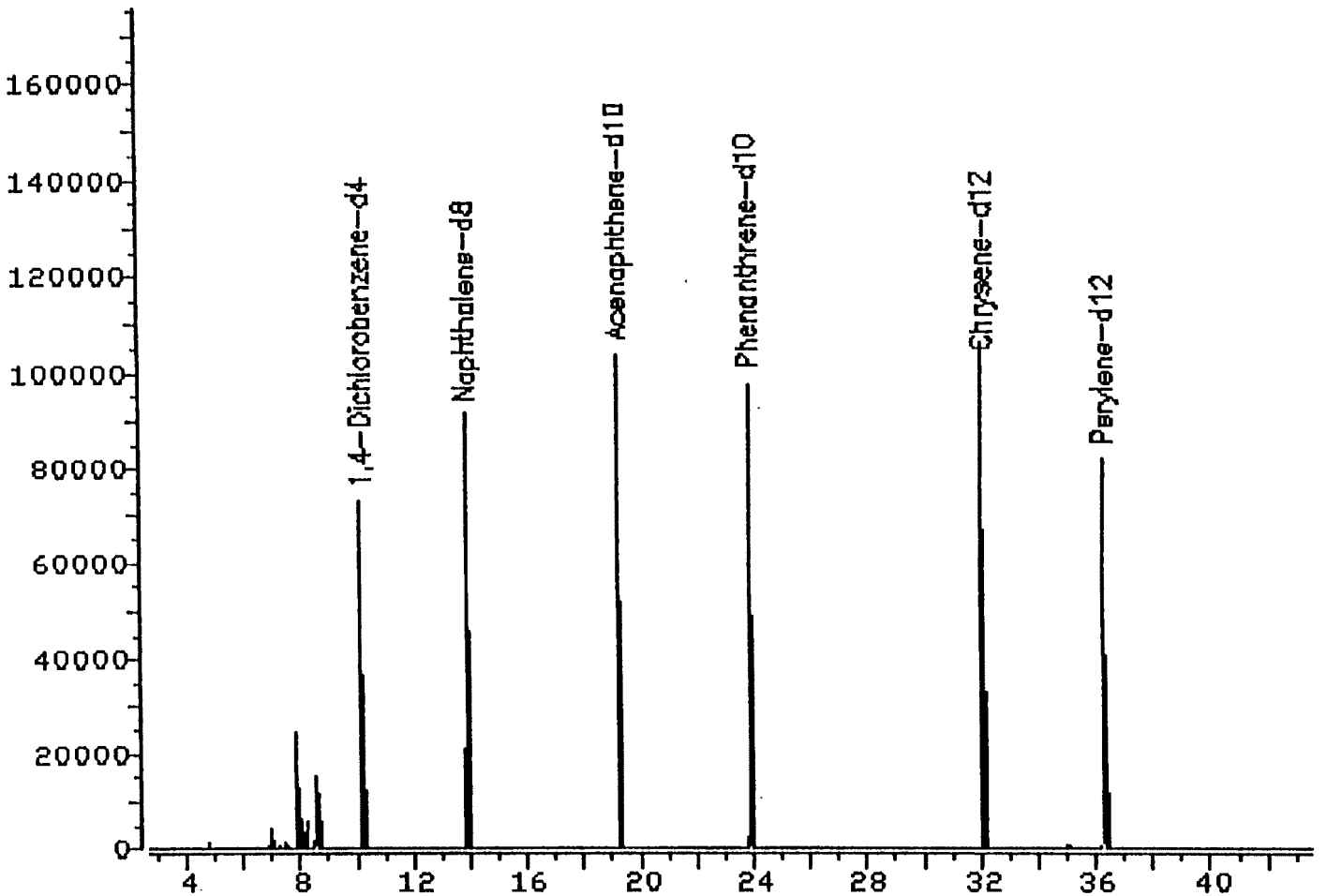

Figure 3. Total Ion Chromatogram of methylene chloride preserved with amylene which has been distilled under normal conditions and concentrated 300:1. Internal standards are at 40ng/ul.

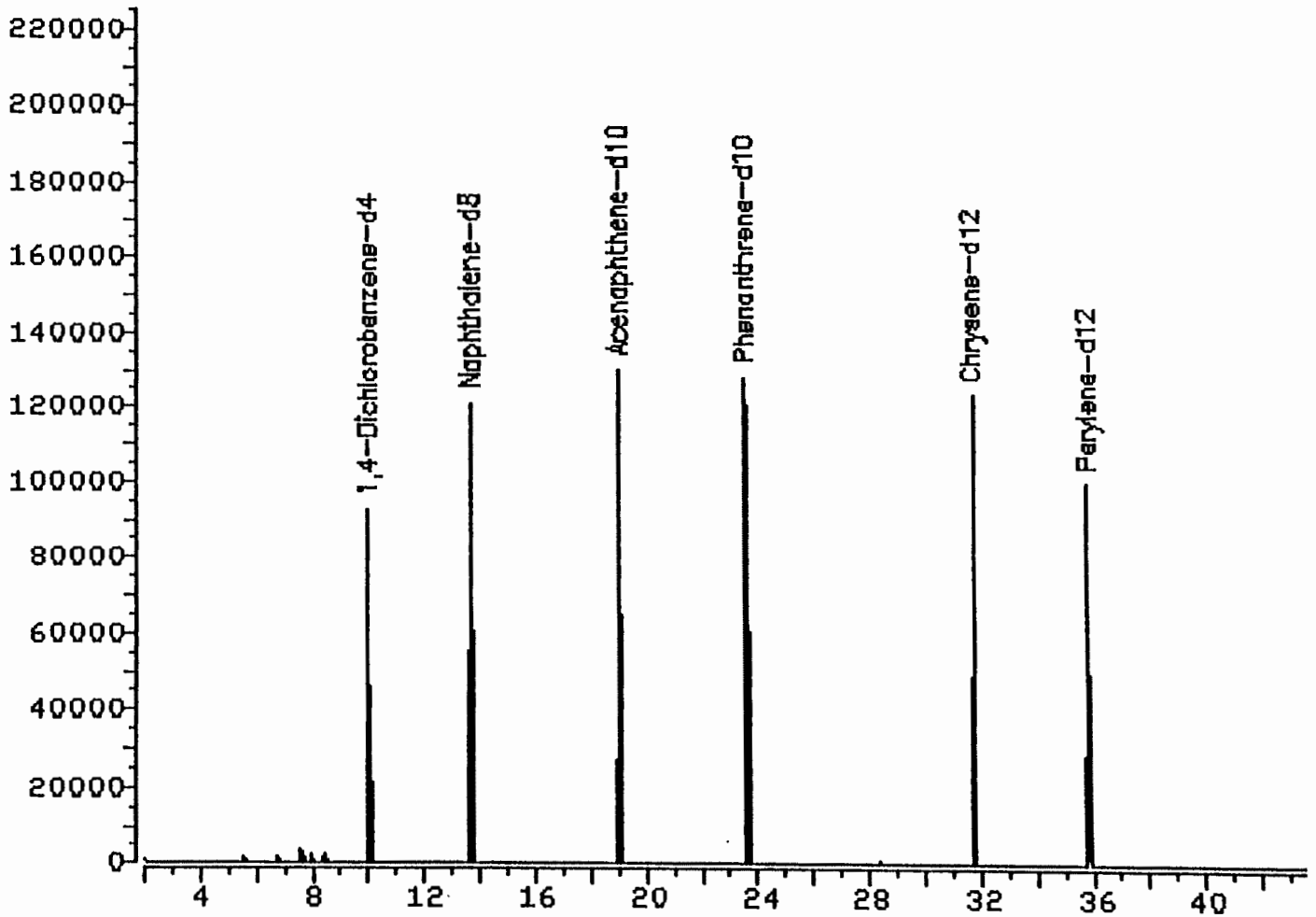

Figure 4. Total Ion Chromatogram of methylene chloride preserved with amylene and methanol which has been distilled under normal conditions and concentrated 300:1. Internal Standards are at 40ng/ul.

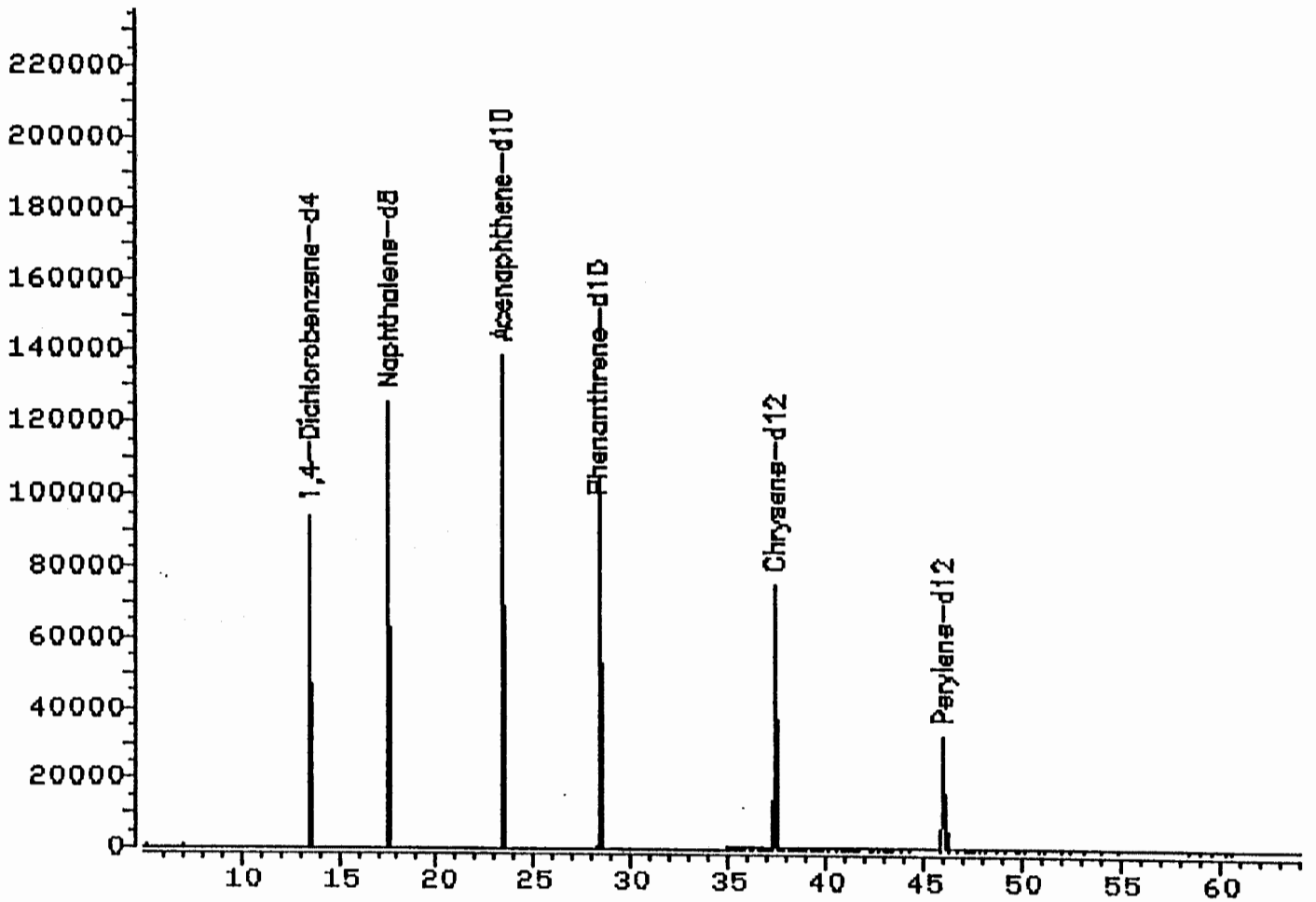

Figure 5. Total Ion Chromatogram of methylene chloride preserved with cyclohexene which has been distilled under the modified conditions and concentrated 300:1. Internal standards are at 40ng/ul.

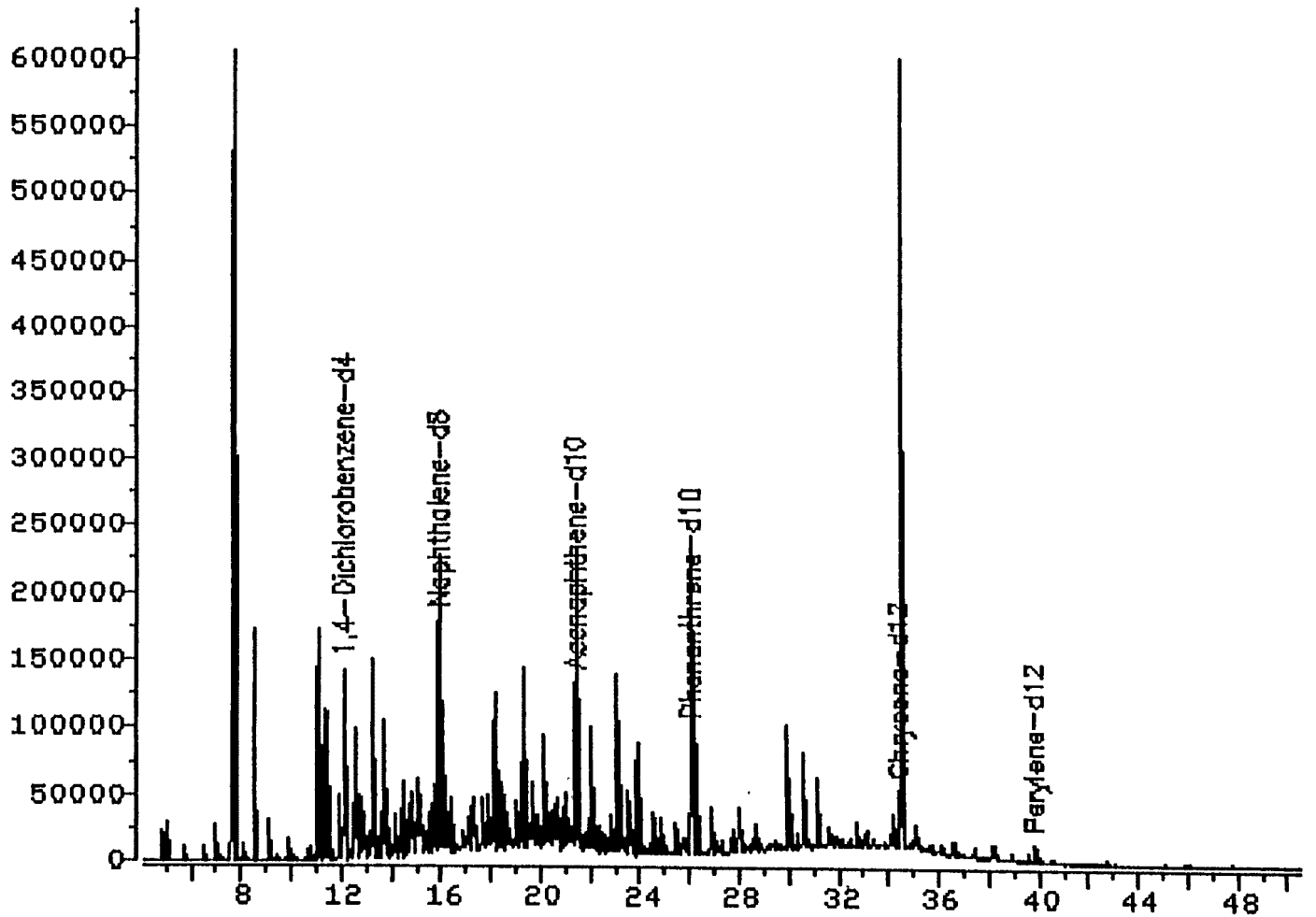

Figure 6. Total Ion Chromatogram of Gel Permeation Chromatograph methylene chloride waste concentrated 300:1. Internal standards are at 40ng/ul.

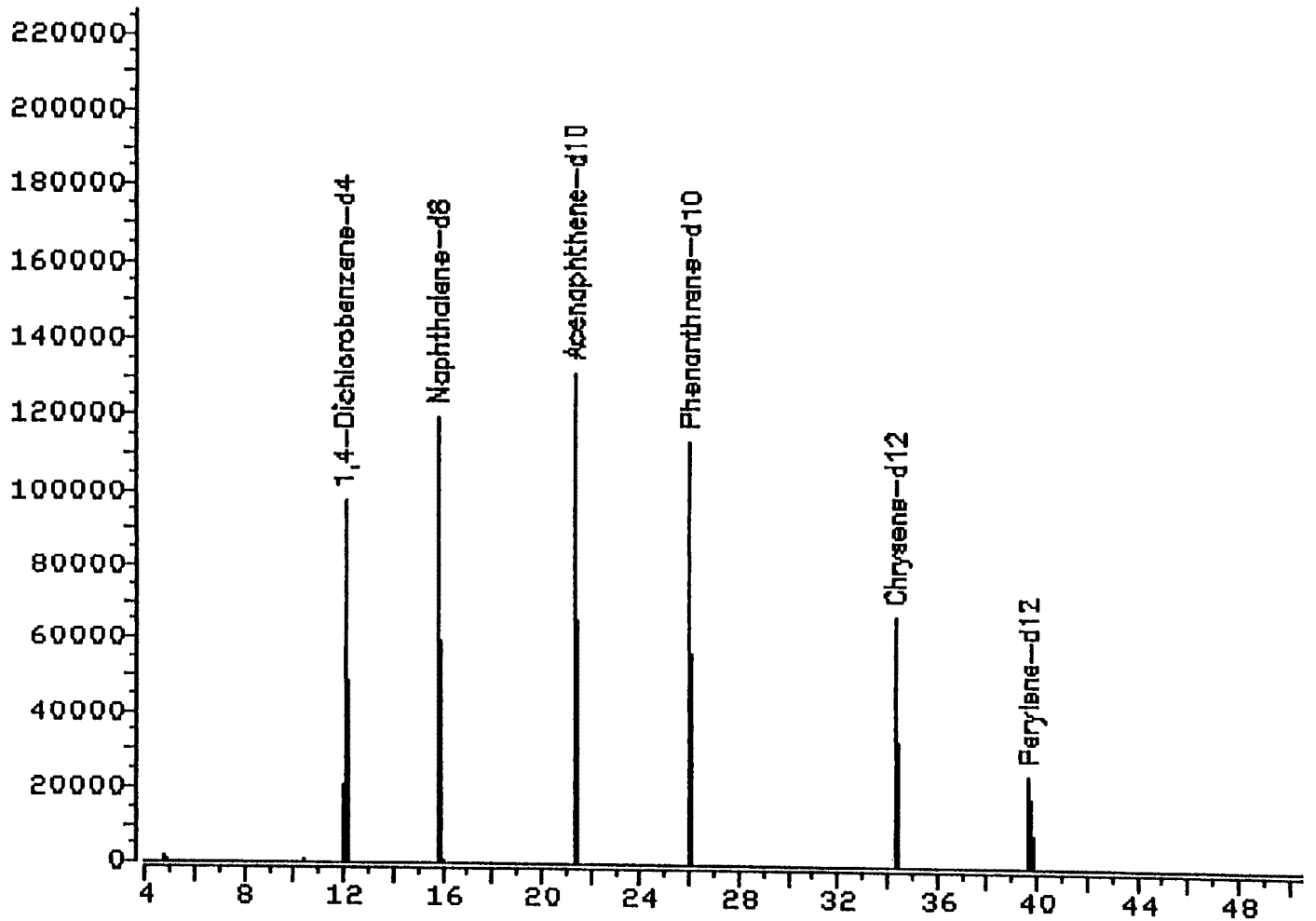

Figure 7. Total Ion Chromatogram of Gel Permeation Chromatograph methylene chloride waste which has been distilled under the modified conditions and concentrated 300:1. Internal standards are at 40ng/ul.

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APPROACHES TO QUALITY CONTROL OF NON-LINEAR CALIBRATION RELATIONSHIPS FOR SW-846 CHROMATOGRAPHIC METHODS

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ABSTRACT

As part of the revisions to Method 8000B in the Third Update to the Third Edition of the SW-846 manual, EPA provides a hierarchy of approaches that may be used to address calibration of instruments for organic analyses. The intent of this approach is to provide the analyst with options to the traditional approach of calibration factors or response factors that are assumed to pass through the origin, and is necessitated, in part, by the use of instrumentation such as particle beam mass spectrometry the response of which is best described by a non-linear relationship. The hierarchy progresses from the simplest, traditional approach, evaluating the relative standard deviation of the calibration or response factors, to a polynomial regression model up to third order that is evaluated on the basis of the weighted coefficient of the determination, a statistical measure of the variability in the calibration data that is explained by the calibration model.

INTRODUCTION

One feature of the SW-846 manual is the series of "base methods" which describe the general approach to specific analytical techniques. Example base methods include Method 3500 (extraction procedures), Method 3600 (cleanup procedures), and Method 8000 (chromatographic procedures). These base methods provide details on the many common aspects of the procedures, including concentration techniques, calibration requirements, calculations, and quality control procedures. The revision to Method 8000 (8000B) proposed in the Third Update to the Third Edition of SW-846 provides specific guidance on the use and evaluation of both linear and non-linear calibration relationships.

Traditionally, most EPA analytical methods have relied on a linear calibration, where the instrument response to known amounts of analyte can be modeled as a first order (linear) equation. For methods for organic analytes, this equation is assumed to pass through the origin (0,0). The methods call for calculating calibration factors (CFs) for external standard calibration procedures or response factors (RFs) for internal standard calibration procedures. Although the forms of the calculations differ, these factors represent the slope of a line between the origin and the response of the instrument to the standard.

SW-846 chromatographic methods specify a five-point initial calibration, thus five CF or RF values are generated. The relative standard deviation

(RSD) is used as a measure of the similarity of the five slopes. An RSD of 0% means that the slopes are identical. This approach has been adequate for most methods and offers advantages of ease of use and understanding (i.e., lower RSD values are "better"). However, as EPA has investigated new analytical techniques and reviewed existing ones with an eye to increasing productivity and lowering costs, the limitations of the linear model have become more apparent.

NEW APPROACH

In Method 8000B, OSW is proposing a hierarchy of calibration approaches that may be employed. The hierarchy consists of the following four approaches to instrument calibration:

- Traditional linear model, evaluated on the basis of the RSD
- Narrower linear range, evaluated on the basis of the RSD
- Linear regression, not through the origin, evaluated on the basis of the regression coefficient (R^2)
- Polynomial regression model, evaluated on the basis of the weighted coefficient of the determination (COD)

The first step in the hierarchy is to attempt to use the traditional linear calibration model that passes through the origin. The RSD of the CFs or RFs is used to evaluate linearity. As in earlier versions of this base method, Method 8000B specifies a maximum RSD of 15% for most GC and HPLC methods. For GC/MS and HPLC/MS methods, the QC limit for the RSD of the initial calibration is generally 20%.

If the RSD for an initial calibration fails to meet the QC specifications, then the second approach is to employ a narrower concentration range with the linear model, again using the RSD to evaluate the linearity. This can be accomplished by eliminating one or more standards from the upper or lower end of the calibration and recalculating the RSD. If the new RSD meets that QC specification for the method, then the analyst must prepare additional calibration standards within the narrower range, as a total of five standards are still necessary. If the RSD of the new calibration range meets the QC specification, then the analyst may proceed with sample analyses.

Narrowing the range involves several trade-offs. First, as noted above, five standards are still necessary for the initial calibration, so at least one new standard must be prepared. However, assuming that this new range is truly appropriate for the instrument in question, these standards should not need to be prepared often. Rather, the analyst has simply better defined the working range of the particular instrument. The second significant trade-off is that narrowing the calibration range may mean that more samples will require dilution to keep their responses within the narrower linear range. This will likely be the case when standards from the high end of the original range are eliminated.

The last obvious trade-off involves reporting sample results when the standards eliminated come from the lower end of the original range. The analyst must consider the regulatory limits associated with the analysis and ensure that the lowest standard in the calibration is at or below a sample concentration that corresponds to the regulatory limit in question. Otherwise, the analysis will not be able to demonstrate compliance with the regulatory limit.

The third option is to use a linear calibration that does not pass through the origin. In this case, a linear regression of the instrument response versus the concentration of the standards is performed treating the instrument response as the dependent variable (y) and the concentration as the independent variable (x), in the form:

$$y = ax + b$$

where:

y = Instrument response
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The correlation coefficient of the regression (R^2) is used to evaluate the linearity of the calibration. The analyst must take care *not* to force the line through the origin, either by including 0,0 as a calibration point, or by using software that forces the line through the origin. Forcing the line through the origin is analogous to using the RSD to evaluate the calibration. Since the traditional calibration approach must be attempted first, the analyst can be assured that the approach of forcing the line through the origin will not meet the QC specifications. OSW believes that including 0,0 as a calibration point is inappropriate for organic methods, as it tends to skew the data in the lower end of the calibration range.

A regression coefficient of 0.99 is necessary when using this option. This R^2 is, in fact, greater than that which would be calculated for the traditional calibration approach with an RSD of ≤15%. The increased R^2 requirement is intended to limit the use of the option of a linear regression that does not pass through the origin to those instances where it is truly appropriate, and not simply to avoid appropriate cleaning and maintenance of the instrument, or to compensate for questionable standards.

In calculating sample concentrations, the regression equation is rearranged to solve for the concentration (x), as shown below.

$$x = \frac{(y - b)}{a}$$

The intercept value (b) generated from the regression must also be evaluated before reporting sample results. A positive value for the intercept may indicate that there is some threshold instrument response

which is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three times (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable. These adjustments to the quantitation limits will apply to all samples analyzed using the regression line.

The fourth calibration option is to employ a polynomial equation up to third order, in the form:

$$y = ax^3 + bx^2 + cx + d$$

As with the linear regression model, the polynomial must treat the instrument response as the dependent variable (y) and the concentration as the independent variable (x). The model also must produce a unique concentration for each response. In order to provide enough data to adequately model a non-linear calibration, the analyst must either perform triplicate analyses of five calibration standards, or single analyses of ten, more widely-spaced, standards.

The difficulty with non-linear (higher order) calibration models is that a large number of polynomials may be fit to the observed results. Therefore, it can be difficult to assess the "goodness of fit" of a particular model relative to any other polynomial. In response, Method 8000B stipulates that the non-linear model be evaluated on the basis of the weighted coefficient of the determination (COD). The COD represents the percentage of the observed variability in the calibration data that is accounted for by the non-linear equation chosen as the model. The COD is calculated as:

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration point (i.e., 10 observed responses for the 10-point curve, and 15 observed responses for the three replicate 5-point curves)

$\bar{y}$ = Mean observed response from the 10-point calibration or from all three 5-point calibrations

Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)

n = Total number of calibration points (i.e., 10, for a single 10-point calibration, and 15, for three 5-point calibrations)

p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

SUMMARY

The proposed approach to calibration in Method 8000B offers a number of advantages to the analyst, including:

- Increased flexibility for the analyst.
- Applicability to a broader range of analytical techniques and instruments, including HPLC-particle beam-MS, which exhibits a second-order response to many analytes.
- A prescribed hierarchical approach that specifies attempting the simplest model first.
- A straight forward numerical approach to evaluating the results, i.e., small RSD values are better and R^2 or COD values should approach 1.0.

While one of the aims of this new approach is to provide added flexibility to the analyst, there are a number of restrictions detailed in Method 8000B. First, the purpose of the hierarchical approach is *not* to allow the analyst to employ any of the non-traditional procedures in order to avoid necessary and appropriate instrument maintenance or to compensate for detector saturation. Second, whatever procedure is used, it must result in a unique concentration for each instrument response. In other words, no parabolic functions or other models that would predict two or more concentrations for a given instrument response.

Other potential disadvantages include the fact that some of the calculations are different and some, such as the COD, are more involved than a simple RSD calculation. However, none of these calculations are beyond the sophistication of most instrument data systems. The approach of using a narrower linear range may require the preparation of new calibration standards and/or dilution of more samples to keep the results within the calibration range.

The use of a linear regression that does not pass through the origin requires that the intercept be evaluated relative to reporting sample results. The polynomial regression approach requires the analysis of more standards than the other approaches, either triplicate five-point calibrations or a single ten-point calibration. Lastly, the QC

specifications are increasingly stringent as one progresses through the hierarchy, in order to discourage inappropriate uses of higher order calibrations.

Despite these potential disadvantages, this hierarchy of approaches may be applied to either external standard or internal standard calibrations, starting from the simplest approach (linear, through the origin), and proceeding through non-linear calibration, as necessary. It should be applicable to any of the SW-846 8000 series chromatographic methods and will be essential in the use of methods such as HPLC-particle beam-MS.

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HOW LOW CAN WE GO - ACHIEVING LOWER DETECTION LIMITS WITH MODIFIED "ROUTINE" ANALYTICAL TECHNIQUES

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ABSTRACT

As illustrated by the Regulatory Issue Workshop at this Symposium, there is a demand for lower detection limits for many environmental pollutants. Because most EPA methods can be adapted to provide lower limits of quantitation, it is our experience that modification of routine methods is almost always the fastest and most cost-effective approach to achieving additional measurement sensitivity. The techniques for modifying routine methods include:

- the extraction of larger samples
- collection of large samples with stack sampling trains
- additional concentration of the final extract
- incorporation of additional cleanup procedures to reduce background signal
- derivatization of specific analytes
- use of more sensitive instrumentation
- reduction of laboratory contamination.

As with any laboratory measurement technique, modified methods must be tested to document their performance with the particular sample matrix of concern to the client. This presentation will provide strategies for achieving lower quantitation limits illustrated using several specific examples. In addition, recommendations for testing proficiency with modified methods and quality control practices suitable for low detection level analyses are provided.

INTRDUCTION

More than 10 years ago the US EPA developed prescriptive methods for the Superfund Contract Laboratory (CLP). These methods have come to be treated as the "defacto" methods for the determination of semivolatile organics, extractable organics, organochlorine pesticides and metals in water and soil. While standard methods such as those prescribed by the CLP can facilitate the inter comparison of data, they can also limit the use of newer techniques for sampling and sample preparation. Prescriptive methods can also slow the adoption of new more sensitive chemical instruments that can allow analysts to achieve lower detection limits. SW-846 uses a modular approach for describing analytical methods. Compatible modules for extraction/digestion, sample preparation and measurement are combined to provide an analytical scheme that satisfies project data quality objectives (DQOs) such as lower detection limits.

Because SW-846 modules are designed for regulatory applications, they are rugged, reproducible and contain embedded quality assurance

procedures. Each module undergoes several levels of performance testing and review before it considered by an SW-846 workgroup. These constraints generally limit the analysts ability to select true state-of-the-art techniques(*e.g.*, capillary zone electrophoresis). Rather, analysts are limited to modifying standard methods in order to achieve the desired performance, such as lower detection limits. Depending on the analyte(s) and the matrix to be analyzed, lower detection limits may be achieved by:

- extracting/digesting larger samples (water and soil)
- collecting larger air samples with stack sampling trains
- concentrating the final extract/digestate prior to analysis
- use additional cleanup procedures to reduce background signals that interferes with the target analyte
- derivatization of specific analytes in order to increase signal-to-noise
- use more sensitive analytical instrumentation
- reducing laboratory contamination
- minimizing contamination during sample collection.

Use of the DQO process is central modifying routine analytical techniques. Targets for quantitation limits, accuracy, precision and matrix suitability are established through this process. The sections below describe specific modifications to analytical procedures that allow these targets to be achieved.

EXTRACTION OF LARGER SAMPLES

Environmental analysis requires that target analytes be isolated from sample matrices (air, water, leachates, soil, sediment or tissue). An obvious way to lower detection limits is to increase sample size or to improve the selectivity of the sampling process. Analysts are cautioned that collection larger samples can increase the heterogeneity of the material taken to the laboratory. This can be in the form of spatial heterogeneity (*i.e.*, larger samples contain more volume of incompletely mixed environmental matrices) or temporal heterogeneity (*i.e.*, larger samples can include pollutants generated during discontinuous events).[1]

Increasing the size of an air or stack sample is more complex than just using a larger sampling time or a larger sampling train. Analysts must ensure that target analytes do not break through the sorbant during sampling. Analysts must also establish that the sample collected over a longer time is representative of discontinuous emission events (*e.g.*, different plant processes or changes in incinerator feedstock).

Most air and stack samples are still collected using Tenax (VOST 0030) or XAD II and Tenax (Semi-VOST 0010). Charcoal is needed to retain some volatiles for some applications. Anasorb 747 (a beaded, activated carbon) is preferred over normal charcoal because it is easier to desorb target analytes from Anasorb. Use of newer sampling materials is not adopted until thorough ruggedness and performance testing of those materials is completed. Based on such tests, the Summa canister (Method TO-14) is currently gaining favor for some air sampling applications.

Lower detection limits for volatile organic analytes (VOAs) in water can be achieved using 25-mL purge vessels or azeotropic distillation for polar VOAs (Method 5031).

Larger water samples can be extracted in order to achieve lower detection limits for semivolatile organics (Semi-VOA's) and organochlorine pesticides using larger glassware, continuous extraction processes or solid phase extraction (draft Method 3535). Investigators at the EPA Laboratory in Duluth/Grand Isle and Ed Furlong of the USGS are using custom-made solid phase materials to extract water samples that are greater than 5 liters. Pesticide manufacturers like Zenica (formerly ICI) also use solid phase materials to improve the selectivity of extractions. ICI demonstrated that passing a water sample through a strong anion exchange material before using a C_{18} sorbant can remove analytical interferences and increase the capacity of the solid phase sorbant for specific apolar target analytes (*e.g.*, pyrethroid insecticides). In some cases, the recovery of apolar analytes using C_{18} media can be improved by adding salt to a water sample prior to extraction.

Ionic or ionizable pollutants such as 2,4-D can be extracted by adjusting the sample pH to produce a cationic or anionic form of the target analyte. The water sample is then passed through an ion exchange resin in order to remove the target ionic species. After extraction, an appropriate acid or base is used to change the ionic form of the compound to a neutral molecule which is eluted with solvent.

Large soil samples (100 - 500 g) are often required to achieve the low quantitation limits required for modern pesticides[2]. They are extracted with methanol or methanol/water using a shaker table or a wrist action shaker. After extraction, particulates are removed by centrifugation or filtration. Target analytes are back extracted into methylene chloride after adding salt or water to the aqueous methanol extract. This back extraction step partitions apolar and semi-polar compounds away from polar interferences extracted by the methanol. The final extract is dried using sodium sulfate. This technique will be considered for the fourth update of SW-846 as proposed method 3570 after performance testing as a multianalyte procedure.

Minimum sample size should be established during project planning as part of the DQO process. This exercise requires that the analyst back-calculate the sample size using the target quantitation limit, instrument quantitation limit (IQL), final extract volume and the anticipated analytical recovery:

$$\text{target quantitation limit} = (\text{concentration in sample}) \,/\, (\text{recovery})$$

$$(\text{target quantitation limit} \times \text{sample size}) / \text{final extract volume} = \text{IQL}$$

$$\text{sample size} = \text{IQL} \times \text{final extract volume} / \text{target quantitation limit}$$

where recovery $< 100\%$
IQL = instrument quantitation limit

MINIMIZE CONTAMINATION DURING SAMPLE COLLECTION

The contamination of samples collected for lead analysis was documented by Patterson and Settle[3] in response to the tuna fish contamination scare of the 1970s. Fitzgerald and Gill[4] adopted a similar approach for environmental mercury analysis. Both groups found that the use of acid washed Teflon collection vessels, trained staff and frequent changes of gloves can minimize contamination of samples collected for metals analysis. VOA contamination can also present problems, particularly when gasoline powered vehicles or generators are in use during sampling.

Contamination is not the only problem encountered during sampling. Reactive or volatile analytes (*e.g.*, mercury and VOAs) can be lost during transport and storage if the proper preservatives or other precautions are not employed.[5] Minimizing the loss of analytes is a critical aspect of trace-level analysis.

ADDITIONAL CLEANUP PROCEDURES TO REDUCE BACKGROUND SIGNAL

Analysis of environmental samples often requires a multi-step sample preparation process to isolate trace-level components from the sample matrix. The purpose of these steps is to isolate and concentrate the target analytes into a final extract that can be analyzed with good accuracy and precision. Cleanup and derivatization can minimize:

- false positives due to non-target peaks that elute within the analyte retention time window (HPLC and GC)
- false negatives due to degradation of labile analytes (GC)
- poor quantitation due to elevated baselines (GC and HPLC)
- quantitation limits above the action limits (GC and HPLC)
- retention time shifts due to column overloading (GC and HPLC)
- damage to chromatography columns caused by deposited materials (GC and HPLC)
- instrument downtime due to the need to clean injector ports or to replace precolumns (GC and HPLC).

Sample cleanup can be accomplished using mini-columns (e.g., Pasteur pipettes), open chromatography columns, solid phase cartridges, porous disks (Empore™) or glass fiber disks (SIMDisk™). Disks generally have higher sample capacity than solid phase cartridges or mini-columns and do not require the training needed for open column techniques. However, open columns should be used if large sample capacity is required.

Polar organic materials (e.g., phenols, humic acids or amines) are absorbed onto the stationary phase (Florisil™, silica or alumina) Cleanups based on absorption techniques (Methods 3610, 3620 and 3630) are generally suitable for neutral or slightly polar compounds. An organic solvent is used to elute the less polar analytes while leaving the polar interferences in place. Columns should not be overloaded.

The ability of the absorbent to retain chemicals is called its activity. The addition of water (or a wet extract) will reduce the activity of any of these absorbents. The ability of a solvent to elute compounds from the absorbent is called its elutropic strength (methanol>ethyl acetate>methylene chloride>ethyl ether>toluene>hexane). The least polar compounds elute from the solid absorption media earliest, elution of more polar material require additional volumes of solvent or stronger solvents.

Reversed phase cleanup is achieved through the interaction of the analytes and interferences with silica derivatized with silyl ethers (e.g., C_8 or C_{18}) or with styrene divinylbenzene. This technique is called reversed phase because the mobile phase is more polar than the stationary phase. Apolar compounds are retained on the column and semipolar analytes are eluted with aqueous methanol or aqueous acetonitrile. Ionic species are generally eluted using water or buffer. Reversed phase cleanups are generally accomplished using solid phase cartridges and porous disks. HPLC can also be used for reversed phase cleanups; however, it is an expensive and relatively labor intensive.

Reversed phase cleanups can also be used for ionic species when ion pairing reagents are added to the elution solvent. Quatenary ammonium salts are added to extracts to form ion-pairs with anions (e.g. phenolates) which then behave like neutral molecules and are retained on the reversed phase media. The retained ionic species can are eluted by removing the ion pairing reagent from the mobile phase.

Metal ions or ionizable organic compounds can be isolated using ion exchange media. The extract pH is adjusted in order to ionize target analytes as cations or anions. The extract is then passed through ion exchange media. Cleanups using ion exchange media can be highly selective allowing the separation of very polar species that are not amenable to solvent partitioning techniques.

Apolar and polar organic constituent in extracts can be separated by the use of partitions between non-miscible solvents (e.g., methylene chloride/water or hexane/acetonitrile). Generally, apolar target analytes dissolve into the less polar solvent while polar species partition into the polar solvent, "like dissolves like".

Gel permeation cleanup (GPC) is a size exclusion technique using a styrene divinylbenzene column. This column packing has numerous pores that allow the entry of small molecules while excluding high molecular weight chemicals. Large, unretained molecules elute earlier while smaller molecules have longer retention times. High molecular weight interferences that can be removed by GPC include waxes, resins, paraffins, humic acid and lipids. There are two forms of GPC systems, (1) a higher capacity, low pressure system that requires more solvent and (2) a more modern lower capacity, high efficiency system that uses a higher pressure pump.

Using either type of GPC for environmental analysis requires that the column be calibrated with the target analytes and several molecular size indicators (usually corn oil, diethylhexyl phthalate and pentachlorophenol). Most semi-VOAs elute from the GPC after the

phthalate esters and before pentachlorophenol. GPC cleanup of samples containing organophosphorous insecticides (OPs) is not appropriate as some OPs elute with the corn oil.

Mercury or shiny copper is used to remove elemental sulfur from sediment extracts prior to analysis for organochlorine pesticides (Method 3660). The sulfur is reduced to sulfide ion and the mercury or copper is oxidized to the di-cation, a black insoluble solid. Whenever sulfur contamination is a problem, copper or mercury should be added to the extracts until no additional sulfide is formed.

Use of mercury to remove sulfur is in decline due to environmental concerns. Granular copper is an alternative; it should be prepared by first pouring dilute hydrochloric acid over the copper granules. This shiny copper should be rinsed with reagent water and drained to remove the hydrochloric acid before it is added to the extract. Acid washing the copper is necessary because even a thin coat of oxidized copper will prevent its reaction with sulfur.

CONCENTRATE THE FINAL EXTRACT PRIOR TO ANALYSIS

Lower detection limits can be achieved by decreasing the final volume of extracts and digestates; however, that approach has significant limitations. Analytical precision decreases significantly when the final volumes are less than 0.5 mL primarily because it is difficult to (1) reliably reproduce these volumes and (2) quantitatively transfer small volumes. While dioxin methods (*i.e.*, 8280 and 8290) use stable labeled analogs to correct for these problems, isotope dilution methods are not really practical for routine environmental analysis.

Use of smaller final extract volumes for organic analysis can also result in the oiling out of apolar interferences or phase separation in autosampler vials due to the presence of residual water. Insoluble oils can trap both semi-VOAs and pesticides. Drying extracts to remove water can result in the loss of polar analytes such as 2,4-D, even when acidified sodium sulfate is prepared according to the instructions in Method 8151. Analysts must carefully inspect final extracts for evidence of heterogeneity whenever concentration techniques are used to achieve lower detection limits.

DERIVATIZE SPECIFIC ANALYTES TO INCREASE SIGNAL-TO-NOISE

Analytes with reactive organic functionalities may be derivatized to decrease detection limits. Analysts are cautioned that these derivatizing reagents react somewhat unselectivly and can significantly increase the potential for false positives. Pentafluorobenzyl bromide (PFBBr) is used to prepare pentafluorobenzyl esters of carboxylic acids and PFB ethers of phenols prior to GC/ECD analysis. Samples are is added to aqueous sodium carbonate and the PFBBr is added in methylene chloride. Tetrabutylammonium hydrogen sulfate serves as a phase transfer catalyst for the reaction. While this two phase reaction system limits the hydrolysis of PFBBr and reduces the amount of interferences from the sample extract, PFBBr derivatives of

environmental samples are complex with many large peaks resulting from the derivatives of non-target compounds.

The use of PFBBr has other disadvantages. It is a lachrymator and is unpleasant to use. PFBBr derivatives cannot be stored for more than several days, and some lots of PFBBr have many impurities which makes interpretation of results nearly impossible. Despite these difficulties, derivatization with PFBBr is often the only way to achieve low detection/quantitation limits required for the analysis of some compounds.

Certain compounds (particularly pesticides and pharmaceuticals) can be derivatized to produce fluorescent species which greatly improve the sensitivity and selectivity of HPLC analysis. Florescent derivatives may be produced by the reaction of molecules in the sample extract prior to analysis or by a post-column derivatization reaction.

Fluorescent species can also be produced in a post-column reaction. Analysis of carbamate insecticides (Method 8315) is one such application of a post-column derivatization technique. Resolution of related analytes is less of a challenge using post-column methods because the derivatives are formed after the chromatographic separation.

Certain pesticides containing sulfur are oxidized to make them suitable for GC analysis or to generate a common moiety from related metabolites. Oxidations are usually accomplished with meta-chloroperbenzoic acid (MCPBA). In methods for Aldicarb, Fenamiphos and Fenthion, the parent pesticide and the sulfoxide (S=0) in its metabolite are oxidized to the corresponding sulfone (0=S=0).

USE MORE SENSITIVE ANALYTICAL INSTRUMENTATION

A number of manufacturers have developed more sensitive analytical instrumentation. The inductively coupled plasma/mass spectrometer (ICP/MS, Method 6020) is capable of measuring many metals at an order of magnitude lower than optical ICP instruments (Method 6010). The ion trap mass spectrometer can achieve detection limits an order of magnitude lower than most full scan quadrupole instruments. GCs with electronic pressure control in the injector port produce narrower peaks for late eluting compounds. This improvement in chromatography can result in lower detection limits.

REDUCE LABORATORY CONTAMINATION

Lower detection limits means that laboratories must reduce contamination that interfere with the measurement of target analytes. Dr. C. Patterson[2] first raised this issue for the analysis of lead in food. Dr. E. Heithmar at the EMSL-LV (personal communication) found that low levels of laboratory contamination limited the lower detection limits that could be achieved using Chelex™ resin and ICP/MS. These investigators documented that metals can be introduced by dust, including the particles found in the hair of analysts. Use of cleanroom techniques, "tacky mats" to limit the introduction of dusts as well as

gloves, coats and hats limited to trace level analyses. Bloom[6] and Prevatt[7] recently reviewed the requirements for cleanroom techniques suitable for environmental analysis.

Analysis of volatile organic chemicals is also subject to contamination problems. This is most clearly demonstrated by the increased reporting levels for acetone and methylene chloride used by routine analytical services laboratories. These increased reporting levels are generally the result of contamination of samples by the solvents used to extract water and soil samples. Some laboratories minimize contamination by maintaining separate air supplies for their volatile and semivolatile laboratories. This solution is most appropriate when designing a new facility and has only limited application for an existing laboratory. Field laboratories are often plagued with benzene and xylene contaminants introduced by the combustion of fuels (e.g., from field generators).

Lopez-Avila and Beckert[8] documented the source and ubiquitous nature of phthalate esters that can interfere with the analysis of semi-VOAs and pesticides.

Elimination of laboratory contamination is a serious concern in trace level analysis. Bloom[6] describes a need for "paranoid zeal" in order to successfully eliminate these contaminants.

DEMONSTRATE LABORATORY PROFICIENCY WITH SENSITIVE ANALYSES

Proficiency testing is particularly critical when modifying analytical procedures to provide improved performance such as lower detection limits. SW-846 describes the process of demonstrating laboratory proficiency in Section 8 of Method 8000B. As a first step:

> 8.4 Each laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods that it utilizes, by generating data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made.

Analysts and laboratory management should evaluate the results of initial proficiency tests in terms of accuracy, precision, percent of false positives, percent of false negatives and the number of rejected analyses. The evaluation should include of interferences and calibration data. Some laboratories are able to satisfy the requirement for a 20% relative standard deviation for the initial calibration despite a not detect at the low-point calibration. This is not acceptable for trace-level analysis. The low-point calibration analysis should produce a signal at least 10 times the chromatographic or mass spectral background level in order to be suitable for analyzing environmental extracts containing target analytes at that concentration.

An initial demonstration of proficiency ensures that the laboratory staff is capable of trace-level analysis and demonstrates that laboratory contamination is under control. However, it does not necessarily ensure that the laboratory or analyst is capable of analyzing real-world samples at the target quantitation limit. This requires analysis of characterized contaminated matrices or spiked real-world matrices spiked at the target quantitation limit. Use of real-world performance materials is described in the next section.

SPECIFIC QA/QC PROCEDURES

Trace-level measurements require an analytical system that is under reliable statistical control.[9] This control is central to a comprehensive measurement QA program described in Chapter 1 of SW-846. One aspect of this measurement QA program is a demonstration of laboratory proficiency in trace level analysis. The laboratory must analyze environmental matrices spiked at the target quantitation limit. Analyses of these spiked materials should provide the method accuracy and precision specified in the project DQO. Whenever appropriate, characterized reference materials containing target analytes at or near the target quantitation limit should also be analyzed as part of the demonstration of laboratory proficiency. Spiked surrogates, matrix spikes and duplicate analyses described in SW-846 Chapter 1, or other appropriate methods, also help demonstrate laboratory proficiency and document the performance of modified methods. In addition, the determination of incorporated, non-target, pollutants may provide an additional measure of method performance. For example, analysts using SW Method 8081B or Method 8082 for the analysis of trace-level organochlorine pesticides or PCBs in tissues should expect to see DDE, a near universal contaminant of animal tissues, in the chromatographs of all trace level analyses, even after application of sulfuric acid/permanganate cleanup (Method 3670).

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NON-PHTHALATE PLASTICIZERS IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Phthalate plasticizers are on all EPA "lists." However only drinking water regulates a non-phthalate plasticizer, bis(2-ethylhexyl) Adipate. In a recent water quality monitoring project on the Chester River, in Maryland, we had authentic standards previously obtained from a former plasticizer manufacturer on the Chester River by the Md Dept. of Natural Resources. These materials included both phthalate and non-phthalate plasticizers. The non-phthalates included adipates, maleates, a sebacate, a benzoate, and a trimelliate. All the materials were a technical grade, containing the various isomers of that material. One of the adipates manufactured at the Chester River site, di-octyl adipate, is one of the compounds on the original consent decree list. One of it's isomers, di(ethylhexyl) adipate is a drinking water analyte. We were examining river sediments at low ppb levels. Most of the plasticizers supplied were "non-target compounds." Our results indicated both phthalate and non-phthalate plasticizers were present in the samples. We feel the results show non-phthalate plasticizers could be useful indicators at sites where non-phthalate plasticizers have been used, typical applications being in lubricants, coatings and low temperature applications for plastics, particularly polyvinyl chloride formulations.

Introduction

Environmental Chemists deal with the effects of industrial chemical processes, but may not be familiar with a particular industry, or uses of a common chemical in a variety of industries. Even a novice environmentalist is aware of the wide use of polyvinyl chloride (PVC) and the effects of it's monomer, vinyl chloride. They may also be aware that phthalate plasticizers are widely used in PVC and other plastics, but what about the non-phthalate plasticizers. In a recent study to determine any effects of airborne industrial pollutants on water quality in the Chester River in Maryland, we had reason to address that problem. In the early 1980's while monitoring for permit violations by a firm located in Chestertown, MD on the Chester River, which manufactured plasticizers, we had received samples of the products made by this firm, which included both phthalate and non-phthalate plasticizers. The problem was settled administratively, and the materials were never really looked at, or utilized. In the fall of 1994 CRL agreed to do analytical work for the State of Maryland, Dept of Natural Resources to survey pollutants in the Chester River sediment. It was realized that the previously obtained materials were still available. The list of compounds included phthalates we had never heard of, and non-phthalates such as adipates, a maleate, a sebacate, a benzoate, and a melliate. While we were aware that ethylhexyl adipate was a drinking water analyte, and vaguely aware that adipates were a group of non-phthalate plasticizers, we had never heard of some of the other compounds such as 7-11 phthalate, and Trioctyl trimelliate. These compounds are listed in table one. Realizing that we had C4, C6, and C10 dibasic acid esters, and the aliphatic dibasic acids being an important class of industrial materials, we felt it might be interesting to see which of these materials, as well other diesters in their grouping, i.e. adipates, were in the NBS75k Mass Spectral library, which is the one we use for analytical work. Also what other groupings, C3, C5, C7, C8 and C9 might be present in this library. These are presented in table 2.

NOTICE

Due to time constraints, this paper was not subjected to Agency review. Therefore it does not necessarily reflect the views of the U.S. Environmental Protection Agency, and no official endorsement should be inferred.

Experimental

A set of sediment samples from sampling stations on the Chester River were analyzed by our usual procedures for the organic semi-volatile Base Neutral Acid fraction. All sediment samples at our laboratory are extracted by RCRA Method 3540A, Soxhlet Extraction. Analysis is by capillary column GC Mass Spectrometry Using CRL BNA SOP R3-QA201.0 which is consolidated procedure derived from SDWA 525.2, NPDES 625, RCRA 8270 and the current CLP Statement of Work. A 30 meter DB-5,1 micron thickness capillary column was utilized . Before acquisition of any sample data, the mass spectrometer is calibrated by obtaining the spectrum of a known compound (DFTPP). All mass assignments and relative abundances are found to be in acceptable ranges or the instrument is adjusted until an acceptable spectrum of DFTPP is obtained, according to the Superfund CLP Organic Low/Medium Statement of Work (SOW). Immediately before analysis, each sample is spiked with the internal standard mix used in the current CLP Statement of Work for semi-volatile. All quantitation or estimates of concentration are made in comparison to the internal standard nearest the compound of interest. Mixed standards of Extractable Priority Pollutants and CLP Hazardous Substances List Compounds (10-100ng range) are analyzed before each group of samples. These are traceable standards obtained from certified vendors. The target compound results are not reported here but are available. bis(2-ethylhexyl) Adipate was run as a separate standard.

For each group of samples extracted, a method blank is prepared and examined for laboratory introduced contamination. All reported target compound values are qualified with a "B" if less than or equal to 10x the concentration determined in the field and/or laboratory blank. All samples were spiked with a mixture of six surrogate compounds prior to extraction. The percent recovery for each was determined to check for matrix effect. The target limits are those established for the Superfund CLP Organic Low/Medium SOW. Eighty-six of ninety surrogates recoveries were within the recommended Quality Control Limits. These results are not reported here, but are available. Two aliquots of sample 941121-17 were spiked with a priority pollutant cocktail containing twelve compounds at 100 ng/uL (in the extract). These spiked samples were then carried through both the extraction and GC/MS analysis. The percent recovery for each spiked compound was determined to check for matrix effect. The percent recoveries have been corrected for target compounds present in the sample. The target limits are those established for the Superfund CLP Organic Low/Medium SOW. Eighteen of twenty-four matrix spike recoveries and six of twelve RPDs were within acceptable QC limits for this case. The semi-volatile that were of the utmost interest in this case, plasticizers (phthalates/adipates) did not seem to have suffered from matrix effects as evidenced by the MS/MSD results. These results are not reported here but are available.

Discussion

Beside analyzing the plasticizers we had, the various environmental databases were searched for information on these compounds, particularly the odd mixtures. What chemical you have exactly is important with industrial chemicals, since use of synonyms is somewhat loose. The toxic release inventory(1) indicated that the dioctyl adipate we had, from the Chestertown manufacturer was actually bis(ethylhexly) adipate, which was later confirmed. According to the TRI there had been a release in 1987.

The plasticizers were run at 100 ppb to establish retention times and spectra, then rerun to establish quantitation limits. Some of the compounds, the monoesters, had very high limits (>100 ppb) and would not be seen except in spill situations. Two of the phthalates are already target compounds and separate standards were not prepared. The phthalates found were the usual low level target phthaltes and are not reported in this paper. It was interesting to us, that 7-11 Phthalate was listed in reference 2, and is a mixed group of akyl phthaltes in that the carbon atom range, as figure (1) indicates. The mixed phthalate esters are also a multipeak mixture of akyl phthalates. We couldn't find out (easily so we gave up) what 6-10 phthalate was. But a drum sample or a spill of these mixed esters could plaster the characteristic 149 ion across most of a typical 30-300 deg. C chromatogram.

The information from the TRI database indicated the Chester River facility may have changed owners, confusing the issue as to Di-n-octyl adipate or Bis(2-ethylhexyl) adipate. The Chester Dioctyl adipate was compared with a known standard of the ethylhexyl adipate. Spectra and retention times indicated the Chester River material was Bis(2-ethylhexyl) adipate (fig. 2,3). The other available materials listed in table one were also run except for the epoxidized soybean oil, which looked as thought it had polymerized. These materials and other diesters from C3-C10 were searched for CAS numbers(2). The NBS spectral library we utilize was then searched for entries. We were looking for patterns such as the phthalate 149, 167 masses that could be utilized. The adipates have masses at 129 and 147 for most of the isomers we had spectra for. It did seem as though diesters with aklyl groups higher than diethyl would fragment to give the same base peak. The sebacates apparently are widely used, but the spectra didn't show any useful patterns.

In our routine sample analysis target compounds are identified and quantitated, then tentatively identified compounds (TICs) are reported. However our program which is typical of most instrument software only peaks those peaks which are at 20% of the nearest internal standard to avoid doing library searches on noise, but this can miss low level contaminants, and in our initial sample run it did. We then generated ion chromatograms at masses 99, 129, 105, and 305, since once contaminants are identified you can quantitate them at lower levels. The only mass that was present, other than the 149 phthalates, were the 129, 147 adipate masses. Bis(2-ethylhexyl) adipate was added to our normal quantitation program as an external standard. The results are reported in table 3. We were somewhat surprised that we had the adipate in our blanks, since the standards had been kept sealed and refrigerated. Reviewing sample blanks data on archived magnetic tapes indicated the presence of adipates in some blanks. This, and the wide range of adipates with extremely similar spectra has implications for drinking water analysis by method 525, in that retention time windows are as important as spectra.

Mixed texanol benzoates another multi-peak mixture gave the usual 105 base peak for benzoic acid for all the components. So we have another target compound, that can have it's quantitation ion across most of the mass chromatogram. The Trioctyl Trimelliate (fig. 4) is a specialty plasticer whose major use according to the Harzardous Subtances Database(HSDB) (4) is in PVC for electrical applications. This could help in targeting sources at specific waste sites related to electrical manufacturing.

CONCLUSION

It is important to be aware that there are other types of materials used as plasticizers besides the phthalates, The non-phthalate materials are widely used as additives, plasticizers, in paints, synthetic lubricants, and hydraulic fluids. the adipates offer a group which has consistent masses, 129 and 147 which can be easily monitored, and in the case of ethylhexyl adipate are regulated. Other non-phthalate plasticizers also seem to have consistent base peaks with the longer alkyl groups, a search program to produce ion chromatograms of these masses including the adipates can easily be set up on the software currently used on most mass spectrometers. Where a hazardous waste site has an industrial categorization that commonly uses the non-phthalate materials, a search for those contaminants could yield additional useful information.

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(4) TOMES Plus, Volume 25, Micromedex Inc.

TABLE 1.

PLASTICIZER OBTAINED FROM CHESTER RIVER SOURCE	CAS Number	Background Information Available in Database
DIOCTYL ADIPATE	000103-23-1	HSDB(1), RTECS(2)
DISODECYL ADIPATE	027178-16-1	(2)
ISODECYL CAPPED 1,3-BUTYLENE ADIPATE	(a)	(a)
TRIDECYL ADIPATE	(a)	(a)
DIBUTYL MALEATE	105-76-0	(2)
6-10 PHTHALATE	(a)	(a)
7-11 PHTHALATE	068515-42-4	(a)
DI-N-BUTYL PHTHALATE	000084-74-2	(1,2,3)
DI-2-ETHYLHEXYL PHTHALATE	000117-81-7	(1,2)
DIISODECYL PHTHALATE	026761-40-0	(1,2)
MIXED PHTHALATE ESTERS	not available	N/A
DI,TRIDECYL PHTHALATE	000119-06-2	(2)
TRIDECYL SEBACATE	(a)	(a)
EPOXIDIZED SOYBEAN OIL	008013-07-8 (6)	RTECS(2)
EPOXY TAllATE	(a)	CHRIS(3)
TRIOCTYL TRIMELLIATE	3319-31-1	HSDB, RTECS

(a) Not found with available resources
(1) Hazardous Substances Data Bank
(2) Registry of Toxic Effects of Chemical Substances
(3) Chemical Hazard Response Information System

TABLE 2.				
Non-Phthalate Potential Plasticizer Materials	CAS #	Source of Spectra	Base Peak or Major Ion	Secodary Ion
Propandioic Acid, diethyl ester	000105-53-3	NBS75K.L	29	115
Propandioic Acid, dimethyl ester	000595-45-0	NBS75K.L	43	73
Propandioic Acid, dimethyl-, diethyl ester	001619-62-1	NBS75K.L	29	88
Propandioic Acid, ethyl-, diethyl ester	000133-13-1	NBS75K.L	160	143
Diethyl methylpropylmalonate	055898-43-6	NBS75K.L	115	174
Propandioic Acid, methyl-,diethyl ester	000609-08-5	NBS75K.L	129	74
Diethyl isopropylmalonate	000759-36-4	NBS75K.L	160	133
Diethyl isobutylmalonate	010203-58-4	NBS75K.L	160	133
Propandioic Acid, ethylmethyl-, diethyl ester	002049-70-9	NBS75K.L	73	87
Butanedioic acid, diethyl ester	000123-25-1	NBS75K.L	101	129
Butanedioic acid, dibutyl ester	000141-03-7	NBS75K.L	101	119
Butanedioic acid, dimethyl ester	000106-65-0	NBS75K.L	115	55
2-Butenedioic acid, diethyl ester	000141-05-9	NBS75K.L	99	127
2-Butenedioic acid, dimethyl ester	000624-48-6	NBS75K.L	113	85
Dibutyl Maleate	000105-76-0	NBS/CRL	99	117
Valeric acid, 2,3-epoxy-3,4-dimethyl-, tert-butyl ester	024222-06-8	NBS75K.L	57	
Valeric acid, 2,3-epoxy-3,4-dimethyl-,ethyl ester, cis	024222-05-7	NBS75K.L	99	115
Hexanedioic acid bis(2-ethylhexyl) ester	000103-23-1	NBS/CRL	129	147
Hexandioic acid, dihexyl ester	000110-33-8	NBS75K.L	129	147
Hexandioic acid, dioctyl ester	000123-79-5	NBS/CRL	129	147
Hexandioic acid, dicyclohexyl ester	000849-99-0	NBS75K.L	129	147
Hexandioicacid, bis(1-methylpropyl) ester	000141-04-8	NBS75K.L	129	147
Hexandioicacid, mono 2-ethylhexyl ester	004337-65-9	NBS75K.L	129	147
Hexandioic acid, dipropyl ester	000106-19-4	NBS75K.L	129	142
Hexandioic acid, bis(1-methylethyl) ester	006938-94-9	NBS75K.L	129	142
Hexandioic acid, dimethyl ester	000627-93-0	NBS75K.L	59	
Hexandioic acid, dibutoxyethyl ester	000141-18-4	NBS75K.L	41	99
Hexandioic acid, dibutyl ester	000105-99-7	NBS75K.L	185	129
Hexandioic acid, 2,2-dimethyl-,dimethyl ester	017219-21-5	NBS75K.L	157	129
Tridecyl Adipate	*	CRL STD	129	147
Diisodecyl Adipate	27178-16-1	CRL STD	129	147
Isodecyl Capped, 1,3-Butylene Adipate	*	CRL STD	129	147
Azelaic Acid, bis(2-ethylhexyl ester)	000103-24-2	NBS75K.L	171	
Azelaic Acid, dibutyl ester	000103-24-3	NBS75K.L	171	
Azelaic Acid, dimethyl ester	000103-24-4	NBS75K.L	152	
Decanedioic acid, bis(2-ethylhexyl) ester	000122-62-3	NBS75K.L	185	112
Decanedioic acid, dibutyl ester	000109-43-3	NBS75K.L	241	185
Decanedioic acid, diethyl ester	000110-40-7	NBS75K.L	55	60
Decanedioic acid, dimethyl ester	000106-79-6	NBS75K.L	55	74
Didecyl Sebacate	002432-89-5	NBS75K.L	57	71
Tridecyl Sebacate	*	CRL STD	57	71
Epoxy Tallate	#	CRL STD	57	
Mixed Texanol Benzoates	#	CRL STD	105	
Trioctyl Trimelliate	003319-31-1	CRL STD	305	323

* not found in available library resources

mixtures not identifiable to a given CAS number

TABLE 3.

Sample number	Bis(2-ethylhexyl) Adipate ug/Kg
941121-14, Chester R. Station 9	32.7 B
941121-15, Chester R. Station 8	55.2 B
941121-16, Chester R. Station 7	53.7 B
941121-17, Chester R. Station 6	<10
941121-18, Chester R. Station 5	<10
941121-19, Chester R. Station 4	<10
941123-15, Chester R. Station 3	27.8 B
941123-16, Chester R. Station 2	148.5
941123-17, Chester R. Station 1	<10
11/21 sand blank	<10
11/23-Sand Blank	11.5

FIGURE 1.
STANDARD OBTAINED FROM CHESTER RIVER SITE
7-11 PHTHALATE (MIXED PHTHALATE ESTERS)

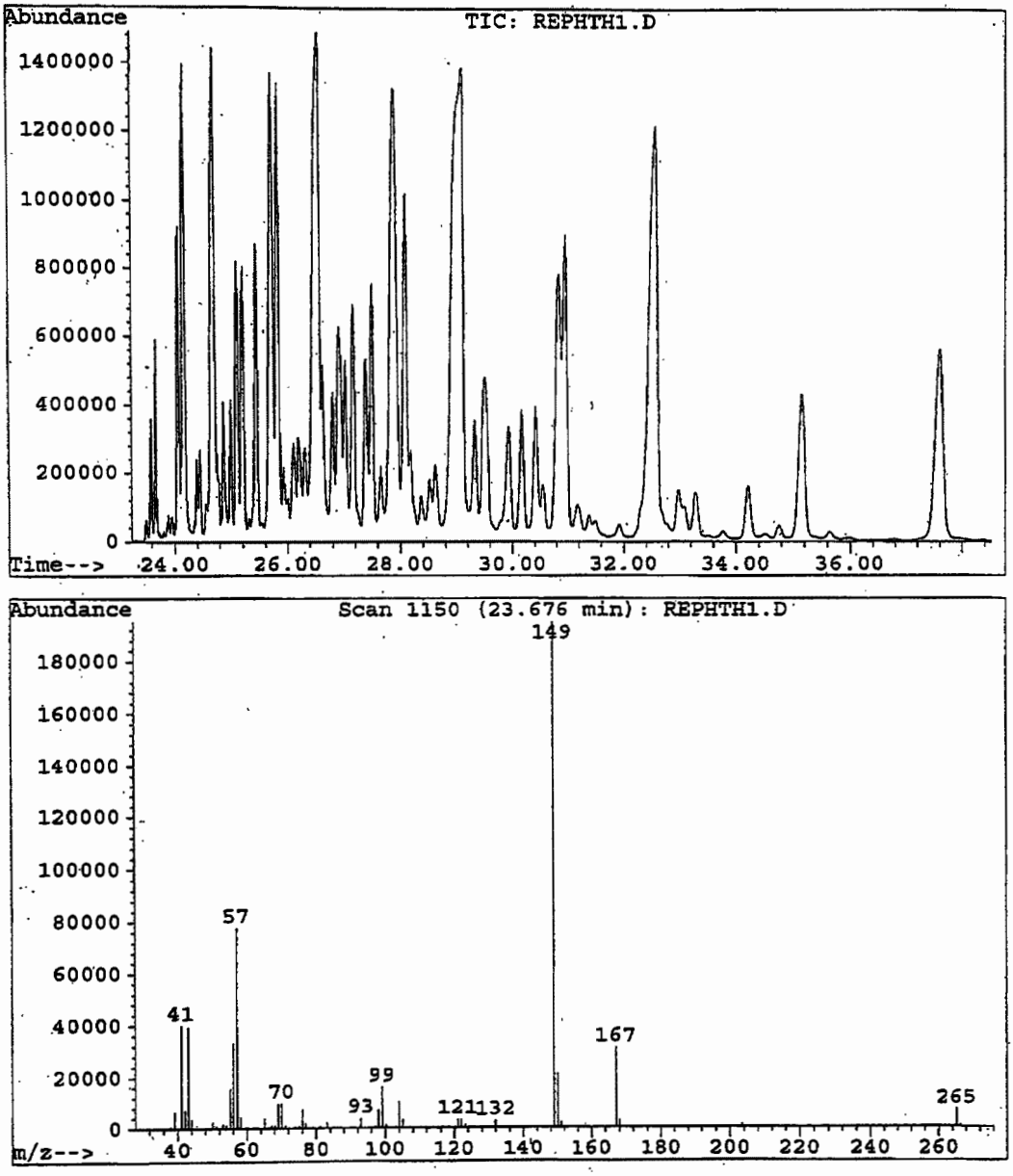


FIGURE 2.
STANDARD OBTAINED FROM CHESTER RIVER SITE
DI-OCTYL ADIPATE

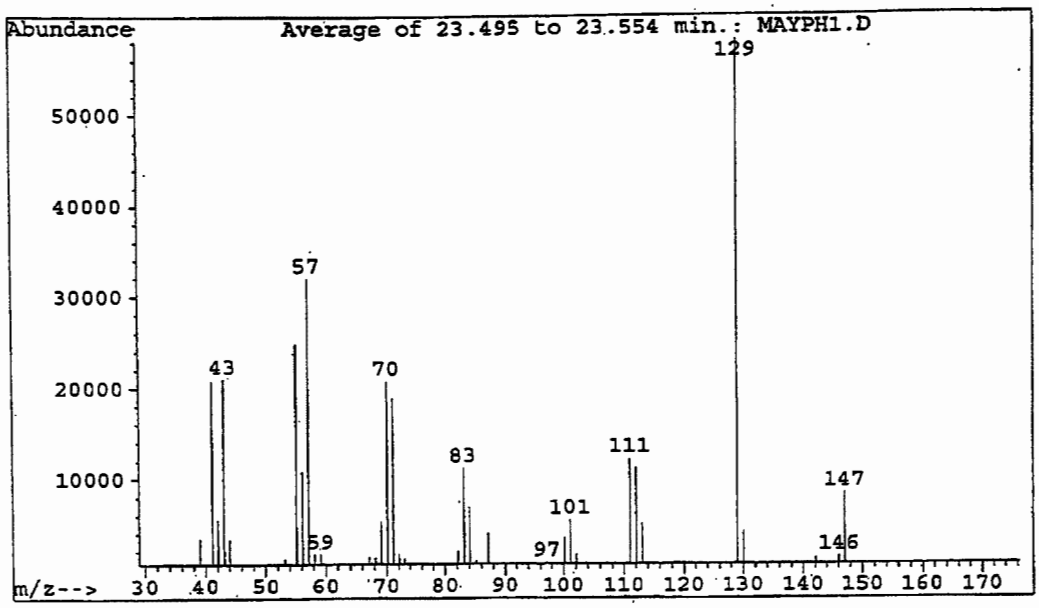


FIGURE 3.
STANDARD OBTAINED FROM ALDRICH CHEMICAL
BIS(2-ETHYLHEXYL) ADIPATE

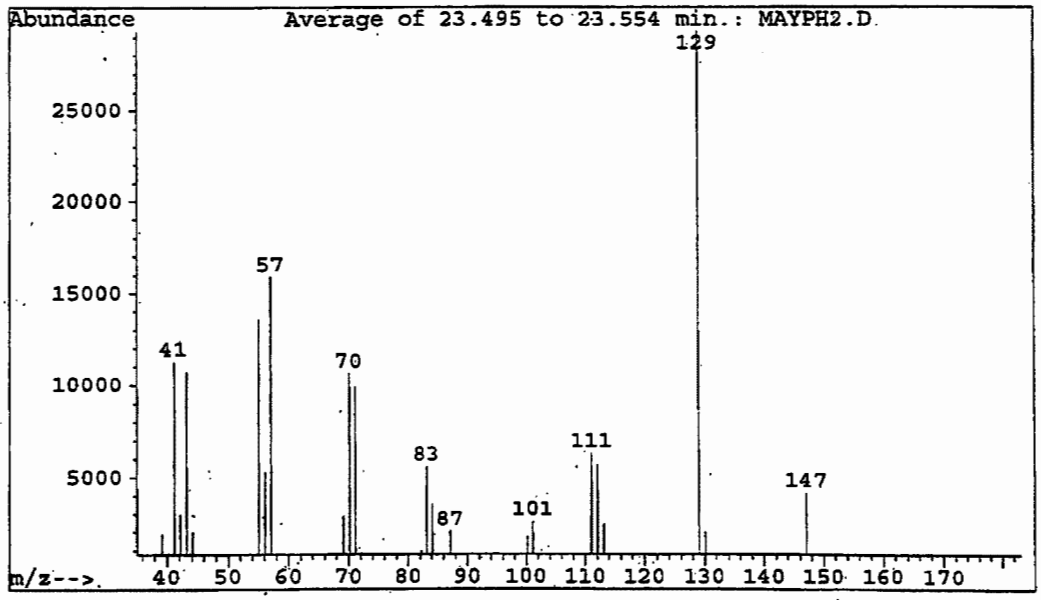
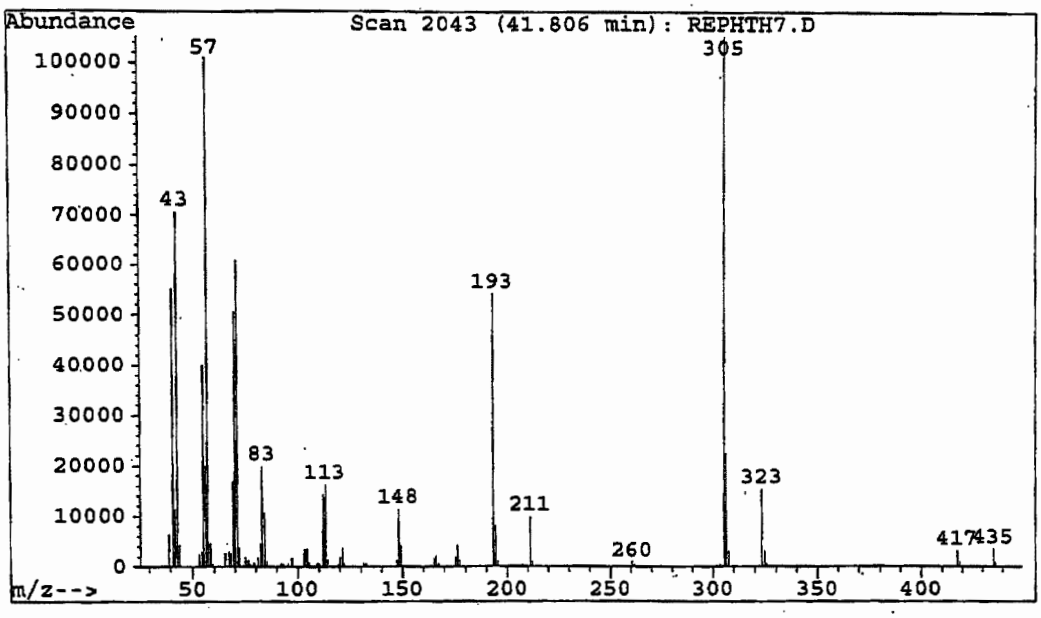


FIGURE 4.
STANDARD OBTAINED FROM CHESTER RIVER SITE
TRIOCTYL TRIMELLIATE



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MICROWAVE-ASSISTED EXTRACTION FROM SOIL OF COMPOUNDS LISTED IN SW-846 METHODS 8250, 8081, AND 8141A

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ABSTRACT

This study, which is part of an ongoing U.S. Environmental Protection Agency (EPA) research program, carried out by the Environmental Monitoring Systems Laboratory-Las Vegas, evaluates new sample-preparation techniques that minimize generation of waste solvents, improve target analyte recoveries, and reduce sample preparation costs. We have continued with developing a microwave-assisted extraction (MAE) procedure designed to extract pollutants from soil and sediment matrices, and are reporting results of MAE for 187 compounds and four Aroclors listed in SW-846 Methods 8250, 8081, and 8141A. All MAE experiments were performed on 5-g sample portions at 115°C/10 min with 30 mL 1:1 hexane/acetone. Of 89 semivolatile and six surrogate compounds spiked on soil, extracted by MAE, and analyzed by GC/MS, the spike recoveries for 79 compounds were between 80 and 120%, and for 14 compounds less than 80% (benzo(b)fluoranthene and benzo(k)fluoranthene were counted as one compound, because they could not be resolved on the DB-5 column; the recovery of 7,12-dimethylbenz(a)anthracene was 128%). Of the latter, recoveries for five compounds were below 20% (benzidine at 0%, α,α-dimethylphenethylamine at 7.0%, 2-picoline at 7.7%, dibenzo(a,j)acridine at 10.6%, and 2,4-dinitrophenol at 17.2%). When the spiked samples were aged for 24 h in the presence of moisture before being extracted, spike recoveries were between 80 and 120% for 46 compounds, and below 80% for 47 compounds. Of 45 organochlorine pesticides spiked on soil, extracted by MAE, and determined by dual column/dual ECD GC, spike recoveries of 38 compounds ranged from 80 to 120%, six ranged from 50 to 80%, and only the captafol recovery was above 120%. Spike recoveries in the range 100 ± 20% were obtained for 29 compounds when moistened samples were aged for 24 h before MAE, and for only 15 compounds after aging for 14 d.

Recoveries for Aroclors (in spiked, native, or reference materials) from nine different matrices ranged from 82 to 93% for Aroclor 1016 and 1260, and from 75 to 157% for Aroclor 1248 and 1254 (concentrations ranged from 0.022 to 465 mg/kg). Organophosphorus pesticide recoveries (47 compounds) were in general slightly lower than those achieved for the other pollutant groups tested.

For 15 compounds in a reference soil, the recoveries of 14 compounds by MAE were equal to or better than recoveries obtained by Soxhlet extraction (naphthalene being the exception). For selected organochlorine pesticides, recoveries from spiked soil samples were at least 7% higher for MAE than for either Soxhlet or sonication extraction.

The results of this study further demonstrate that MAE of pollutants from soil samples is a viable technique for sample preparation. With the use of MAE, many of the compounds of

concern to the EPA can be extracted in a single step in 10 min with a small amount of organic solvent.

NOTICE

The U. S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), had this abstract prepared for a proposed oral or poster presentation. It does not necessarily reflect the views of the EPA or ORD. Readers should note the existence of a patent (Paré, J.R.J., et al., U.S. Patent 5,002,784, March 1991) describing the use of microwave-assisted extraction for biological materials.

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A TOXIC CONGENER SPECIFIC, MONOCLONAL ANTIBODY-BASED IMMUNOASSAY FOR PCBs IN ENVIRONMENTAL MATRICES

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The most toxic PCB congeners are ortho unsubstituted and coplanar. They occur in much smaller amounts than the less toxic congeners in industrial PCB formulations and environmental samples. There is growing recognition that specific analysis of the toxic PCB congeners in the environment is required for an objective evaluation of risk and environmental impact. However, the time, effort and expense associated with the congener specific analysis of these compounds by instrumental methods such as capillary gas chromatography places substantial constraints on the scope of risk assessment and site evaluation studies. Immunoassay based analytical methods have demonstrated value for specific, high throughput screening as well as quantitiative analyses of many environmental analytes. We have developed an enzyme immunoassay (EIA) which is specific for the most toxic, coplanar PCB congeners. This EIA is based on a coplanar hapten derived monoclonal antibody and a novel competitor labeled enzyme conjugate. The coated tube format of this assay can be completed in less than 30 minutes. The EIA has a minimum detection limit of less than 0.2 ppb and an I_{50} of less than 1 ppb for the 3,3',4,4'-tetrachloro and 3,3',4,4',5-pentachlorobiphenyl congeners. Cross-reaction with several of the common Aroclor congeners including 4,4'-dichloro-, 2,2',5,5'-tetrachloro- and 2,2',4,4',5,5'-hexachlorobiphenyl is less than 0.01%. This presentation will describe optimization and performance characteristics of the EIA with emphasis on preparation of various environmental matrices and the relation of toxic congener quantification to the total PCB content of a sample.

ACCELERATED SOLVENT EXTRACTION OF CHLORINATED HYDROCARBONS INCLUDING DIOXIN AND PCB FROM SOLID WASTE SAMPLES

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Abstract

Accelerated Solvent Extraction (ASE) applies temperature and pressure to accelerate extraction processes and improve the efficiency of solvent extraction. This paper reports the results of a study of chlorinated hydrocarbons found at trace levels on a variety of matrices. PCB contaminants have been extracted from solid wastes including sewage sludge, urban dust and soil. Recoveries from these incurred samples were equivalent or better than from the Soxhlet extractions of equivalent samples. Dioxins at ppb levels were also extracted by ASE from a number of incurred samples from a range of environmental sources. A review of the data again shows that ASE gives equivalent or better recoveries compared to the traditional techniques. For a 10-g sample, the automated ASE system typically requires about 15 minutes to complete an extraction with a total solvent requirement of from 13 to 15 mL.

Introduction

Organic solvents required to extract solid samples can comprise the largest source of waste in the environmental analysis laboratory. Typical solvent volumes can range from 50 mL to over 400 mL per sample analysis procedure. At the present time, federal and state regulatory agencies are placing increased demands to reduce solvents in the analytical laboratory. However, most states require that only 40CFR promulgated methods be used in RCRA work. This requirement limits the typical contract and industrial laboratories to the solvent intensive methods described under SW-846: Method 3510 (separatory funnel), 3540 (Soxhlet), 3541 (automated Soxhlet) and 3550 (ultrasonic extraction).

A new extraction technique, accelerated solvent extraction (ASE) has recently been introduced (1). This technique uses conventional liquid solvents at elevated pressures (1500-2000 psi) and temperatures (50-200°C) to extract solid samples quickly, and with much less solvent than conventional techniques. With ASE, a solid sample is enclosed in a stainless steel vessel which is filled with an extraction solvent and heated to temperature. The sample is allowed to statically extract in this configuration for 5-10 minutes, with the expanding solvent vented to a collection vial. Following this period, compressed nitrogen is used to purge the remaining solvent into the same vial. The entire procedure is completed in 12-17 minutes per sample, and uses approximately 15 mL of solvent for a ten gram sample. ASE takes advantage of the increases in analyte solubilities which occur at temperatures above the boiling points of commonly used

solvents. At the higher temperatures used by ASE, the kinetic processes for the desorption of analytes from the matrix are accelerated compared to the conditions when solvents at room temperature are used. Solvent usage is reduced as a result of the higher analyte solubility in the heated solvent.
In this study, data will presented from the extraction of soils contaminated with PCBs and Dioxins.

Methods

Materials. All solvents used were pesticide grade or better. Certified PCB contaminated soil was purchased from Resource Technology Corporation (Laramie, WY).

Extraction. ASE extractions were performed at a pressure of 2000 psi and a temperature of 100 or 150°C. Additional information on the operation of ASE are reported in separate papers (1,2). Stainless steel extraction vessels with internal volumes of 11 mL were used. The extraction method was designed so that the vessel containing the sample was pre-filled with solvent, and then allowed to heat and extract statically for a total elapsed time of 10 minutes. The static valve was controlled so that it opened briefly when the cell pressure exceeded 2200 psi. The solvent that was expelled during this valve opening was routed to the collection vial. A schematic diagram of ASE is shown as Figure 1.
Following the combined heat-up and static extraction period, the static valve was opened, and fresh extraction solvent was introduced for a period of 10-15 seconds (approximately 8 mL), followed by a purge with nitrogen gas at 150 psi. The final volume of the extraction solvent was approximately 15 mL; the total extraction time was approximately 12 minutes per sample. All PCB containing samples were extracted with hexane/acetone at 100°C. Dioxin containing samples were extracted with toluene at 150°C. Fly ash samples were extracted with toluene acidified with phosphoric acid. All extracts were collected into amber, precleaned 40 mL vials purchased from I-Chem (New Castle, DE).

Quantitation. Analysis of the PCB extracts was performed by GC/ECD according to EPA Method 8080. Analysis of dioxin extracts was by GC/MS.

Results

PCBs
PCBs have been extracted from a variety of matrices, including oyster tissue, soils sludges and sediments. All of the extractions were performed according to the following method: 100C, 2000 psi, 12 minutes, using hexane/acetone as the extraction fluid. Table I summarizes data obtained from the extraction of sewage sludge. This sample was dried and ground prior to extraction. Percent recovery values are based on Soxhlet extraction results. Results presented in Table 2 were obtained by extracting a reference soil with certified levels of arochlor 1254. Analysis of these extracts were performed by an independent contract laboratory and show excellent correlation with the certified value.

Dioxins

Dioxins and furans have been extracted from a number of matrices as well. Dioxin samples were extracted at 150C, 2000 psi, using toluene as the extraction fluid. The extraction of dioxins requires app. 17 minutes per sample. Data summarized in Tables 3 and 4 show the absolute levels of dioxins and furans recovered from chimney brick by ASE and Soxhlet extraction. In all cases, ASE produced levels which very closely correspond the Soxhlet values.

Conclusion

In this study, accelerated solvent extraction has been shown to produce results comparable to traditional solvent extraction of PCBs and dioxins in much less time (12-17 minutes per sample) and using much less solvent (15 mL for a 10 g sample). Since a single method is capable of extracting the analytes from a variety of matrices, the time normally required for method development is significantly reduced.

ASE has previously been shown to be equivalent to Soxhlet extraction of BNAs, chlorinated pesticides, organophosphorus herbicides and shaker extraction of herbicides (1,2). Based on these data, ASE will be included as extraction Method 3545 in update III of CFR 40 (3).

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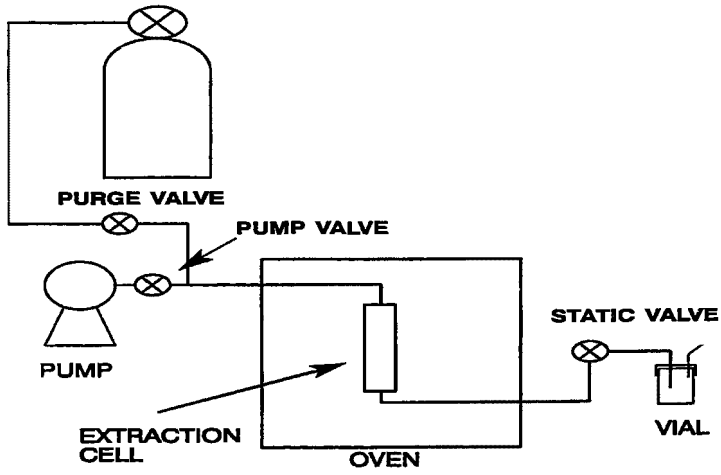

Figure 1. Schematic diagram of accelerated solvent extraction (ASE).

Table 1. Recovery of PCBs from Sewage Sludge

PCB Congener	Avg. (%), n=6	RSD (%)
PCB 28	118.1	2.5
PCB 52	114.0	4.7
PCB 101	142.9	7.4
PCB 153	109.5	5.8
PCB 138	109.6	3.9
PCB 180	160.4	7.5

Analyte concentration range: 160-200 μg/kg/component

Table 2.
Recovery of PCBs from Contaminated Soil
(1340 µg/kg certified, Arochlor 1254)

Run Number	µg/kg
1	1290
2	1366
3	1283
4	1369
Avg.	1327 (99.0%)
RSD	3.5%

Table 3. Dioxins from Chimney Brick

Congeners	Soxhlet (ng/kg)	ASE (ng/kg)
2,3,7,8-Tetra CDD	0.006	0.006
1,2,3,7,8-Penta CDD	0.052	0.057
1,2,3,4,7,8-Hexa CDD	0.046	0.052
1,2,3,6,7,8-Hexa CDD	0.12	0.13
1,2,3,7,8,9-Hexa CDD	0.097	0.10
1,2,3,4,6,7,8-Hepta CDD	1.0	0.88
Octa CDD	2.9	2.6

Table 4. Furans from Chimney Brick

Congeners	Soxhlet (ng/kg)	ASE (ng/kg)
2,3,7,8-Tetra CDF	0.16	0.18
1,2,3,7,8-Penta CDF	0.43	0.47
1,2,3,4,7,8-Hexa CDF	1.1	1.1
1,2,3,6,7,8-Hexa CDF	0.54	0.57
1,2,3,7,8,9-Hexa CDF	0.042	0.042
1,2,3,4,6,7,8-Hepta CDD	2.1	2.0
Octa CDD	2.0	2.0

Robust SFE Sample Preparation Methods for PCB and OCPs submitted to the US EPA SW 846 for consideration as a draft SFE method 3562

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Environmental laboratories are now in the process of examining the feasibility of replacing traditional sample preparation techniques that use macro quantities of chlorinated hazardous organic solvents with supercritical fluid extraction (SFE). Method development and validation have been underway for at least the past three years in many laboratories around the world. These new, emerging technology alternatives primarily use carbon dioxide with only a fraction of the organic solvent used in traditional methods such as Soxhlet or sonication.

We will present SFE techniques and robust methods for the sample preparation of polychlorinated biphenyls (PCBs) and organochlorine pesticides(OCPs) from solid wastes and fish tissue. In each case, the conditions for the extraction and cleanup prior to analysis will be given. Validation data will include to the recovery and precision results for representative reference samples. This validation data has been presented to the organic work group of the US EPA SW-846 solid waste operation for consideration as a draft method, which would be designated Method 3562.

The presented methods will maximize unattended operation and minimize the use of organic solvents. For a typical SFE sample preparation of a fish tissue sample containing PCBs and OCPs, approximately one hour of time is required with no further external sample cleanup or evaporation/concentration steps (in-situ sample cleanup). A typical traditional sample preparation technique which would require 12-18 hours of time, 250-500 milliliters of organic solvent, and a separate, manual column chromatography cleanup step with a Florisil column or silica treated with sulfuric acid. The manual column chromatography manipulation would result in a volume of organic solvent which needs concentration prior to analysis.

The deliverables data include the recovery of PCB congeners and OCP analytes as listed below.

Table 1 **PCBs**

Compounds	empirical formula	IUPAC numbers
2,4,4' Trichlorobiphenyl	$C_{12}H_7Cl_3$	CB 28
2,5,2',5' Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	CB 52
2,4,5, 2',5' Pentachlorobiphenyl	$C_{12}H_5Cl_5$	CB101
2,4,5, 3',4' Pentachlorobiphenyl	$C_{12}H_5Cl_5$	CB 118
2,3,4, 3',4' Pentachlorobiphenyl	$C_{12}H_5Cl_5$	CB 105
2,3,4, 2',4',5' Hexachlorobiphenyl	$C_{12}H_4Cl_6$	CB 138
2,3,4, 2',3',4' Hexachlorobiphenyl	$C_{12}H_4Cl_6$	CB 128
2,3,6, 2',4',5' Hexachlorobiphenyl	$C_{12}H_4Cl_6$	CB 149
2,4,5, 2',4',5' Hexachlorobiphenyl	$C_{12}H_4Cl_6$	CB 153
2,3,4,5 ,3',5' Hexachlorobiphenyl	$C_{12}H_4Cl_6$	CB 156
2,3,4,5, 2',4',5'Heptachlorobiphenyl	$C_{12}H_3Cl_7$	CB 180
2,3,4,5, 2',3',4' Heptachlorobiphenyl	$C_{12}H_3Cl_7$	CB 170

a IUPAC nomenclature

There are potentially 209 members of a class of compounds known as Polychlorinated Biphenyls. In this class of compounds, biphenyl is the backbone and between one and ten chlorine atoms are substituted on this biphenyl nucleus. Of the possible 209 CBs only about 120 have been detected in environmental samples.

Table 2 OCPs

Compounds	CAS #
Aldrin	**309-00-2**
b-Hexachlorocyclohexane (b-BHC)	**319-85-7**
d-Hexachlorocyclohexane (d-BHC)	**319-86-8**
g-Hexachlorocyclohexane (g-BHC)[b]	**319-87-9**
a-Chlordane	**5103-71-9**
4,4'-DDD	**72-54-8**
4,4'-DDE	**72-55-9**
4,4'-DDT	**50-29-3**
Dieldrin	**60-57-1**
Endosulfan	**115-29-7**
Endrin	**72-20-8**
Endrin aldehyde	**7421-93-4**
Heptachlor	**76-44-8**
Heptachlor epoxide	**1024-57-3**

a Chemical Abstracts Registry Number

b Also known as Lindane

RESULTS :

The following tables summarizes all the recovery, bias, precision, minimum detectable limit (MDL) and the Reliable Quantitatio Limit as prescribed in your letter.:

Table 3 PCB Deliverable Data

	bias	Precision % rsd	MDL mg/Kg	RDL mg/Kg
EC 1	95.7	8.2	10.7	42.8
SRM 1941	85.8	2.2	1.7	6.8
EC 5	104.0	3.6	3.1	12.4
CRM 481	79.0	4.7	5.2	20.7
Michigan Bay	108.7	2.6	5.5	22.1
CRM 392	91.8	2.7	15.1	60.6
SRM 2974	83.2	3.0	5.0	19.9
GRAND MEANS	92.6	3.9	6.6	26.2

Table 4 OCP Deliverable Data

	bias	Precision % rsd	MDL mg/Kg	RDL mg/Kg
Delhi 250	107.9	5.3	0.9	3.4
Delhi 5	74.3	5.2	0.6	2.4
McCarthy 250	102.0	4.0	0.7	2.8
McCarthy 5	85.9	7.4	1.3	5.0
Auburn 250	79.4	4.4	0.6	2.5
Auburn 5	87.8	5.5	0.6	2.5
GRAND MEANS	89.6	5.3	0.8	3.1

The poster session will include much more experimental data regarding the types of samples which were used for the data obtained. It would appear that this is a robust method which was tested in four different laboratories in the United States and in Canada on a wide variety of certified samples and in the case of the organochlorine pesticides, spiked samples on reference soils.

ABSTRACT FOR ENVIRACS MEETING, WASHINGTON DC, JULY 1995

ANALYSIS OF DIOXIN IN WATER BY AUTOMATED SOLID PHASE EXTRACTION COUPLED TO ENZYME IMMUNOASSAY

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An automated system has been developed for solid phase extraction of liquid samples, based in part on the fluidics and control portions of the automated FMS Dioxin-Prep™ System. The SPE-Prep™ System has been used to develop a method for the extraction of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) from water. Also, an enzyme immunoassay (EIA) system has recently been developed for rapid screening of TCDD from a variety of matrices. These two novel methods have been coupled to produce a rapid and simple method for the screening of water samples for dioxin contamination. Water analysis can be performed by EIA directly following extraction and solvent exchange with no extract clean-up. Sensitivity for TCDD in the EIA is approximately 100 pg per analysis. Thus sensitivity to 0.1 ppt TCDD in water is possible using 1-2 liters of sample. Scaling the sample size to 50 liters allows better than 10 ppq sensitivity. Total time for sample preparation and EIA analysis is less than 4 hours for a 1-2 liter sample. Larger samples can be extracted by running the automated system overnight, with the same approximate analyst time required for extraction and EIA analysis. Optimization of the automated SPE system and its interface to the EIA will be described. Results from EIA and GC-MS analysis of both spiked and field samples will be presented.

MICROWAVE-ASSISTED SOLVENT EXTRACTION OF PAHS FROM SOIL- REPORT OF AN INTER-LABORATORY STUDY

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ABSTRACT

Solvent extractions are among the oldest and most widely practiced sample preparation techniques for chemical analysis. Normally, solvents are selected to dissolve target analytes based on the affinity between solvent and solute and range from highly polar molecules like water to lipophilic hydrocarbons, depending on the target analyte. Although traditional extraction methods are labor intensive and often time consuming, newer extraction techniques using microwave heating more efficiently leach additives from plastics (1), natural products from botanicals (2), and pollutants from sediment (3-5). Microwave extractions that are performed in closed vessels achieve higher temperatures and pressures, thus they take less time than traditional methods. Controlled dielectric heating with microwave sources is more reproducible than room temperature sonications or open vessel Soxhlet methods. This improves extraction precision.

INTRODUCTION

This presentation discusses optimization of extraction parameters for releasing polycyclic aromatic hydrocarbons (PAHs) from a reference sediment, SRM 1941a using methylene chloride, and presents results obtained at NIST by reverse phase liquid chromatography (4). Both extraction time and temperature were systematically varied to evaluate the two most important experimental parameters in order to establish the optimum extraction conditions. Although microwave recoveries showed improvement with increasing temperatures from 40 to 100 °C, the average ranged from 93-106% of the Soxhlet value. When the isothermal extraction was varied from 10-30 minutes, similar recovery efficiencies were found although some degradation was seen at longer times. The presence of moisture speeded the attainment of the target temperature, however, extraction efficiency did not improve. Neither did the addition of sodium sulfate as a drying agent improve recovery.

A protocol was subsequently developed for conducting an interlaboratory study to compare the recovery efficiency of the microwave method with conventional extraction techniques. It consisted of a 15 minute extraction in 30 mL of methylene chloride (pesticide grade) at 100 °C. Participants included a regional EPA lab, a municipal environmental lab, one small and one large private lab and one national laboratory. Instructions to analysts included a request to extract the sediment by their conventional method and to analyze the PAHs of environmental interest in both extracts by the best available method, i.e., GC, GC-MS, or HPLC. In all cases, that analytical method turned out to be a GC-MS, similar to EPA Method 8270. Information on conventional extraction methods, sample sizes and analytical methods are summarized in the following table.

Table I. Conventional Methods of Preparation, Analytical Technique and Sample Sizes for the Interlaboratory Study

	Methods		Spikes &	Sample Size, g	
Lab#	Preparation	Detection	Surrogates	Conven	μwave
1	Sonication	GC-MS	d_8, d_{10}, d_{12}	5	5
2	Sonication	GC-MS	d_8, d_{10}, d_{12}	10	2
3	Sonication	GC-MS	d_4, d_8, d_{10}, d_{12}	5	1
4	Wrist Shaker/auto	GC-MS	d_{12}, terphenyl	1	1
5	Tumbling	GC-MS	d_8, d_{10}, d_{12}	1	1

For the study a batch consisted of six vessels comprising three sample replicates, one solvent blank and two controls which permitted analysts to run either a surrogate, laboratory QC or check sample, or a standard or reference material. Vessels were weighed both before and after microwave heating to identify any potentially compromised vessel that may have vented during the heating step. Only one lab reported > 0.1 g weight lost for any vessel during the 25 minutes of elapsed time which includes ~ 10 minutes for the six-vessel complement to reach 100 °C. After cooling to room temperature samples were centrifuged and the solvent decanted. Sample cleanup in most instances meant removal of elemental sulfur with copper. A final solvent exchange and blown down in hexane was effected for the chromatography.

RESULTS

Results comparing the percent recovery for typical PAHs found in soil will be presented for the microwave extraction technique. Spike recoveries for the deuterated compounds averaged from ~ 65% to slightly over 100%. When compared to the NIST certified value (6) for the specific PAH, recoveries were often > 100 %. Additional comparisons between the microwave extract recoveries and conventional extractions of PAHs will be presented for each participating laboratory.

DISCUSSION

The results presented demonstrate that with dielectric heating sufficient energy is transferred to solution, with solvents such as methylene chloride, to raise the solution temperature to well above the boiling point in a matter of minutes. At these elevated temperatures, the rate of analyte extraction or desorption from the soil surface and interstices is enhanced. In addition, the solubility of these relatively non-polar analytes in methylene chloride is substantially improved. Extraction efficiency thus is a function of the increased temperatures afforded by the closed vessel technique. This technology has been shown to be comparable to conventional methods of extraction (5). In systems where even more polar solvents such as acetonitrile or aliphatic alcohols are used, similar enhancements can be expected. This approach may lead to still more efficient and environmentally friendly extraction systems. With automated cleanup, improved sample throughput is possible.

CONCLUSIONS

We can report that study participants uniformly appreciated the opportunity to dramatically reduce the solvent volumes needed to accomplish extractions of pollutants from sediments. In addition, laboratory efficiency may have been improved because of the time savings realized when closed vessel microwave extraction was used.

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OPTIMIZING AUTOMATED SOXHLET EXTRACTION OF SEMIVOLATILES

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ABSTRACT

Automated Soxhlet Extraction was recently promulgated as an official USEPA method (SW-846 Method 3541). Because of more efficient extraction design, the revised technique is faster than traditional Soxhlet Extraction (Method 3540) and uses less solvent than traditional Soxhlet extraction or Ultrasonication Extraction (Method 3550). In the first stage of Method 3541 extraction, sample is immersed in boiling solvent, facilitating extraction of target analytes and thus shortening total extraction time. Following this the sample thimble is separated from contact with the extraction solvent and there is a second refluxing extraction stage which is similar to a Soxhlet-type of extraction in that condensed solvent percolates down through the sample.

The Soxtherm extraction system performs SW-846 Method 3541 and automates all steps of sample processing including macro concentration of the sample extracts and collection of evaporated solvent for recycling or disposal. Samples up to 30 grams in size are extracted in two hours using less than half the solvent required by traditional methods. A variety of target compounds of environmental interest are efficiently extracted from different matrices.

Since automated concentration of the sample extract is included in Soxtherm processing, an assessment of losses traceable to the evaporation technique is useful. This work examines effects on evaporative losses of changes in extraction system operation such as solvent type, heater and coolant temperatures, extraction vessel and thimble sizes, and final concentrate volume. Very good recoveries of easy to lose semivolatile analytes were demonstrated with excellent precision. Six replicate aliquots of 1:1 acetone and methylene chloride (115 mL) spiked with 25 μg of each analyte were concentrated to final volumes ranging from 4 mL to 11 mL, with an average recovery of 99.5% for all eleven of the compounds. The same procedure when conducted using 102 mL of 100% methylene chloride yielded an average of 94.4% recovery with final volumes ranging from 5 to 12 mL.

The system used for this work provides high throughput with minimal labor requirement, and presents opportunities for laboratories to decrease turnaround time, minimize hazardous waste generation, obtain operator independent results, and economize on labor costs.

INTRODUCTION

Soxhlet extraction is a proven technique for recovery of organic analytes, is simple to implement, and suffers from few disadvantages; however, one drawback has been the method time requirement of 16 to 24 hours. Recently an updated technique was promulgated as SW-846 Method 3541, "Automated Soxhlet Extraction", which cites a two hour extraction cycle. A recent publication[1] showed that extraction times can be shortened relative to those specified in the method without substantial decrease of analyte recoveries. Fast extraction time relative to the traditional method stems from direct exposure of the sample to boiling solvent during the initial portion of the procedure.

Soxtherm performs Method 3541 in the most automated fashion possible, with all steps under microprocessor control. Following an initial reflux period during which the sample is immersed in boiling solvent, the system separates the sample thimble from the extract by evaporating a portion of the refluxing solvent. The second reflux period which follows serves to complete recovery of extractable material and assures precise results. Further reduction in volume of the sample extract can take place following that reflux period.

Some semivolatile target compounds are easily lost when extracts are reduced to small volumes. Maximum utility of the automated Soxhlet procedure depends on recovering such analytes in a volume of concentrate that is small enough to require minimal further processing, yet large enough to avoid extensive evaporation losses. Some recent work at US EPA Region 6 Laboratory in Houston, Texas used concentrates from Soxtherm which were subjected to further evaporation in Labconco RapidVap™ N_2*, a nitrogen blowdown apparatus. These showed moderate losses in recovery for more volatile analytes upon GC/MS analysis (Table 1). However, prior work involving extraction of spiked samples[2], in which Soxtherm evaporation was stopped at 10-20 mL final volume and the concentrate gently blown down by hand to a smaller volume and analyzed by GC/FID (Table 2) indicates that evaporation losses were minimal and that recoveries were affected principally by matrix effects.

Comparison of the two sets of prior work cited indicates that users of this technique should be able to routinely concentrate samples automatically to some final volume between 1 mL and 10 mL with very minimal evaporation losses. This work is aimed at determining how low in volume Soxtherm concentrates can be made without encountering significant evaporation losses. Recovery losses traceable to the evaporation stage of sample processing are assessed and sensitivity of analyte recoveries to changes in extraction system operating conditions such as temperatures and final concentrate volume are determined.

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* RapidVap is a trademark of the Labconco Corporation.

Table 1. Spiked Blanks with Final Evaporation Completed in RapidVap

ANALYTE	AVER. (6 REPL)	STD. DEVIATION
2-Fluorophenol	46	3.4
Phenol-d5	61	4.6
2-Chlorophenol-d4	56	5.0
1,2-Dichlorobenzene	63	6.3
Nitrobenzene-d5	62	5.6
2-Fluorobiphenyl	66	4.1
2,4,6-Tribromophenol	77	3.3
Terphenyl-d14	97	2.9
Phenol	52	3.8
2-Chlorophenol	51	4.8
1,4-Dichlorobenzene	49	5.3
N-nitrosodi-*n*-propylamine	70	5.5
1,2,4-Trichlorobenzene	59	5.0
4-Chloro-3-Methylphenol	68	4.0
Acenaphthene	71	4.0
4-Nitrophenol	84	3.5
2,4-Dinitrotoluene	74	3.1
Pentachlorophenol	95	4.0
Pyrene	96	2.8

Table 2. Recoveries from Spiked Samples Using Gentle Nitrogen Blowdown

Analyte	Blank	Sand/Clay	Loam
2-Fluorophenol	93	80	78
Phenol	92	83	86
1,2-Dichlorobenzene	82	60	45
1,2,4-Trichlorobenzene	88	84	85
Acenaphthene	90	80	85
Hexachlorobenzene	96	86	96
o-Terphenyl	93	85	96

Average of three or four replicates

EXPERIMENTAL PROCEDURE

Extraction System Operating Parameters

No samples were used during these investigations; however, the extraction system was allowed to proceed in a manner consistent with sample extraction so that any evaporation losses traceable to the extraction period would be duplicated. Initial solvent volume during automated Soxhlet extraction must be large enough to cause the sample to be covered with boiling solvent. Therefore, solvent volumes were chosen to equal amounts required to process various sizes of environmental samples ranging up to thirty grams. Example Soxtherm operating parameters are shown below in Table 3. The automated extraction system was programmed with an extraction temperature (i.e. heater control temperature) sufficient to produce adequate reflux action. During the thirty minutes of boiling time the system was in total reflux, which produces rapid extraction.

The number of 15 mL aliquots removed during the first solvent reduction period was chosen to reduce extract volume to an amount that would be low enough to uncover the extraction thimble, thus suspending it above the boiling extract. For the standard extraction beaker (ca. 48 mm. i.d.) the volume remaining after the first reduction period was approximately 40 mL.

Table 3. Example Soxtherm Operation Conditions

Parameter	Value
Extraction temperature	150° C
Boiling time	30 minutes
Solvent reduction A	5 x 15 mL
Extraction time	45 minutes
Solvent reduction B	2 x 15 mL
Solvent cooling time	15 minutes
Air pulse interval	5.5 minutes
Air pulse duration	3 seconds
Chiller water temperature	15° C

Following the first solvent reduction period an extraction time of 45 minutes was employed. This would serve to rinse additional extractable materials from the sample contained within the thimble. After extraction was completed a second solvent reduction period was used to concentrated the extract to a small volume (5 to 15 mL).

Extraction and Evaporation

Solvent was measured and placed into each extraction beaker and a solution of eleven semivolatile compounds (25 μg of each contained in 1 mL of 1:1 acetone and DCM) was spiked directly into the solvent. Processing was initiated using a recirculating chiller (Neslab CFT-33) to cool water for the condensers. No gaskets were placed between the extraction beakers and the condensers. Omission of gaskets that contain extractable material eliminates a potential source of contamination cited in Method 3541. Following the automated extraction and evaporation the concentrated extract was allowed to cool for a few minutes with a foil cap covering the extraction beaker to prevent further solvent losses, then the concentrate was removed using a syringe to measure its volume and the beaker was rinsed with two or more small portions of solvent.

Quantitation

Concentrates were adjusted in volume to 10.0 mL and analyzed using a Hewlett-Packard 5890A gas chromatograph equipped with an Rtx™-5 column* (0.53 mm i.d. x 15 meter, 1 micron film thickness) and a flame ionization detector. Peak areas from analysis of recovered extracts were referenced against those from solutions of spiking standard diluted to 10.0 mL and 25.0 mL, with one set of standard injections performed for each three samples that were analyzed.

RESULTS & DISCUSSION

Table 4 shows recoveries after evaporation for the semivolatile compound spiked into either a 1:1 mixture of acetone and methylene chloride (DCM) or into 100% DCM. Measured volumes of the concentrated "extracts" showed similar sizes and variability for the two experiments, with volumes ranging between 4 and 12 mL, with average volumes of 8.3 mL and 9.2 mL, respectively. These compare well with calculated final volumes of 10 mL and 12 mL respectively for the two experiments (starting volume less amount expected to be removed during solvent reduction steps) and indicates that losses of solvent vapor due to leakage were consistent and not very large. The final volumes achieved in these experiments are convenient for further concentration of extracts, when necessary to achieve detection limit goals, using nitrogen blowdown or the microSnyder apparatus.

As expected, evaporation of 1:1 mixture produced a concentrate that was enriched in acetone. Weighing extracts from the 1:1 experiment and computing the ratio to the measured volumes produced a calculated density of 0.919 g/mL, which corresponds to a mixture containing about 25% DCM.

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* Rtx is a trademark of Restek Corporation.

Table 4. Evaporation Recoveries for Solutions Containing Semivolatile Analytes

Six replicate evaporations using Soxtherm

Analyte	System A		System B	
	Rec(%)	s.d.	Rec(%)	s.d.
2-Fluorophenol	103	3.0	93	2.9
Phenol	102	2.8	94	2.0
1,4-Dichlorobenzene	101	2.7	94	1.3
1,2-Dichlorobenzene	97	2.2	94	1.5
Hexachloroethane	93	1.7	93	1.3
Nitrobenzene	98	2.5	95	1.7
bis-(2-Chloroethoxy)methane	101	2.9	97	3.8
Naphthalene	98	2.4	95	2.0
Hexachlorobenzene	97	2.1	94	1.0
2-Fluorobiphenyl	99	2.6	96	1.8
Acenaphthene	104	5.3	93	1.9

SYSTEM A = 115 mL of 1:1 acetone and methylene chloride

SYSTEM B = 102 mL of methylene chloride

Both experiments produced very good recoveries with single analyte precision (standard of deviation) values ranging from 1.0% to 5.3%. Very little loss was measured for even the most volatile of the compounds tested (2-fluorophenol and phenol) and there was no discernible difference between recoveries of the most volatile and least volatile analytes. Overall measured recoveries for the eleven analytes were higher for the experiment with 1:1 acetone and DCM than for the experiment with 100% DCM, 99.5% average versus 94.4%, respectively.

SUMMARY & CONCLUSIONS

Data from further experiments not available for this manuscript will be presented at the conference. Parameters which may be investigated include the effect of increasing heater or coolant water temperatures and the effect of decreasing final concentrate volumes. The following conclusions have been drawn from the data accumulated thus far.

1. Soxtherm evaporates extracts to a small volume in a predictable fashion and accomplishes the macro concentration function efficiently and automatically.

2. For the acetone and DCM experiment, the average final concentrate volume was 8.3 mL, versus a projected final volume of 10 mL (115 mL starting volume less 7 x 15 mL removed during solvent reduction steps). This indicates that losses due to leakage during evaporation are minimal under these conditions.

3. Recoveries were very good for all analytes in both solvent systems, and there were no statistically significant differences in recoveries between the more volatile and less volatile of the analytes tested. recoveries also showed no dependence on the measured volumes of the final concentrates. This indicates that there are no appreciable evaporation losses during evaporation to final volumes between 4 mL and 12 mL.

4. Recoveries were higher by an average of 5% for evaporation of 1:1 acetone and DCM mixture than for evaporation from DCM alone. Unless this result is due to measurement errors, it indicates that evaporation of DCM without acetone carries off small amounts of target compounds as high boiling as acenaphthene.

REFERENCES

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TESTS OF IMMUNOASSAY METHODS FOR 2,4-D, ATRAZINE, ALACHLOR, AND METOLACHOR IN WATER

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ABSTRACT

There is high level of public concern about pesticides that might be dispersed into water systems in the United States as a result of misapplication, improper disposal, or natural disasters (e.g., flooding). EPA has an interest in immunoassay as rapid, reliable, low-cost screening method for environmental and floodwater samples. The EPA Office of Pesticide Programs (OPP) tasked SAIC to conduct a systematic validation of immunochemical methods for 2.4-D, atrazine, alachlor, and metolachlor using surface water samples spiked at three different concentrations. Seven replicate samples were prepared at each of three fortification levels and analyzed using EPA Methods 3510/8151 (515.1) and 507; those results were compared with results obtained using commercially available immunochemical test kits. The fortification levels of atrazine, alachlor and metolachlor corresponded to the estimated detection limit (EDL), the limit of quantitation (LOQ, 3 x EDL), and ten times the LOQ specified in method 507. In the case of 2,4-D, the measurement limit for the immunoassay test kit was higher than that EDL specified in method 515.1. Therefore, those fortification levels were selected according to the limits of the test kit.

The tests of the kits for 2,4-D, alachlor, and metolachlor were fully successful. The major problem identified during testing was false positives and poor accuracy using the atrazine test kits. This problem may have been the result of a bad calibration standard supplied with the kit (the manufacturer has since changed suppliers) or cross-reacting materials in the sample. No triazine herbicides or degradation products were detected in the matrix blanks using GC/MS (<0.05 ug/mL).

	low	medium	high
2,4-D Recovery (%)	110.8	91.7	124.3
Standard Deviation	28.5	25.2	13.6
RSD (%)	25.7	27.5	10.9
Alachlor Recovery (%)	89.8	96.4	113.2
Standard Deviation	12.8	18.9	10.3
RSD (%)	14.3	19.6	9.1
Metolachlor Recovery	81.1	126.2	78.8
Standard Deviation	10.2	2.9	15.4
RSD (%)	12.6	2.3	19.5
Atrazine Recovery (%)	193.4*	197.8*	143.8*
Standard Deviation	29.9	13.1	11.1
RSD (%)	15.5	6.6	7.7

* Failed to meet project data quality objectives (DQOs)

INTRODUCTION

Immunoassay was one of the major topics at EPA's Tenth Annual Waste Testing and Quality Assurance Symposium (ENVIRACS) held last July. It appears that the efforts of manufacturers, Regulatory Agencies as well as academic, government and commercial laboratories have resulted in reliable products that can be used to screen for pollutants in the environment using immunochemistry. A number of immunoassay screening procedures have been promulgated or will be proposed for the RCRA program in SW-846. These include methods for pentachlorophenol, PCBs as Aroclors, petroleum hydrocarbons and Toxaphene.

The Office of Pesticide Programs also has an interest in immunoassay as a low-cost, reliable screening procedure for monitoring pesticides in the environment. Based on immunoassay results, investigators from the University of Iowa reported the presence of pesticides in mid West flood water samples during the Spring of 1993. However, their sampling and analysis procedures were not well documented. OPP chose SAIC to systematically test the validity of immunoassay kits for screening samples for contamination from 2,4-D, Alachlor, Metolachlor and Atrazine. SAIC was specifically tasked to provide data that could be used to evaluate the timeliness, costs, accuracy, and precision of immunoassay.

This task was specifically authorized to establish the suitability of immunoassy for screening flood water samples. However, the mid-Western flood waters had receded by the time that the SAIC work assignment was in place. As a result, each analyte was added to surface waters from San Diego County in order to simulate flood water.

Immunoassay Binding

The measurement technology used in immunoassay kits is formally called Enzyme Linked Immunosorbant Assay (ELISA). Antibodies used in test kits are immobilized on the walls of test tubes, 96-well assay plates, magnetic particles, or membranes. Immunoassay measurements are accomplished by competitive binding between pollutants extracted from a sample and a pollutant-enzyme-conjugate supplied as part of the kit. When the extract of a highly contaminated sample is analyzed, most antibody sites bind the extracted pollutants. When a non-contaminated sample or a blank is analyzed, most antibody sites bind the pollutant-enzyme-conjugate. The antibody tubes or assay plates are then washed to remove any unbound extract.

Antibody reagents can be used to measure pollutants directly in aqueous samples. However, antibodies are incompatible with organic extraction solvents, most oily matrices and certain reactive wastes. As a result, solids must be extracted with methanol and diluted before antibody binding. Additional cleanup procedures may be required to make immunoassay suitable for measuring pollutants in oily and reactive matrices.

Visualization Technique

The difference in the amount of pollutant in sample extracts, blanks,

and standards becomes apparent during the second incubation of the ELISA procedure. All of the bound enzyme-conjugate reacts with a substrate to produce a colored product. Therefore, the observed color by the kit is inversely proportionally to the concentration of pollutant in the sample extract: (1) a darker color means a lower concentration in the sample, (2) less color means a higher pesticide concentration in the sample.

Immunoassay screening techniques compare the color produced from sample extracts with a standard that corresponds to the action level in the sample. This relationship is illustrated in Figure 1 (provided by Millipore).

Although not currently authorized by the EPA, immunoassay can be used for quantitative analysis. The upper and lower quantitation range of the method is established by analyzing 3 to 5 calibrators in duplicate. When the concentration of pollutants in a sample extract exceeds the upper calibration range (*i.e.*, is lighter), that extract should be diluted so that it falls within the dynamic range. The precision of immunoassay measurements should be documented by performing duplicate analyses of sample extracts, positive controls and blanks.

Data Review And Quality Assurance Considerations

When reviewing immunoassay data, one must remember that this is a different measurement technology from chromatographic analysis. Therefore, data quality objectives (DQOs) need to be designed for ELISA and not just adapted from monitoring programs that use chromatographic analysis. Immunoassay QA should include performance checks that document photometer performance. In addition, data sheets should provide the ambient temperature when the test was performed, storage conditions for the kits, the lot number of all reagents as well as all recorded raw data. Under no circumstances should reagents from different kits or from different manufacturers be employed to perform a single analysis. Data reviewers should ensure that results for duplicate analyses, positive controls and blanks fall within acceptance windows specified in the method or defined as project DQOs. Reviewers should confirm that sample calculations are provided and that all data reductions are performed properly.

Documentation of analyst training is an important quality assurance consideration for immunoassay techniques. Specific training in performing these methods in the field is particularly important when those measurements may be used to support real-time remediation decisions.

EXPERIMENTAL DESIGN

Laboratory work was conducted following Good Laboratory Practices described according to an approved Quality Assurance Project Plan (QAPP). Water samples were obtained from the Santa Margarita River (San Diego County CA) and fortified with three different concentrations of atrazine, alachlor, metolachlor, and 2.4-D. Seven replicate fortifications of each fortification level were analyzed using EPA Methods 507 and 515.1 (8151); those results were compared with results

obtained using commercially available (Millipore) immunochemical test kits based on ELISA.

Single analyses of each of the seven replicate fortifications were made for each target analyte using the chromatographic methods. Duplicate immunochemical determinations of each replicate fortification were made as specified in the manufacturer's instructions. The mean value of the duplicate immunochemical determinations was used for quantitation. A reagent blank and a matrix blank were analyzed along with each fortification level.

Samples analyzed by method 507 were fortified with a mixture of three target herbicides, atrazine, alachlor, and metolachlor. Samples analyzed by method 515.1 (8151) were fortified with 2,4-D only. Samples analyzed by the immunoassay kit were fortified with the individual target analytes. The fortification levels of atrazine, alachlor and metolachlor correspond to the estimated detection limit (EDL), the limit of quantitation (LOQ, 3 x EDL), and ten times the LOQ specified in method 507. In the case of 2,4-D, the measurement limit for the immunoassay test kit was higher than that EDL specified in Method 515.1 (8151). Therefore, the fortification levels for 2,4-D were selected according to the limits of the 2,4-D test kit.

Instrumentation

Gas Chromatograph Hewlett Packard 5890 Series II GC with a 7673 auto-sampler, and a Vectra 486s/20 with HP Chemstation.

Method 507 chromatographic conditions:

column:	30 m x 0.53 mm ID, 1.5 μm film thickness DB-5
carrier:	helium at 5 mL/min
make up:	helium at 25 mL/min
hydrogen:	3 mL/min
air:	100 mL/min
inj.temp:	200°C
det.temp (NPD):	240°C
inj.volume:	2 μL
initial temp:	130°C
initial time:	5.3 min.
rate 1:	12°C/min
final temp.1:	190°C
final time 1:	0 min.
rate 2:	3°C/min
final temp.2:	230°C
final time 2:	2.37 min.

2,4-dimethyl-nitro-benzene:	4.61 minutes (surrogate)
atrazine retention time:	13.35 minutes
alachlor retention time:	16.30 minutes
metolachlor retention time:	17.80 minutes

Method 515.1 chromatographic conditions:

column:	30 m x 0.53 mm ID, 1.5 μm film thickness DB-5
carrier:	helium at 5 mL/min
make up:	5% methane in argon at 55 mL/min
inj.temp:	200°C
det.temp (ECD):	300°C
inj.volume:	1 μL
initial temp:	150°C
initial time:	0.5 min.
rate:	6°C/min
final temp.	275°C

2.4-D retention time: 8.20 minutes

Photometer - Millipore EnviroQuant™ photometer with filter block, keypad, liquid crystal display, microprocessor, printer, and tube holder. It is a discrete-wavelength, bichromatic photometer. The photometer included a CPU with an automated data reduction algorithm.

Immunochemistry Test Kits: (1) Millipore Envirogard™ Alachlor QuantiTube Test Kit, ENVIR TOO 06, (2) Millipore Envirogard™ 2,4-D QuantiTube Test Kit, ENVIR TOO 03, (3) Millipore Envirogard™ Triazine QuantiTube Test Kit, ENVIR TOO 01, (4) Millipore Envirogard™ Metolachlor QuantiTube Test Kit, SD3P 212S4
All equipment, supplies, and reagents needed for the immunochemistry analysis, including calibration standards, were provided in the specific kits.

TABLE 1. CHEMICAL STANDARDS, SOURCES, PURITY, AND LOT NUMBERS

Analyte	CAS #	Lot #	Purity %	Source
Atrazine	1912-24-9	J210	99.0 (neat)	EPA
Alachlor	15972-60-8	115	99.9 (neat)	EPA
Metolachlor	51218-45-2	124603	97.0 (neat)	Crescent Chemical
2,4-D	94-75-7	JB01257	99.0 (neat)	Ultra Scientific
1,3-dimethyl-2-nitrobenzene (507 surrogate)	89-87-2	H-0052	250-μg/mL	Ultra Scientific

RESULTS

Method 515.1 (Method 8151) for 2,4-D - Two trials of Method 515.1 were performed during this study. Initial evaluation of Method 515.1 was not successful. Calibration was not linear and method recoveries did not satisfy the project DQO criterion for calibration. After consultation with the EPA WAM, laboratory procedures were modified - glassware was cleaned with methanolic potassium hydroxide (10%), 5% methane in argon (P-5) was employed as a detector makeup gas, and commercial 2,4-D methyl esters (Ultra) were used for calibration.

The second trial of Method 515.1 gave mean recovery and precision values meeting project DQOs for 2,4-D at all fortification levels. The calibration data for the target analyte was linear and all calibration check standards gave less than 20% difference from initial calibration. The reagent and matrix blanks did not exhibit response exceeding one half the low level calibration standard response within the retention time window of any of the target analytes. The mean recovery for 2,4-D in samples fortified at 2.0 µg/L (EDL) was 111.9% with a precision of 18.6%. The mean recovery at 6.0 µg/L (LOQ) was 104.1% with a relative standard deviation (RSD) of 17.9% and the mean recovery at 60.0 µg/L (10 x LOQ) was 97.0% with an RSD of 9.3%. These data are presented in Table 2A.

2,4-D immunoassay test kits The test kit gave acceptable 2.4-D recoveries for samples fortified at 2 µg/L (EDL) and at 6.0 µg/L (LOQ). The mean recovery for 2,4-D in samples fortified at 60 µg/L (10 x LOQ) was high. The precision values for samples fortified at the EDL and LOQ were high while the precision for samples fortified at 10 x LOQ was acceptable.

The mean recovery for 2,4-D in samples fortified at 2 µg/L was 110.8% with an RSD of 25.7%. The mean recovery for 2,4-D at 6.0 µg/L was 91.7% with an RSD of 27.5% and the mean recovery for 2,4-D at 60.0 µg/L was 124.3% with an RSD of 10.9%. These data are presented in Table 2B.

The calibration data associated with these samples was linear ($r = 1.0$ and $r = 0.9993$) with all points falling within the expected range. The calibration check standards associated with samples fortified at the EDL and the LOQ exhibited less than 12% difference from initial calibration. However, the calibration check standard associated with the 10 x LOQ group exceeded 20% difference. The matrix blank response was less than one half the low level calibration response for all data sets.

TABLE 2. ANALYSIS OF 2,4-D IN TERMS OF PERCENT RECOVERY

2A. GC/ECD

	Fortification Level		
Replicate #	2.0 µg/L	6.0 µg/L	60.0 µg/L
1	97.9	107.5	96.9
2	93.2	109.3	97.4
3	100.7	111.1	93.0
4	105.8	78.9	82.4
5	104.6	118.3	113.1
6	131.4	78.0	98.1
7	150.0	125.8	97.9
Mean Percent Recovery	111.9	104.1	97.0
Standard Deviation	20.8	18.6	9.0
RSD	18.6	17.9	9.3

2B. IMMUNOASSAY

	Fortification Level		
Replicate #	2.0 µg/L	6.0 µg/L	60.0 µg/L
1	134.0	86.5	96.6
2	83.0	135.0	139.9
3	96.5	101.5	132.9
4	83.5	72.7	127.0
5	159.5	109.8	122.6
6	120.5	64.7	127.1
7	98.5	72.0	123.8
Mean Percent Recovery	110.8	91.7	124.3
Standard Deviation	28.5	25.2	13.6
RSD (%)	25.7	27.5	10.9

Method 507 for atrazine, alachlor, and metolachlor - Method 507 gave mean recovery and RSD values meeting project DQOs (70 - 120% recovery and RSD < 20%) at all fortification levels. The calibration data for all target analytes were linear and all calibration check standards gave less than 20% difference from initial calibration. The reagent and matrix blanks did not exhibit response exceeding one half the low level calibration standard response within the retention time window of any of the target analytes.

Using Method 507, the mean recovery for atrazine in samples fortified at 0.13 µg/L (EDL) was 94.2% with an RSD of 11.2%. The mean recovery for atrazine at 0.39 µg/L (LOQ) was 117.7% with an RSD of 3.9% and the mean recovery for atrazine at 3.9 µg/L (10 x LOQ) was 114.6% with an RSD of 6.9%..

Using Method 507, the mean recovery for alachlor in samples fortified at 0.38

µg/L (EDL) was 101.2% with an RSD of 16.9%. The mean recovery for alachlor at 1.10 µg/L (LOQ) was 107.8% with an RSD of 3.5% and the mean recovery for alachlor at 11.0 µg/L was 89.2% with an RSD of 6.7%.

Using Method 507, the mean recovery for metolachlor in samples fortified at 0.75 µg/L (EDL) was 89.3% with an RSD of 5.9%. The mean recovery for metolachlor at 2.20 µg/L (LOQ) was 103% with an RSD of 3.3% and the mean recovery for metolachlor at 22.0 µg/L was 88.0% with an RSD of 7.0%.

Atrazine immunoassay test kits - The atrazine immunoassay test kit gave high recoveries (> 120%) for atrazine using immunoassay. Furthermore, the matrix blanks gave a positive response for atrazine at levels equivalent to the low level calibration standard (0.05 µg/mL). Analysis of the matrix blank using Method 507 did not show the presence of atrazine but the atrazine detection limit by this method is specified at 0.13 µg/L and so, may not be capable of detecting atrazine at 0.05 µg/L.

A major problem was identified in testing the atrazine immunoassay kit. These kits produced false positives and poor accuracy. The manufacturer (Millipore) believes that the problem is the result of a bad lot calibration standard or if the amount of atrazine in the standard is not appropriate to the capacity of the antibody reagents. Millipore has subsequently changed the source for their standards, but those new kits were not retested.

TABLE 3. ANALYSIS OF ATRAZINE IN TERMS OF PERCENT RECOVERY

3A. GC/NPD

Replicate #	Fortification Level 0.13 µg/L	0.39 µg/L	3.9 µg/L
1	87.1	116.9	121.8
2	85.4	112.8	123.5
3	88.8	126.2	101.4
4	83.2	116.3	113.0
5	102.2	114.4	113.5
6	110.5	116.0	114.4
7	102.3	121.2	113.0
Mean Percent Recovery	94.2	117.7	114.6
Standard Deviation	10.6	4.6	7.9
RSD (%)	11.2	3.9	6.9

3B. IMMUNOASSAY

Replicate #	Fortification Level 0.13 µg/L	0.39 µg/L	3.9 µg/L
1	161.5	220.5	125.6
2	238.5	210.3	159.0
3	230.8	189.7	135.9
4	184.6	189.7	139.7
5	192.3	187.2	147.4
6	176.9	200.2	152.6
7	169.2	187.2	146.2
Mean Percent Recovery	193.4	197.8	143.8
Standard Deviation	29.9	13.1	11.1
RSD (%)	15.5	6.6	7.7

Alachlor immunoassay test kits The test kit gave alachlor recovery and RSD values meeting project DQOs for all fortification levels. A linear response was obtained for the calibration standards over the range 0.1 µg/L to 5 µg/L (r = .9999). The calibration check standards exhibited less than 13% difference from the initial calibration. Matrix blanks did not exceed one half the response of the low level calibration standard (0.1 µg/L).

The mean recovery for alachlor in sample fortified at 0.38 µg/L was 89.9% with an RSD of 14.3%. The mean recovery for alachlor at 1.10 µg/L was 96.4 % with an RSD of 19.6% and the mean recovery for alachlor at 11.0 µg/L was 113.2% with an RSD of 9.1%. Data for the analysis of alachlor are presented in Table 4.

TABLE 4. ANALYSIS OF ALACHLOR IN TERMS OF PERCENT RECOVERY

4A. GC/NPD

Replicate #	Fortification Level 0.38 µg/L	1.10 µg/L	11.0 µg/L
1	96.4	114.5	94.4
2	100.3	104.2	95.6
3	97.1	109.5	78.9
4	74.4	105.7	88.3
5	123.7	105.7	88.1
6	115.2	107.2	90.2
7	96.4	117.1	87.8
Mean Percent Recovery	101.2	107.8	89.2
Standard Deviation	17.1	3.8	6.0
RSD (%)	16.9	3.5	6.7

4B. IMMUNOASSAY

Replicate #	Fortification Level 0.38 µg/L	1.10 µg/L	11.0 µg/L
1	71.1	96.4	122.7
2	81.6	111.8	103.6
3	78.9	130.0	103.2
4	105.3	80.0	121.4
5	92.1	83.6	120.5
6	100.0	78.2	120.9
7	100.0	94.5	100.0
Mean Percent Recovery	89.8	96.4	113.2
Standard Deviation	12.8	18.9	10.3
RSD (%)	14.3	19.6	9.1

Metolachlor immunoassay test kits - The test kit gave acceptable metolachlor recovery and RSD values for samples fortified at 0.75 µg/L (EDL) and at 22 µg/L (10 x LOQ). High recoveries were obtained for samples fortified at 2.20 µg/L (LOQ) although the precision was acceptable. The matrix blank associated with samples fortified at the LOQ also gave a high result, exceeding one half the response of the low level calibration standard. Subtraction of this value, 0.17 µg/L, from the measured concentrations would result in recoveries meeting project DQOs. The matrix blanks associated with the other two sample sets did not exceed one half the low level calibration standard.

The mean recovery for metolachlor in samples fortified at 0.75 µg/L was 81.1% with an RSD of 12.6%. The mean recovery for metolachlor at 2.20 µg/L was 126.2% with an RSD of 2.3% and the mean recovery for metolachlor at 22.0 µg/L

was 78.8% with an RSD of 19.5%. Data for the analysis of metolachlor are presented in Table 5.

The calibration standards associated with samples fortified at the EDL and LOQ gave a linear response (r = 0.9998) with all associated calibration check standards showing less than 16% difference from initial calibration. The calibration standards associated with samples fortified at 10 x LOQ gave a non-linear response with none of the individual standards responding within the test kit specified expectation values. The calibration check standard associated with this group of samples exceeded 20% difference from the initial calibration.

TABLE 5. ANALYSIS OF METOLACHLOR IN TERMS OF PERCENT RECOVERY

5A. GC/NPD

	Fortification Level		
Replicate #	0.75 µg/L	2.20 µg/L	22.0 µg/L
1	92.7	106.4	93.8
2	81.2	101.3	94.5
3	84.4	107.6	77.2
4	93.2	102.4	87.7
5	90.3	99.2	87.3
6	93.9	100.6	87.7
7	83.6	107.5	85.8
Mean Percent Recovery	89.3	102.9	88.0
Standard Deviation	5.2	3.4	6.2
RSD (%)	5.9	3.3	7.0

5B. IMMUNOASSAY

	Fortification Level		
Replicate #	0.75 µg/L	2.20 µg/L	22.0 µg/L
1	69.3	124.1	93.6
2	74.7	129.1	103.6
3	77.3	124.5	65.6
4	72.0	123.2	63.6
5	88.0	124.1	67.3
6	93.3	130.0	74.5
7	93.3	128.6	83.6
Mean Percent Recovery	81.1	126.2	78.8
Standard Deviation	10.2	2.9	15.4
RSD (%)	12.6	2.3	19.5

DISCUSSION

With the exception of the atrazine immunoassay kit, only minor differences were observed between results obtained using immunoassay analyses and using Method 507 or 515.1. Those results are compared using the 95% confidence intervals calculated for each set of replicate analyses obtained by replicate chromatographic and immunochemical analyses. These confidence intervals were calculated using the program InStat™ and are based on a Poisson distribution of the data rather than the Student t test. These data are presented in Table 6.

Comparison of the 2,4-D results obtained using GC/ECD and immunoassay reveal that the measured concentrations correspond to the fortification levels in the samples. However, the 2,4-D kit gave a somewhat positive bias (< 20%) at the highest fortification level (60 µg/L). The immunoassay method gave higher RSDs than Method 515.1 (8151). All 2,4-D analyses were less precise that analyses for atrazine, alachlor and metolachlor.

The chromatographic results for atrazine correspond to the fortification levels in the samples; however, the immunoassay results were consistently higher than the fortification levels. Analysis of blanks produced a positive result corresponding to the low-point fortification level. Consultation with Millipore indicates that there may have been problems with the calibration reagent supplied with the kit. These results indicate that the claimed lower quantitation level for the atrazine kit is greater than the low-point calibration level (>0.13 µg/L).

TABLE 6. CONFIDENCE INTERVALS FOR THE ANALYTES

	Fortification Level		
Analyte/technique	2.0 µg/L	6.0 µg/L	60.0 µg/L
2,4-D GC	1.9-2.6	5.2-7.3	53-63
2,4-D Immunoassay	1.7-2.8	4.1-6.9	67-82
	0.13 µg/L	0.39 µg/L	3.9 µg/L
Atrazine GC	0.11-0.13	0.44-0.47	4.2-4.7
Atrazine Immunoassay	0.22-0.29	0.73-0.83	5.2-6.2
	0.38 µg/L	1.10 µg/L	11.0 µg/L
Alachlor GC	0.33-0.43	1.1-1.3	9.3-10.4
Alachlor Immunoassay	0.30-0.39	0.87-1.25	11.4-13.5
	0.75 µg/L	2.20 µg/L	22.0 µg/L
Metalochlor GC	0.63-0.70	2.2-2.4	18.1-20.4
Metalochlor Immunoassay	0.54-0.68	2.7-2.8	14.3-20.5

Figure 2 provides a graphical representation which summarizes the minor differences observed between chromatographic and immunochemical results in this study. Values obtained using the immunoassay kits are plotted on the X axes; values obtained using chromatographic analyses are plotted on the Y axes. Values obtained for the 4 analytes using both methods are presented on one page to facilitate comparison of these data.

The graph for 2,4-D results illustrates that both chromatographic and immunochemical methods are less precise for this analyte than for the other three analytes. The precision of Method 515.1 is similar to the immunoassay method for the analysis of 2,4-D. There appears to be a significant positive bias for the analysis of 2.4-D using immunoassay at the 60 µg/L fortification level.

The graph for atrazine results illustrates that both chromatographic and immunochemical methods have similar precision. While values obtained using immunoassay are somewhat higher than chromatographic analyses, any comparison of method bias is suspect because of calibration difficulties observed using the immunoassay method for atrazine.

The graph for alachlor results illustrates that both chromatographic and immunochemical methods have similar accuracy and precision. The concentration of alachlor measured using Method 507 was slightly less than the 11.0 µg/L fortification level; the concentration of alachlor measured using immunoassay was slightly more than the 11.0 µg/L fortification level.

The graph for metolachlor results illustrates that both chromatographic and immunochemical methods have similar accuracy. Method 507 appears more precise than the immunoassay method. The metolachlor immunoassay kit had limited testing outside of the factory, it was released as a product by Millipore during this study.

CONCLUSIONS

Immunoassay is a useful technique for environmental monitoring and should become one of the tools used for making environmental decisions. However, immunoassay requires different analytical and data reduction skills from chromatographic analysis. The only way to develop these new skills is through training or by conducting immunoassays. Unfortunately, it seems that our industry places barriers to adopting measurement techniques simply because they are new.

Let us hope that immunoassay does not follow the example of the capillary GC analysis of organochlorine pesticides. It took a decade to get that technique approved for regulatory applications. Now, almost no one uses packed columns for those analyses.

ACKNOWLEDGEMENTS

The authors acknowledge the helpful discussions of Barabara Young of Millipore Corp. and Brian Skoczendki of Immunosystems in conducting this study.

FIGURE 1

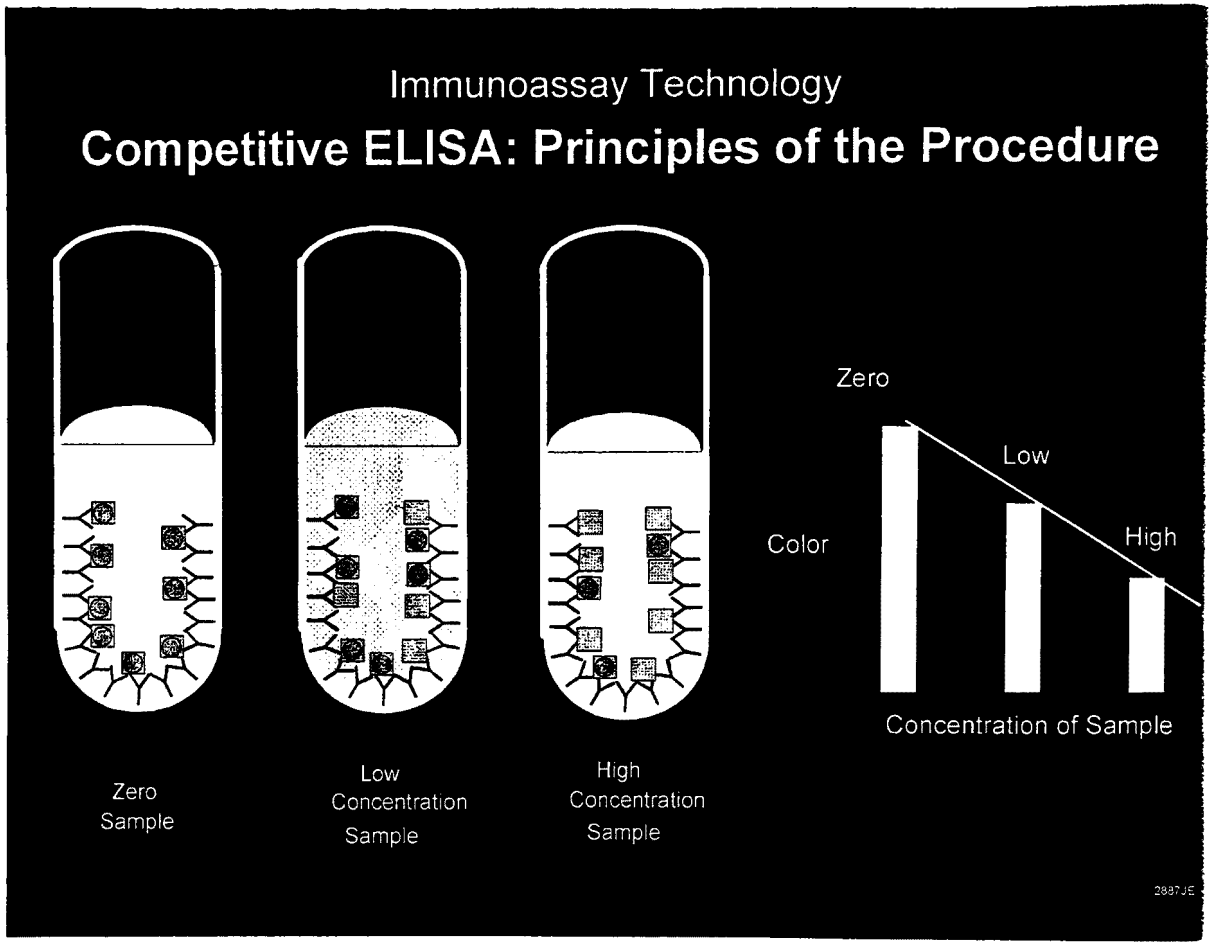
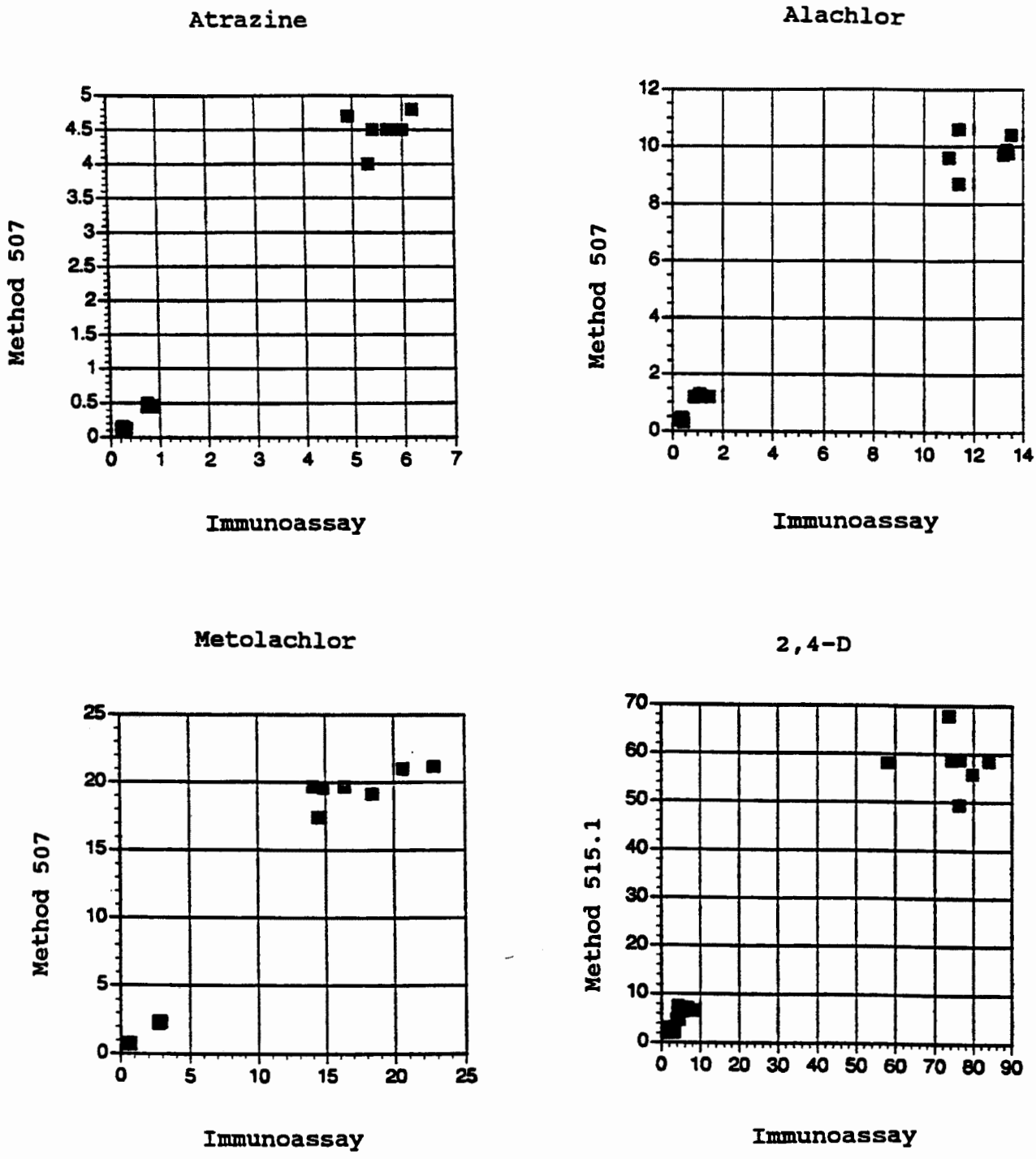

Immunoassay Technology
Competitive ELISA: Principles of the Procedure
Zero
Low
High
Color
Concentration of Sample
Zero Sample
Low Concentration Sample
High Concentration Sample
2887JE

FIGURE 2 - RECOVERY USING METHODS 507/515.1 vs. IMMUNOASSAY



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AUTOMATED LIQUID-LIQUID EXTRACTION OF SEMIVOLATILE ANALYTES

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ABSTRACT

Organic extractions have traditionally been very labor intensive and tend to be time consuming -- especially when care is given to recovery and precision of quality control spikes. Bath temperatures, emulsions, and rate of concentration can directly affect control recoveries by traditional methods. The Region 6 Houston Lab has been actively evaluating various equipment and methodology for performing Organic extractions in order to reduce turn-around time while maintaining a high level of quality control. Our current shift has been away from traditional separatory funnel / K-D, sonication, and continuous extraction devices, to the improved techniques of the Corning Accelerated One-Step™ and automated Soxhlet (Soxtherm™). As part of our ongoing investigation of new and improved extraction techniques, we are evaluating an automated liquid-liquid extraction device produced by Laboratory Automation, Inc. (ABC Instruments), called the ExCell™. We have compared this new device with various other extraction techniques, with emphasis on comparison to the Accelerated One-Step[1] since this is now becoming our main water matrix extraction technique.

This new technique (electrically assisted extraction -- the ExCell) more closely mimics separatory funnel extractions (equilibrium based) than the continuous extraction device in physical interaction. It uses an innovative electric field to provide the water / solvent mixing action as the water sample passes up through aliquots of solvent. Because of the replacement of mechanical mixing with electrically actuated dispersion, emulsions were not encountered with this technique and are much less likely than in separatory funnel extractions. This technique is highly automated up to the point of concentration. For the purposes of this test, the Labconco RapidVap N_2™ was used to concentrate all samples from the ExCell, traditional continuous extractor, and separatory funnel extractions. The main goal of our lab was to evaluate the productivity enhancements that this device could provide to our lab, and attempt to measure how equivalent this technique is to other

[1] One-Step is a trademark of the Corning corporation. ExCell and Soxtherm are trademarks of Laboratory Automation, Inc., a subsidiary of OI Analytical. RapidVap is a trademark of Labconco. TurboVap is a trademark of Zymark Corp. No indorsement is indicated or implied by the U.S. EPA for any of these companies or products. Opinions expressed are expressly of the authors only.

techniques we are currently employing. Equivalency was measured by spiking various matrices with 54-64 semi-volatile target compounds, extracting the samples, and comparing the results of the ExCell with results from other extraction techniques. Precision and accuracy data are presented. The extractions were all carried out at a single acid pH (< 2). Analysis of the extracts were performed by method 8270. For each matrix evaluated, seven replicates at low level (10ug/L) were extracted (for MDL determination) and three replicates were extracted at a high level (500ug/L). The matrices evaluated were TCLP buffer #1 (pH 4.93, ±0.05), DI water, ground water, and waste water. Not all extraction techniques could be compared in all matrices at this time. Results and principles of extractor operation are discussed.

INTRODUCTION

The Houston Lab has been very interested in the wide range of evolutionary developments in the organic extraction field. The reason for this interest is two fold. First, our agency (the EPA) is under an Executive order to reduce the amount of hazardous waste generated by the end of 1999 by half. This has motivated us to look hard at new methods that reduce solvent consumption or allow solvent collection for recycling. The second reason is that there have been many new developments in organic extractions that have improved productivity, decreased labor, and reduced turnaround times in the lab. In the past, our extraction lab has been a bottleneck in the over-all productivity of our organic analysis. This can certainly cause time problems later, especially if the analysis shows possible problems with the original extraction that can only be solved or confirmed by a re-extraction. Through some implementations of new techniques and equipment, our turnaround times have improved significantly from 3-6 days (sometimes longer) to 1-3 days. With the main goal of enhancing these productivity improvements in our lab even further, we contacted ABC instruments about conducting a study on their new ExCell liquid/liquid extraction device to see if it would meet our needs.

The extraction techniques we currently have evaluated, or have experience with, include traditional separatory funnel (SF), traditional continuous extractor (CE), Corning One-Step (OS), Corning Accelerated One-Step (AOS), solid phase extractions (SPE), and the ExCell (EX) for water matrices. For solid matrices, we have evaluated or used sonication, soxhlet, automated soxhlet (Soxtherm™), and organic microwave. In addition to extraction techniques, we have evaluated medium to large (20-500ml) concentration techniques / equipment for the extractions that require a separate concentration step (this would include all the above listed except for OS, AOS, and Soxtherm). These concentration techniques include traditional K-D / water bath, Zymark TurboVap™, Zymark TurboVap 500™, and the Labconco RapidVap N_2™. The methods we currently use for the bulk of our water extractions consists of AOS (semi-volatiles), separatory

funnel (Pesticides/PCBs), and sonication (soil semi-volatiles (ABNs) & Pest/PCBs). We are currently using the RapidVap N_2 for concentrating the extracts (not required for AOS). We are moving to reduce or eliminate the use of separatory funnel extractions as we add AOS hardware, or possibly move to other extraction techniques. A large percentage of our samples are from the Superfund program and we have standardized the bulk of our analysis on the CLP methodologies. This allows us to use a single acid (pH < 2) extraction with a continuous extractor for the majority of our semi-volatile analysis. For these reasons, we have elected to compare the ExCell mainly with the AOS at a single acid pH (< 2).

PRINCIPLES OF OPERATION

For most organic extractions, intimate mixing between aqueous and organic phases is necessary to reach extraction equilibrium and assure good analyte recoveries. How this mixing is physically accomplished can vary and is one means of innovation in the extraction field. Traditional techniques for liquid/liquid extraction accomplish this by mechanical (SF) or kinetic energy (CE) means. The following will provide a brief description of the extraction techniques employed in this comparison.

Separatory Funnel (SF): This is an equilibrium technique in which the aqueous sample is first taken to a pH of < 2. An aliquot of methylene chloride (MeCl) is added and the two phases are mixed by physical shaking of the separatory funnel to the point of equilibrium of analytes between the phases. When the phases separate, the solvent is removed by draining. This process is repeated two more times. All of the solvent aliquots are combined, dried, and concentrated. Traditional concentration of solvent is performed by K-D / water bath and nitrogen blow-down apparatus.

Continuous Extractor (CE): This is an extraction that is not required to reach full equilibrium with the solvent aliquot because the system is being constantly refreshed with new solvent. The sample is taken to a pH of < 2 and added to the CE device. The CE device consists of a boiling solvent reservoir on one

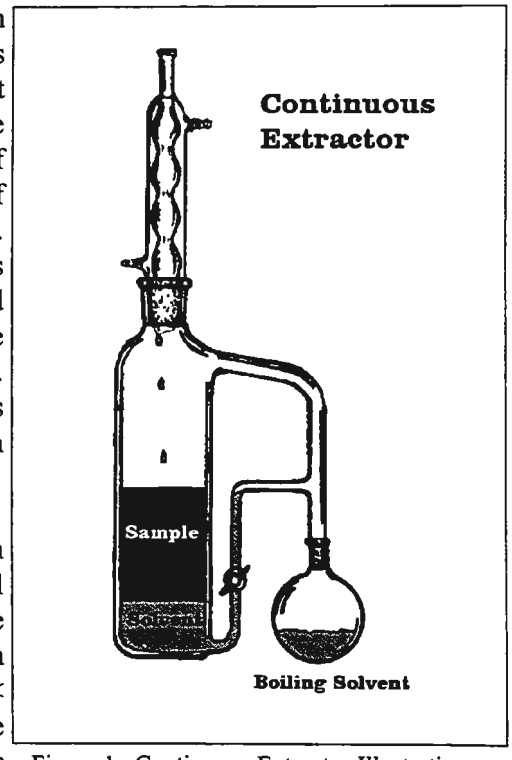

Figure 1: Continuous Extractor Illustration

side, and a sample reservoir on the other with a condenser on top (see figure 1). The boiling solvent vapor transverses to the condenser over the sample, condenses, and then drips into the aqueous sample. The solvent extracts analytes as it passes through the sample and collects in the bottom of the sample vessel. After the solvent reaches a certain level, it siphons back into the boiling vessel to concentrate the analytes and then recycles through the process again, this time as clean distilled solvent vapor. This process continues for 18 to 24 hours, continually providing fresh aliquots (drops) of solvent to extract the sample. The only agitation provided by this method is the drop of solvent falling through the aqueous sample. The aliquots (drops of solvent) are much smaller than the SF, but much more numerous and in contact with the sample over a much longer period of time. At the end of the 18-24 hours, the solvent is collected, dried, and concentrated. Traditional concentration of solvent is performed by K-D / water bath and nitrogen blow-down apparatus.

Accelerated One-Step (AOS): This technique is almost identical to CE with some notable differences. One difference is the addition of a semipermeable hydrophobic membrane on the sample side of the apparatus that the water column sits on (see figure 2). The hydrophobic membrane allows solvent to pass freely through, but does not allow the water to pass through. This membrane holds the water on top, and when the stopcock assembly is open, it allows the solvent to pass directly into the boiling chamber by gravity (no siphon effect required -- thus allowing a faster flow of solvent through the system). The hydrophobic membrane also dries the solvent in the process -- thus eliminating a sodium sulfate drying step required before concentration. Another difference from traditional CE is in the design of the solvent boiling chamber. In the traditional CE this chamber is a boiling flask, in the OS and AOS it more closely resembles a K-D with a three-ball snyder column in shape and function. The bottom of the AOS solvent boiling apparatus contains a water jacketed concentrator tube (thimble) for hot water to provide the heat to boil the solvent. When the solvent return valve (stopcock assembly) from the sample chamber is closed (after extraction is complete), the

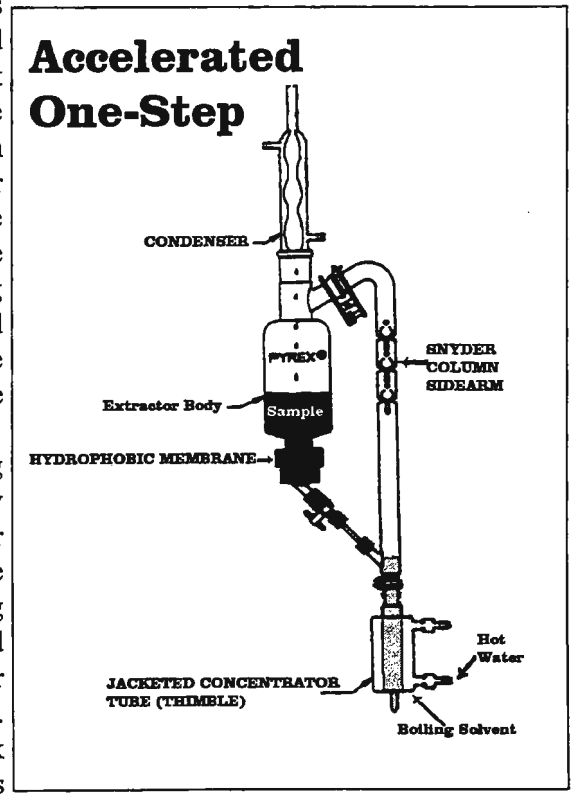

Figure 2: Accelerated One-Step Illustration

concentration of the solvent begins in the jacketed thimble (the solvent boils off and does not return to the thimble, but collects on the sample side). The bottom of the thimble contains a small projection under the hot water jacket of about 0.5 - 1.0 ml that is not heated by the water and thus protects against the extract going to dryness. These modifications to the continuous extractor allow for shorter extraction times (5-6 hrs. verses 18-24 hrs.), uses less solvent (100 ml verses 500 ml), dries, and concentrates the extract all in one device with little operator intervention. It also collects the used solvent for disposal or recycling. The down side to this device is the initial setup time (not very significantly different from CE), glass breakage, hot water distribution, and providing sufficient cooling to prevent solvent and volatile analytes from going out the top of the condensers.

Electrically Assisted Extraction (ExCell): This device seems to work somewhat similarly to both SF and CE, but more closely follows SF in principle. With this device, the aqueous sample is drawn-up through a standing aliquot of solvent in a stream (similar to an upside down CE). This stream is bombarded by an electrical field that provides the mixing action (similar to SF) between the two phases. This method also uses limited fixed aliquots of solvent (also similar to SF).

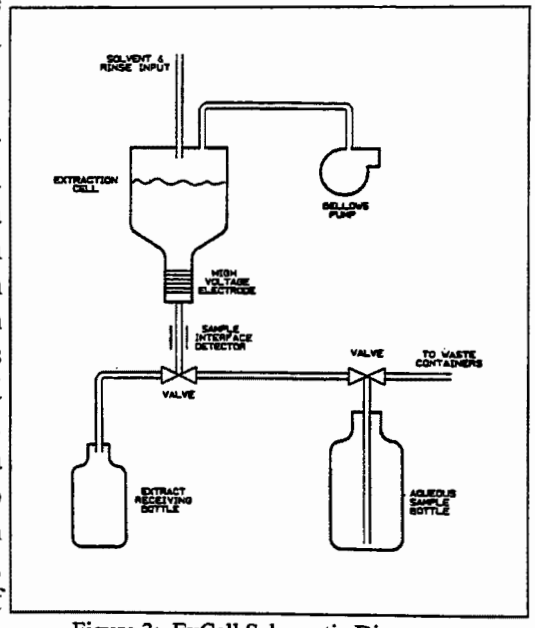

Figure 3: ExCell Schematic Diagram

Workers at Oak Ridge National Laboratory discovered that droplets of a conductive fluid (water) can be dispersed within a non-conductive fluid (MeCl) by application of an electric field[2]. This principle is used in the ExCell automated liquid/liquid extraction system to intimately mix droplets of aqueous sample with solvent as they are pumped through an aliquot of the extraction solvent. The dispersed droplets encounter a field of a different strength and this causes them to recombine as a bulk phase (water) which floats over the extraction aliquot (MeCl), thus greatly reducing the chance of emulsions. The original work used dual internal electrodes; however, the commercially available extraction system combines both in a single, external electrode wrapped around a PTFE funnel, reducing opportunities for corrosion or contamination[3]. The entire

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[2] U.S. Patent No. 4,767,515. Scott, T.C. and Wham R.M. "Surface Area Generation on Droplet Size Control in Solvent Extraction Systems Using High Intensity Electric Fields", Aug. 30 '88.

[3] U.S. Patent No. 5,384,023.

sample is pumped through the extraction solvent aliquot at a rate of approximately 32 ml/min.

If desired, the sample can be made to automatically repeat passage through the extraction aliquot for increased extraction yield. Following the last passage of the aqueous sample through the extraction solvent, the aliquot is automatically separated, collected, dried (if desired) and the extraction can be repeated with fresh aliquots of solvent. Most of the automated extraction work described in this manuscript was performed using three extracts (three fresh solvent aliquots) with the sample making one passage through the extract. Each ExCell extraction instrument will batch extract up to six samples.

RapidVap N_2 Concentration Technique: This technique is much faster than K-D / Nitrogen blow-down and has a design that allows some relief of watching for dryness that the K-D does not have. This device uses a nitrogen stream with physical swirling and heating of the container to evaporate your extract solvent. The bottom of the glass solvent container comes to a low volume point that is not in the heated zone and thus does not go to dryness as rapidly. This device will safely evaporate a 250 ml MeCl extract to 1.5 ml in two hours (by the settings used in our lab).

EXPERIMENTAL PROCEDURE

Sample Preparation & Collection: All samples were measured at 1 liter and spiked with 1 ml of either a high level or low level working mixed standard solution in MeCl to give a concentration of either 500ug/L or 10ug/L for 54 target analytes. A separate working surrogate solution (in MeCl) was used in which 1 ml was spiked to give a concentration of 50 or 100 ug/L (depending on analyte). Stock standards were purchased from Supelco. Some analytes (5 compounds) were not in our initial cocktail and were added later as a separate solution (1 ml) to subsequent sample sets (low level groundwater and waste water only). All samples were spiked with surrogates and target analytes before pH adjustment and subsequent extraction. TCLP buffer #1 was made according to method 1311 of the SW-846[4] with glacial acetic acid and sodium hydroxide to a pH of 4.93 ($\pm$0.05). The waste water was collected in 4 liter glass amber containers at a waste treatment facility in Houston, Texas. The ground water was collected in 4 liter glass amber containers in McBaines, Missouri. The waste water and ground water where kept in the dark and refrigerated at 2-6°C until spiking and subsequent extraction.

Extraction: All of the following extractions were performed at a single pH < 2 (using 6N H_2SO_4 to acidify).

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[4] EPA Test Methods for Evaluating Solid Waste

Separatory Funnel (SF): The technique we employed is from method 3510B of the SW-846. Our extractions were performed with three 60 ml MeCl aliquots at a single pH of less than 2. The extract was dried by a sodium sulfate drying column. Mechanical shakers were employed to perform this extraction.

Continuous Extraction (CE): We followed method 3520B of the SW-846. Approximately 500 ml of MeCl was used as the solvent. The extract was dried by a sodium sulfate drying column.

Accelerated One-Step (AOS): We followed a modification of method 3520B in which the solvent (MeCl) amount was reduced from 500 ml to 100 ml. The extraction time was also reduced from 18-24 hrs. to 5-6 hrs.

Electrically Assisted Extraction (ExCell): All extractions were performed with 3-80ml extracts of 1 pass each. This is similar to what is used in separatory funnel extractions in which you have 3-60ml separate MeCl aliquot extractions of the same sample. The first 80 ml aliquot is added to the ExCell sample container by the technician, and the sample is shaken before being placed into the ExCell instrument. The subsequent solvent metering, solvent addition, timing, rinsing, solvent collection, and sample collection is all automated by the instrument. The finished extracts and used sample go into a separate collection (or disposal) containers at the end of the extraction process, ready for concentrating or a second pH adjustment.

Concentration: Concentrations were performed by the RapidVap N_2 rather than by Kuderna-Danish (K-D) / water bath for all extractions other than the AOS which has a self-contained concentration apparatus similar to K-D. The block temperature on the RapidVap was set to 35°C and the vortex speed set to 45%. Nitrogen gas stream was manually adjusted to an arbitrary flow (just to dimple the surface of the solvent). Additional nitrogen blow-down was required for all methods to adjust the final extraction volume down to 1 ml. This was accomplished using the Organomation Meyer N-EVAP[5].

Analysis: Analysis was performed by GC/MS using method 8270 of the SW-846. Quantitation was performed with a single 50ng/ul standard shot daily and compared with a five-point curve. The instrument used was an HP-5890/5971 with a 30M 0.25mm ID HP-5MS GC column with a 0.25μ film thickness. An HP-7673 autosampler was attached in which we used a 1μl autosampler injection for all samples. This instrument was being used on a continuous basis to analyze a variety of dirty samples during the time of this study and may have been affected by residual effects of such analysis.

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5 The Meyer N-EVAP is a trademark of Organomation Associates Inc.

RESULTS and DISCUSSION

Productivity Comparison: All methods were evaluated for productivity features. This can be a very biased type of analysis since opinions are by nature very operator dependent. Overall, the main technician involved in these extractions preferred the operation of the ExCell over all other methods. This was due to more than mere time considerations (see table 1), but was also due to mechanical operation of hardware and potential safety hazards.

The ExCell is very user friendly and is the most mechanically automated. It is processor controlled and several variables can be programmed (rinse times, number of extracts, number of passes for each extract, etc.). The only glassware required is the sample bottle, receiving bottle, and drying funnel. This reduces the chance of injury due to glassware breakage. The solvents are pumped into the instrument externally, thus eliminating repetitive solvent pouring except for the first addition which we performed manually. Loading and unloading the sample is very easy, but care should be made on positioning of the sample straw. Extract drying may be accomplished on-line with a sodium sulfate drying funnel, or performed separately later.

Table 1:

ESTIMATED TIMES FOR SAMPLE PREPARATION
(in minutes; for six samples)

Function	ExCell		AOS		SF		CE	
	Tech Time	Total Time	Tech Time	Total Time	Tech Time	Total Time	Tech Time	Total Time
Equipment Prep (wash, etc)	35	35	60	60	60	60	60	60
Time of Extraction	0	210	0	360	0	45	0	1,080
Cooling Step	0	0	0	0	0	0	0	60
Drying Step (+ prep)	20	20	0	0	15	15	45	45
Breakdown / Washing	20	20	60	60	35	35	35	35
Concentration Step*	30	180	1	10	30	180	30	240
Nitrogen Blow-down Step**	30	120	30	120	30	120	30	120
Total Time	135	585	151	610	170	455	200	1,640
Amount of Solvent Used	240		100		250		500	

* The RapidVap N_2 was used for all methods that required separate concentration.
** Same nitrogen blow-down method was used for all extraction methods.

The Accelerated One-Step is the second choice for ease of use and speed by the operator. The main productivity feature of this device is that once it is setup and

running, there is very little operator intervention with the extraction and concentration process. After the 5-6 hour extraction time is complete, the operator merely turns the stopcock to concentrate the sample down to about 1.5 ml. The design is such that it is not very likely for the extract to evaporate to dryness, therefore samples are rarely lost for this reason (this problem was also reduced on all other methods by using the RapidVap N_2 rather than K-D for concentration purposes). The problem for the operator is the initial setup and potential injury from glassware breakage. This device is probably more prone to glass breakage than the others due to it's somewhat complex design. Setup is a bit involved, but not difficult once accustom to it.

The Separatory Funnel is probably the most familiar technique used for extractions. The main advantage it holds is in the shorter total amount of time it takes to extract a set of samples (up to 10 + QC?). The AOS may edge this one out at higher sample numbers though. The big disadvantage is the labor-intensive hands-on time required and potential glass breakage / injury.

The Continuous Extractor by far consumes the most time, labor, and solvent compared with the other techniques. It is similar to the AOS in setup and operation, but the separate cool-down, drying, and concentration steps puts it at a disadvantage in operator and total time involved.

Equivalency Comparison: Table 2 shows the accuracy and precision data for low level (10ug/L) DI water spikes for all four sample extraction methods discussed. Table 3 shows data provided by ABC Instruments in which DI water was extracted by the ExCell instrument at different pH. Tables 4 & 5 show the accuracy, precision and MDL[6] data for low level ground water and waste water spikes respectively (ExCell and AOS only). Table 6 shows the recovery data for the high level spike (400-500 ug/L) for all currently available matrices. The main interest for our lab were the CLP target compounds (not all of which were included in this list). Salient aspects of the recoveries afforded using each extraction technique are discussed below.

Separatory Funnel Extraction provided lower recoveries than the continuous extractions for more water soluble analytes, such as phenol and 4-nitrophenol. This is expected since the extraction is not an exhaustive one. Previous workers have noted similar differences between separatory funnel and continuous extractions[7]. Further investigation of our data led to the theory that the separatory funnel extractions may have not been made at a sufficiently acidic pH and the suspected data effected was removed from table 2. Historical data exists for comparison and this part of the experiment will be repeated.

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6 40 Code of Federal Regulations, part 136, appendix B.

7 Valkenburg, C.A., Munslow, W.D., Butler, L.C.; *J. AOAC* 1989, 72(4), 602-608.

Continuous Extractor provided higher recoveries of the more water soluble analytes noted above, but lower recoveries of more volatile analytes (e.g. dichlorobenzenes, hexachloroethane, 1,2,4-trichlorobenzene, or hexachlorocyclopentadiene). This result is expected for an extraction that takes place over a long period of time with reflux in an apparatus that is prone to vapor losses. Again, previous workers have noted similar differences between separatory funnel and continuous extractions[5].

Accelerated One-Step extraction provided higher recoveries of the more water soluble analytes noted above (similar to CE). The tendency to lose volatile analytes was not as great for this technique than for CE. This is probably a consequence of shorter extraction times needed for the AOS technique relative to CE. Losses of volatile analytes were more pronounced at the lower spiking level than the high level in DI water. The difference was less pronounced when the TCLP buffer matrix was extracted. Certain amines were much more readily recovered at the higher spiking level than at lower spiking levels (ex. 4-chloroaniline, 2-naphthylamine, and 4-aminobiphenyl). For these compounds, which are difficult to recover from samples at low pH, AOS provided somewhat higher recoveries than did CE.

Electrically Assisted Extraction (ExCell) provided lower recoveries than the continuous extractions for more water soluble analytes such as phenol and 4-nitrophenol. This is not unexpected since electrically assisted extraction, like separatory funnel extraction, is not exhaustive. Somewhat higher recoveries were obtained from ExCell extraction than from SF extraction for the more water soluble analytes. The ExCell data seems to more closely follow the SF data (with the exception of 4-Aminobiphenyl, once the compounds were removed that were suspect), which is to be expected since they are both an equilibrium process.

Like CE and AOS, ExCell extraction resulted in lower recoveries for some of the more volatile analytes. The increase in recoveries of those analytes in going from low to high spiking levels was less pronounced for ExCell, suggesting that the losses occur by a different mechanism. No heat is applied during ExCell extraction; however, there are periods during which some air is pumped through the extraction aliquots, and losses may be occurring at those times.

ExCell also share the AOS tendency for higher recoveries of amines at the higher spiking level; however, ExCell recoveries for those compounds were generally lower than those from AOS and in some cases these analytes were not recovered at all using the ExCell (aniline). This may also prove true for separatory funnel extractions for those compounds at a strongly acidic pH. Table three shows results of work performed at the manufacturer's laboratory in Columbia Missouri

at various pH that indicated better recovery for the amines (and other compounds) mentioned. There were also a few other analytes for which recoveries showed a strong dependence on spiking level only for the ExCell technique (e.g. terphenyl, di-n-octyl phthalate, and 7,12-dimethylbenz[a]anthracene).

CONCLUSIONS

Although recoveries were often lower using ExCell extraction, the technique can reduce the cost and complexity of sample preparation while increasing worker safety. Therefore instrument method optimization will be attempted to bring recoveries closer to those obtained using other extraction techniques. Most of the compounds that did not perform well by the ExCell were not CLP target compounds. For those that were, this is a concern that will be investigated further in an effort to optimize the method. It is believed that future investigation will show this method to be closer to the separatory funnel technique in performance. Ruggedness of this method needs to be investigated with a wider variety of real sample matrices. This instrument could be a real benefit to the overall productivity of the lab and will be investigated further.

Table 3 (provided by ABC Instruments):

COMPARATIVE AMINE RECOVERY AT DIFFERENT PH CONDITIONS FOR THE EXCELL*

#	Compound	acid then base	pH 4	base then acid	table 2 ExCell
4	Aniline	2	4	50	0
16	N-Nitrosomorpholine	53	30	54	68
17	N-Nitrosodi-n-propylamine	49	36	49	84
27	4-Chloroaniline	21	28	54	0
29	N-Nitrosodi-n-butylamine	50	38	50	83
36	2-Nitroaniline	62	55	61	69
41	Dibenzofuran	50	42	48	67
42	2-Naphthylamine	39	65	73	0
48	Diphenylamine	66	68	69	34
49	1,3,5-Trinitrobenzene	88	87	90	49
52	4-Aminobiphenyl	63	87	96	0
56	Methapyrilene	0	0	83	0
58	p-Dimethylaminoazobenzene	91	92	95	66
60	2-Acetylaminofluorene	111	106	115	81
64	7,12-Dimethylbenz[a]anthracene	66	54	79	16

*80ug/L in DI water, GC/FID

SUMMATION OF LOW LEVEL DI WATER RECOVERIES
(Table #2)

			ACCURACY DATA				PRECISION DATA			
Semivolatile Compounds	Spike Amount	Analyte Number	Avg % Rec EXCELL	Avg % Rec AOS	Avg % Rec SF	Avg % Rec CE	%RSD EXCELL	%RSD AOS	%RSD SF	%RSD CE
N-Nitrosodimethylamine	0.000	1*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
N-Nitrosomethylethylamine	10.000	2*	72.9%	77.0%	52.8%	82.1%	7.1	12.6	9.1	7.3
N-Nitrosodiethylamine	0.000	3*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
Aniline	10.000	4*	0.0%	27.3%	Suspect	14.8%	ERR	15.7	Suspect	25.5
Phenol	10.000	5	48.7%	74.1%	34.6%	83.1%	4.2	12.4	10.5	7.1
bis(2-Chloroethyl)ether	10.000	6	72.4%	86.6%	78.9%	83.7%	6.3	12.1	7.0	4.7
2-Chlorophenol	10.000	7	62.3%	68.4%	76.6%	71.7%	5.2	13.4	7.9	7.9
1,3-Dichlorobenzene	10.000	8	49.5%	61.9%	69.7%	53.6%	15.0	12.1	7.4	14.8
1,4-Dichlorobenzene	10.000	9	51.4%	63.5%	73.1%	55.9%	14.1	11.9	8.3	13.4
Benzyl Alcohol	0.000	10*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
1,2-Dichlorobenzene	10.000	11	52.9%	64.9%	73.5%	57.9%	11.8	12.3	7.7	12.3
2-Methylphenol	10.000	12	59.6%	68.0%	61.5%	72.2%	8.7	11.7	9.0	6.4
bis(2-Chloroisopropyl)ether	10.000	13	72.7%	85.0%	76.5%	81.0%	4.2	11.3	7.4	6.7
N-Nitrosopyrrolidine	0.000	14*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
o-Toluidine	0.000	15*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
N-Nitrosomorpholine	10.000	16*	67.6%	76.2%	48.3%	80.7%	3.4	8.3	13.2	6.1
N-Nitrosodi-n-propylamine	10.000	17	83.5%	82.1%	74.5%	85.7%	3.0	9.5	10.4	5.0
4-Methylphenol	10.000	18	59.2%	68.9%	61.0%	74.2%	6.3	11.2	8.3	5.4
Hexachloroethane	10.000	19	39.7%	51.6%	61.5%	45.4%	19.3	14.1	8.1	21.1
N-Nitrosopiperidine	0.000	20*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
2-Nitrophenol	10.000	21	63.2%	64.2%	74.5%	71.1%	5.6	10.9	8.4	6.8
2,4-Dimethylphenol	10.000	22	50.1%	61.2%	62.9%	57.2%	42.1	9.9	19.3	10.5
bis(2-Chloroethoxy)methane	10.000	23	75.6%	81.2%	79.2%	82.6%	3.4	8.9	7.8	5.8
2,4-Dichlorophenol	10.000	24	62.4%	64.0%	70.5%	72.3%	3.8	10.8	6.8	5.8
1,2,4-Trichlorobenzene	10.000	25	52.8%	65.4%	72.7%	57.2%	11.3	10.0	6.5	12.7
2,6-Dichlorophenol	10.000	26*	63.3%	69.7%	75.1%	73.1%	4.4	9.1	7.7	4.6
4-Chloroaniline	10.000	27	0.0%	62.5%	Suspect	56.9%	ERR	7.1	Suspect	9.6
Hexachlorobutadiene	10.000	28	32.4%	56.3%	52.8%	47.4%	26.3	12.7	7.6	24.1
N-Nitrosodibutylamine	10.000	29*	82.9%	81.5%	72.9%	86.2%	4.3	5.6	11.9	4.7
4-Chloro-3-methylphenol	10.000	30	71.4%	74.5%	79.4%	80.9%	2.9	5.2	7.0	3.8
1,2,4,5-Tetrachlorobenzene	10.000	31*	56.7%	72.1%	73.3%	62.0%	10.6	6.7	7.2	12.8
Hexachlorocyclopentadiene	10.000	32	26.1%	25.6%	43.1%	30.1%	35.4	18.8	11.8	26.9
2,4,6-Trichlorophenol	10.000	33	66.1%	68.3%	76.6%	76.8%	2.6	5.9	6.9	3.3
2,4,5-Trichlorophenol	10.000	34	67.6%	75.0%	77.2%	78.9%	2.1	4.6	8.1	3.8
2-Chloronaphthalene	10.000	35	60.4%	73.3%	81.7%	68.5%	7.0	5.9	7.1	7.4
2-Nitroaniline	10.000	36	69.1%	68.5%	73.4%	76.0%	3.4	2.7	12.8	3.8
Dimethyl phthalate	10.000	37	80.4%	88.1%	91.4%	86.3%	5.8	1.7	7.5	3.6
3-Nitroaniline	0.000	38	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
2,4-Dinitrophenol	10.000	39	18.3%	9.4%	0.0%	24.3%	21.3	49.9	ERR	20.4
4-Nitrophenol	10.000	40	29.7%	53.0%	12.9%	67.9%	6.3	4.1	41.4	5.2
Dibenzofuran	10.000	41	66.8%	72.3%	79.1%	72.3%	5.4	3.6	10.9	4.6
2-Naphthylamine	10.000	42*	0.0%	54.2%	Suspect	35.2%	ERR	5.4	Suspect	21.6
2,3,4,6-Tetrachlorophenol	10.000	43*	69.1%	72.6%	56.1%	82.9%	4.1	1.6	22.3	4.5
Diethyl phthalate	10.000	44	90.0%	95.6%	94.8%	92.5%	16.4	3.1	7.1	3.9
4-Chlorophenyl-phenylether	10.000	45	70.2%	83.8%	82.2%	77.5%	6.3	1.9	7.7	6.8
4-Nitroaniline	0.000	46	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
4,6-Dinitro-2-methylphenol	10.000	47	48.7%	44.0%	44.9%	58.3%	6.0	9.8	15.4	6.9
Diphenylamine	10.000	48*	34.2%	42.6%	48.7%	41.8%	15.3	2.3	10.0	3.7
1,3,5-Trinitrobenzene	10.000	49*	49.3%	44.1%	64.1%	57.6%	4.3	8.2	13.2	5.5
4-Bromophenylphenyl ether	10.000	50	78.8%	90.6%	80.3%	82.3%	4.2	2.0	7.6	6.8
Hexachlorobenzene	10.000	51	52.8%	85.9%	75.9%	75.5%	7.4	1.7	7.0	4.7
4-Aminobiphenyl	10.000	52*	0.0%	44.2%	59.6%	26.6%	ERR	4.5	7.1	17.6
Pentachlorophenol	10.000	53	57.9%	42.5%	4.7%	60.4%	6.2	9.9	125.6	8.3
2-sec-Butyl-4,6-dinitrophenol	10.000	54*	55.6%	48.9%	44.7%	62.5%	5.7	9.3	22.9	4.9
Di-n-butylphthalate	10.000	55	85.9%	89.1%	101.2%	91.2%	8.5	1.7	3.8	17.3
Methapyrilene HCL	10.000	56*	0.0%	18.5%	Suspect	7.1%	ERR	26.2	Suspect	63.0
Benzidine	0.000	57*	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
p-Dimethylaminoazobenzene	10.000	58*	66.5%	76.9%	88.6%	69.4%	10.9	2.9	9.1	10.7
Butylbenzylphthalate	10.000	59	90.1%	96.5%	100.2%	89.8%	8.2	2.8	3.7	4.8
2-Acetylaminofluorene	10.000	60*	81.3%	75.3%	92.0%	92.1%	3.0	4.0	9.7	2.4
3,3'-Dichlorobenzidine	0.000	61	Not Added	Not Added	Not Added	Not Added	Not Added	Not Adde	Not Adde	Not Adde
bis(2-ethylhexyl)phthalate	10.000	62	56.3%	100.2%	91.4%	93.5%	13.8	8.9	26.0	5.8
Di-n-octyl phthalate	10.000	63	44.1%	90.5%	84.6%	76.5%	12.3	3.5	29.3	5.9
7,12-Dimethylbenz(a)anthracen	10.000	64*	16.5%	67.7%	68.6%	63.9%	24.7	16.0	41.2	11.1

* Compounds are not on CLP target list.

SUMMATION OF LOW LEVEL GROUND WATER RECOVERIES
(Table #4)

			ACCURACY DATA		PRECISION DATA		MDL DATA	
Semivolatile Compounds	Spike Amount	Analyte Number (Arbitrary)	Avg % Rec EXCELL	Avg % Rec AOS	%RSD EXCELL	%RSD AOS	Calc MDL EXCELL	Calc MDL AOS
N-Nitrosodimethylamine	10.000	1*	37.6%	73.3%	6.9	5.8	0.81	1.33
N-Nitrosomethylethylamine	10.000	2*	72.5%	82.4%	15.5	4.8	3.54	1.23
N-Nitrosodiethylamine	10.000	3*	78.0%	78.8%	6.9	6.2	1.68	1.54
Aniline	10.000	4*	0.0%	49.7%	ERR	8.6	0.00	1.35
Phenol	10.000	5	50.8%	95.5%	5.6	4.7	0.90	1.41
bis(2-Chloroethyl)ether	10.000	6	85.8%	97.4%	6.7	4.2	1.81	1.30
2-Chlorophenol	10.000	7	77.2%	87.9%	5.1	3.8	1.24	1.05
1,3-Dichlorobenzene	10.000	8	77.2%	90.2%	7.6	5.9	1.84	1.66
1,4-Dichlorobenzene	10.000	9	77.9%	91.1%	6.9	5.1	1.70	1.46
Benzyl Alcohol	10.000	10*	0.0%	0.0%	ERR	ERR	0.00	0.00
1,2-Dichlorobenzene	10.000	11	81.5%	91.8%	7.0	5.4	1.80	1.57
2-Methylphenol	10.000	12	67.2%	83.5%	5.9	5.5	1.24	1.43
bis(2-Chloroisopropyl)ether	10.000	13	87.7%	95.7%	8.3	5.0	2.30	1.52
N-Nitrosopyrrolidine	10.000	14*	69.6%	93.8%	5.9	7.2	1.29	2.13
o-Toluidine	10.000	15*	1.4%	58.1%	26.5	8.2	0.11	1.50
N-Nitrosomorpholine	10.000	16*	66.9%	76.1%	5.2	6.2	1.09	1.48
N-Nitrosodi-n-propylamine	10.000	17	89.7%	91.4%	4.9	6.8	1.37	1.94
4-Methylphenol	10.000	18	68.1%	91.4%	5.6	5.2	1.20	1.48
Hexachloroethane	10.000	19	66.6%	83.6%	9.8	7.1	2.01	1.87
N-Nitrosopiperidine	10.000	20*	87.0%	88.4%	4.0	6.3	1.09	1.75
2-Nitrophenol	10.000	21	81.0%	90.0%	6.8	5.1	1.73	1.46
2,4-Dimethylphenol	10.000	22	71.4%	79.5%	3.8	5.3	0.85	1.31
bis(2-Chloroethoxy)methane	10.000	23	87.1%	95.8%	6.7	6.0	1.83	1.82
2,4-Dichlorophenol	10.000	24	74.1%	79.0%	6.4	5.8	1.48	1.44
1,2,4-Trichlorobenzene	10.000	25	79.3%	90.5%	6.8	5.3	1.70	1.50
2,6-Dichlorophenol	10.000	26*	80.8%	85.8%	6.2	5.1	1.58	1.37
4-Chloroaniline	10.000	27	7.4%	86.1%	22.6	6.8	0.52	1.83
Hexachlorobutadiene	10.000	28	53.5%	75.8%	10.9	8.0	1.83	1.91
N-Nitrosodibutylamine	10.000	29*	89.9%	85.8%	5.2	6.0	1.46	1.63
4-Chloro-3-methylphenol	10.000	30	85.5%	91.2%	4.8	4.4	1.30	1.27
1,2,4,5-Tetrachlorobenzene	10.000	31*	78.6%	85.3%	7.2	6.8	1.78	1.83
Hexachlorocyclopentadiene	10.000	32	54.8%	53.3%	10.1	11.6	1.75	1.94
2,4,6-Trichlorophenol	10.000	33	88.1%	87.4%	5.6	4.7	1.55	1.28
2,4,5-Trichlorophenol	10.000	34	90.8%	91.6%	5.2	3.9	1.49	1.12
2-Chloronaphthalene	10.000	35	91.3%	97.5%	7.0	5.5	1.99	1.70
2-Nitroaniline	10.000	36	87.0%	92.4%	5.3	3.5	1.46	1.02
Dimethyl phthalate	10.000	37	99.4%	101.6%	2.4	2.4	0.75	0.78
3-Nitroaniline	10.000	38	48.6%	92.6%	18.2	3.0	2.79	0.88
2,4-Dinitrophenol	10.000	39	13.4%	5.6%	28.7	108.0	1.21	1.89
4-Nitrophenol	10.000	40	37.3%	74.1%	4.6	8.7	0.54	2.02
Dibenzofuran	10.000	41	94.0%	99.3%	5.3	3.8	1.55	1.19
2-Naphthylamine	10.000	42*	1.8%	63.7%	35.1	3.5	0.20	0.70
2,3,4,6-Tetrachlorophenol	10.000	43*	81.2%	76.1%	3.1	4.4	0.79	1.06
Diethyl phthalate	10.000	44	103.5%	112.2%	1.6	2.3	0.52	0.83
4-Chlorophenyl-phenylether	10.000	45	89.6%	96.3%	4.9	3.2	1.37	0.97
4-Nitroaniline	10.000	46	70.1%	99.7%	4.0	3.4	0.89	1.08
4,6-Dinitro-2-methylphenol	10.000	47	61.1%	67.0%	4.9	5.9	0.95	1.23
Diphenylamine	10.000	48*	96.6%	94.3%	3.2	2.6	0.98	0.77
1,3,5-Trinitrobenzene	10.000	49*	72.9%	80.8%	3.3	4.0	0.75	1.02
4-Bromophenylphenyl ether	10.000	50	85.8%	92.8%	5.0	3.4	1.35	0.99
Hexachlorobenzene	10.000	51	80.0%	90.3%	3.5	3.6	0.87	1.03
4-Aminobiphenyl	10.000	52*	3.0%	78.4%	86.4	3.2	0.81	0.79
Pentachlorophenol	10.000	53	23.3%	7.3%	25.4	61.3	1.85	1.41
2-sec-Butyl-4,6-dinitrophenol	10.000	54*	61.1%	58.4%	6.1	7.5	1.17	1.38
Di-n-butylphthalate	10.000	55	105.1%	117.5%	2.2	1.8	0.74	0.66
Methapyrilene HCL	10.000	56*	0.0%	46.7%	170.8	10.8	0.02	1.59
Benzidine	10.000	57*	0.0%	0.0%	ERR	ERR	0.00	0.00
p-Dimethylaminoazobenzene	10.000	58*	89.2%	91.5%	9.3	2.3	2.60	0.65
Butylbenzylphthalate	10.000	59	100.7%	113.6%	4.0	3.3	1.26	1.16
2-Acetylaminofluorene	10.000	60*	108.5%	100.7%	2.7	3.6	0.91	1.14
3,3'-Dichlorobenzidine	10.000	61	28.7%	31.1%	35.6	13.5	3.21	1.32
bis(2-ethylhexyl)phthalate	10.000	62	120.0%	117.7%	3.9	3.5	1.49	1.30
Di-n-octyl phthalate	10.000	63	83.5%	117.2%	6.4	4.0	1.69	1.46
7,12-Dimethylbenz(a)anthracen	10.000	64*	54.7%	71.3%	11.3	3.9	1.95	0.88

* Compounds are not on CLP target list.

SUMMATION OF LOW LEVEL WASTE WATER RECOVERIES
(Table #5)

Semivolatile Compounds	Spike Amount	Analyte Number (Arbitrary)	ACCURACY DATA Avg % Rec EXCELL	Avg % Rec AOS	PRECISION DATA %RSD EXCELL	%RSD AOS	MDL DATA Calc MDL EXCELL	Calc MDL AOS
N-Nitrosodimethylamine	10.000	1*	28.9%	63.7%	3.5	6.7	0.32	1.34
N-Nitrosomethylethylamine	10.000	2*	52.3%	72.6%	4.9	4.7	0.80	1.07
N-Nitrosodiethylamine	10.000	3*	65.9%	74.1%	4.0	3.6	0.84	0.85
Aniline	10.000	4*	0.0%	19.4%	ERR	35.5	0.00	2.17
Phenol	10.000	5	40.4%	87.5%	4.5	2.6	0.57	0.71
bis(2-Chloroethyl)ether	10.000	6	74.2%	81.3%	5.0	6.4	1.17	1.64
2-Chlorophenol	10.000	7	64.6%	78.4%	4.3	4.3	0.88	1.06
1,3-Dichlorobenzene	10.000	8	65.6%	73.8%	8.6	5.3	1.77	1.23
1,4-Dichlorobenzene	10.000	9	68.1%	78.7%	8.7	5.7	1.86	1.40
Benzyl Alcohol	10.000	10*	0.0%	0.0%	ERR	ERR	0.00	0.00
1,2-Dichlorobenzene	10.000	11	69.9%	77.3%	7.7	5.5	1.68	1.33
2-Methylphenol	10.000	12	50.2%	80.1%	4.6	3.3	0.73	0.82
bis(2-Chloroisopropyl)ether	10.000	13	76.7%	80.2%	4.4	4.8	1.06	1.21
N-Nitrosopyrrolidine	10.000	14*	59.1%	80.6%	4.3	2.7	0.81	0.68
o-Toluidine	10.000	15*	0.0%	45.1%	ERR	7.8	0.00	1.10
N-Nitrosomorpholine	10.000	16*	57.2%	70.1%	4.3	1.8	0.78	0.40
N-Nitrosodi-n-propylamine	10.000	17	80.5%	72.7%	4.7	3.1	1.20	0.70
4-Methylphenol	10.000	18	52.3%	84.5%	4.3	3.6	0.70	0.94
Hexachloroethane	10.000	19	53.4%	72.3%	11.7	6.1	1.96	1.38
N-Nitrosopiperidine	10.000	20*	77.0%	75.9%	5.1	2.5	1.23	0.60
2-Nitrophenol	10.000	21	72.8%	83.8%	5.1	3.8	1.16	1.01
2,4-Dimethylphenol	10.000	22	25.7%	72.7%	23.4	3.3	1.89	0.74
bis(2-Chloroethoxy)methane	10.000	23	78.2%	82.8%	4.7	5.1	1.15	1.33
2,4-Dichlorophenol	10.000	24	65.9%	80.3%	4.5	3.2	0.93	0.81
1,2,4-Trichlorobenzene	10.000	25	69.2%	77.6%	8.0	5.3	1.74	1.29
2,6-Dichlorophenol	10.000	26*	70.2%	85.8%	5.0	4.3	1.11	1.16
4-Chloroaniline	10.000	27	0.7%	38.9%	17.1	5.5	0.04	0.67
Hexachlorobutadiene	10.000	28	44.4%	71.1%	12.8	6.7	1.79	1.50
N-Nitrosodibutylamine	10.000	29*	81.4%	69.4%	5.2	2.8	1.34	0.62
4-Chloro-3-methylphenol	10.000	30	72.9%	91.6%	5.2	1.6	1.19	0.47
1,2,4,5-Tetrachlorobenzene	10.000	31*	68.7%	77.7%	7.7	5.5	1.65	1.36
Hexachlorocyclopentadiene	10.000	32	42.2%	56.7%	13.1	8.0	1.74	1.43
2,4,6-Trichlorophenol	10.000	33	79.9%	94.5%	5.0	2.0	1.26	0.59
2,4,5-Trichlorophenol	10.000	34	80.8%	92.6%	4.1	1.6	1.03	0.46
2-Chloronaphthalene	10.000	35	80.6%	86.8%	6.3	3.4	1.59	0.92
2-Nitroaniline	10.000	36	70.7%	68.3%	5.9	4.8	1.31	1.02
Dimethyl phthalate	10.000	37	90.0%	88.7%	3.4	2.0	0.96	0.55
3-Nitroaniline	10.000	38	12.9%	45.4%	33.2	7.4	1.35	1.05
2,4-Dinitrophenol	10.000	39	28.4%	37.8%	18.6	30.9	1.66	3.67
4-Nitrophenol	10.000	40	39.9%	84.7%	7.6	8.3	0.96	2.20
Dibenzofuran	10.000	41	84.7%	79.0%	4.5	2.2	1.20	0.56
2-Naphthylamine	10.000	42*	1.1%	1.5%	30.8	7.2	0.11	0.03
2,3,4,6-Tetrachlorophenol	10.000	43*	79.7%	77.9%	3.5	4.8	0.87	1.17
Diethyl phthalate	10.000	44	94.6%	93.8%	3.0	1.3	0.88	0.37
4-Chlorophenyl-phenylether	10.000	45	81.9%	85.8%	4.4	2.2	1.13	0.58
4-Nitroaniline	10.000	46	32.0%	63.7%	8.0	8.0	0.80	1.60
4,6-Dinitro-2-methylphenol	10.000	47	66.6%	71.4%	8.0	7.0	1.68	1.58
Diphenylamine	10.000	48*	63.9%	78.8%	10.1	2.8	2.03	0.69
1,3,5-Trinitrobenzene	10.000	49*	73.4%	64.3%	4.6	1.9	1.06	0.39
4-Bromophenylphenyl ether	10.000	50	77.5%	79.9%	4.5	3.4	1.10	0.86
Hexachlorobenzene	10.000	51	72.2%	77.9%	4.9	2.0	1.12	0.49
4-Aminobiphenyl	10.000	52*	1.1%	0.7%	24.0	110.1	0.08	0.26
Pentachlorophenol	10.000	53	63.6%	33.5%	14.3	76.0	2.86	8.00
2-sec-Butyl-4,6-dinitrophenol	10.000	54*	70.1%	72.7%	4.7	8.1	1.04	1.84
Di-n-butylphthalate	10.000	55	94.9%	96.7%	6.4	1.8	1.92	0.54
Methapyriene HCL	10.000	56*	0.0%	45.7%	264.6	4.1	0.04	0.59
Benzidine	10.000	57*	0.0%	0.0%	ERR	ERR	0.00	0.00
p-Dimethylaminoazobenzene	10.000	58*	73.4%	74.0%	7.7	1.6	1.77	0.38
Butylbenzylphthalate	10.000	59	90.6%	97.0%	3.4	1.9	0.97	0.59
2-Acetylaminofluorene	10.000	60*	99.8%	85.3%	3.4	2.6	1.07	0.70
3,3'-Dichlorobenzidine	10.000	61	0.0%	0.0%	ERR	ERR	0.00	0.00
bis(2-ethylhexyl)phthalate	10.000	62	128.9%	119.4%	11.3	13.7	4.58	5.13
Di-n-octyl phthalate	10.000	63	78.2%	96.8%	5.9	2.7	1.44	0.82
7,12-Dimethylbenz(a)anthracen	10.000	64*	9.4%	66.8%	37.2	5.8	1.09	1.21

* Compounds are not on CLP target list.

SUMMATION OF ALL HIGH LEVEL RECOVERIES
(Table #6)

Semivolatile Compounds	Spike Conc (ug/L)	Analyte Number (Arbitrary)	ACCURACY DATA DI Water Avg % Rec EXCELL	ACCURACY DATA DI Water Avg % Rec AOS	ACCURACY DATA Ground Water Avg % Rec EXCELL	ACCURACY DATA Ground Water Avg % Rec AOS	ACCURACY DATA Waste Water Avg % Rec EXCELL	ACCURACY DATA Waste Water Avg % Rec AOS	ACCURACY DATA TCLP Buffer #1 Avg % Rec EXCELL	ACCURACY DATA TCLP Buffer #1 Avg % Rec AOS
N-Nitrosodimethylamine	500	1*	Not Added	Not Added	40.1%	87.7%	Not Added	Not Added	Not Added	Not Added
N-Nitrosomethylethylamine	500	2*	67.3%	82.0%	70.4%	98.5%	66.9%	86.2%	57.1%	87.6%
N-Nitrosodiethylamine	500	3*	Not Added	Not Added	83.6%	101.5%	Not Added	Not Added	Not Added	Not Added
Aniline	500	4*	0.0%	24.0%	0.8%	33.3%	0.8%	29.0%	0.3%	16.7%
Phenol	500	5	43.5%	77.8%	45.3%	89.9%	41.5%	88.4%	40.3%	84.2%
bis(2-Chloroethyl)ether	500	6	78.6%	86.3%	81.3%	92.3%	85.4%	73.3%	72.0%	86.3%
2-Chlorophenol	500	7	70.2%	83.3%	79.7%	95.7%	80.3%	97.4%	65.3%	91.6%
1,3-Dichlorobenzene	500	8	63.4%	84.2%	70.9%	87.5%	73.6%	87.2%	62.1%	93.3%
1,4-Dichlorobenzene	500	9	64.7%	84.0%	73.2%	88.6%	74.4%	87.3%	64.1%	93.0%
Benzyl Alcohol	500	10*	Not Added	Not Added	0.0%	0.0%	Not Added	Not Added	Not Added	Not Added
1,2-Dichlorobenzene	500	11	67.2%	85.7%	75.6%	90.1%	78.3%	89.9%	65.6%	94.5%
2-Methylphenol	500	12	67.3%	84.6%	68.8%	88.2%	65.2%	82.6%	62.6%	89.7%
bis(2-Chloroisopropyl)ether	500	13	74.6%	77.7%	85.1%	93.3%	88.5%	93.3%	63.2%	80.1%
N-Nitrosopyrrolidine	500	14*	Not Added	Not Added	73.6%	94.5%	Not Added	Not Added	Not Added	Not Added
o-Toluidine	500	15*	Not Added	Not Added	3.4%	64.5%	Not Added	Not Added	Not Added	Not Added
N-Nitrosomorpholine	500	16*	62.0%	80.6%	75.5%	98.0%	63.3%	103.9%	54.5%	83.3%
N-Nitrosodi-n-propylamine	500	17	70.6%	75.1%	90.4%	95.9%	92.2%	96.8%	63.4%	77.2%
4-Methylphenol	500	18	67.3%	88.8%	67.9%	92.1%	63.5%	90.0%	61.1%	92.3%
Hexachloroethane	500	19	46.9%	79.9%	64.1%	82.8%	66.8%	85.7%	47.6%	86.2%
N-Nitrosopiperidine	500	20*	Not Added	Not Added	91.0%	105.9%	Not Added	Not Added	Not Added	Not Added
2-Nitrophenol	500	21	82.1%	92.4%	84.3%	93.7%	89.3%	96.0%	75.8%	98.1%
2,4-Dimethylphenol	500	22	75.6%	88.4%	73.5%	81.6%	71.4%	88.8%	68.3%	91.8% -
bis(2-Chloroethoxy)methane	500	23	81.1%	89.6%	85.7%	95.0%	89.7%	95.2%	73.7%	93.8%
2,4-Dichlorophenol	500	24	81.1%	94.8%	78.9%	91.1%	81.6%	92.2%	73.9%	98.3%
1,2,4-Trichlorobenzene	500	25	65.8%	93.6%	77.4%	92.4%	82.0%	94.8%	63.6%	100.6%
2,6-Dichlorophenol	500	26*	79.7%	91.1%	82.0%	92.6%	85.8%	93.2%	73.0%	95.9%
4-Chloroaniline	500	27	12.0%	84.2%	14.6%	92.6%	13.5%	88.1%	7.4%	78.8%
Hexachlorobutadiene	500	28	48.1%	85.3%	67.7%	93.0%	70.0%	95.0%	47.0%	91.2%
N-Nitrosodibutylamine	500	29*	76.1%	80.6%	89.9%	97.3%	92.8%	76.0%	66.4%	82.6%
4-Chloro-3-methylphenol	500	30	78.6%	90.2%	78.2%	91.0%	77.6%	91.4%	68.2%	90.8%
1,2,4,5-Tetrachlorobenzene	500	31*	62.8%	89.4%	81.9%	96.6%	84.6%	98.5%	58.1%	93.5%
Hexachlorocyclopentadiene	500	32	53.3%	87.2%	74.5%	89.6%	74.0%	90.9%	52.2%	94.7%
2,4,6-Trichlorophenol	500	33	80.4%	93.6%	87.1%	95.7%	89.8%	96.8%	73.8%	96.9%
2,4,5-Trichlorophenol	500	34	78.7%	89.3%	86.4%	94.7%	88.9%	96.7%	71.3%	93.6%
2-Chloronaphthalene	500	35	73.3%	95.8%	85.0%	96.3%	88.9%	97.9%	66.8%	97.6%
2-Nitroaniline	500	36	78.6%	89.4%	93.0%	100.8%	91.4%	81.2%	71.0%	91.3%
Dimethyl phthalate	500	37	82.3%	93.7%	92.4%	97.9%	95.8%	96.2%	75.1%	95.5%
3-Nitroaniline	500	38	Not Added	Not Added	68.9%	113.3%	Not Added	Not Added	Not Added	Not Added
2,4-Dinitrophenol	500	39	90.2%	115.1%	87.4%	110.7%	98.3%	106.4%	87.4%	113.3%
4-Nitrophenol	500	40	48.0%	98.3%	51.3%	97.8%	44.6%	98.0%	41.1%	95.6%
Dibenzofuran	500	41	75.0%	91.1%	94.2%	102.0%	95.5%	102.1%	64.8%	91.6%
2-Naphthylamine	500	42*	33.0%	101.5%	21.0%	108.3%	16.5%	47.2%	19.0%	105.1%
2,3,4,6-Tetrachlorophenol	500	43*	81.8%	91.8%	92.3%	100.0%	94.7%	102.3%	74.6%	96.3%
Diethyl phthalate	500	44	80.0%	89.0%	97.5%	99.5%	107.5%	96.6%	72.6%	91.0%
4-Chlorophenyl-phenylether	500	45	74.5%	92.7%	91.1%	99.9%	91.8%	99.1%	62.9%	94.4%
4-Nitroaniline	500	46	Not Added	Not Added	90.8%	102.4%	Not Added	Not Added	Not Added	Not Added
4,6-Dinitro-2-methylphenol	500	47	91.4%	102.8%	94.1%	98.8%	95.1%	97.1%	80.0%	97.6%
Diphenylamine	500	48*	44.4%	50.4%	96.9%	97.8%	97.3%	53.7%	39.5%	51.5%
1,3,5-Trinitrobenzene	500	49*	80.2%	95.6%	103.1%	104.8%	103.1%	101.0%	72.7%	94.6%
4-Bromophenylphenyl ether	500	50	71.5%	91.7%	89.1%	98.1%	89.9%	100.4%	63.4%	95.9%
Hexachlorobenzene	500	51	68.4%	90.7%	85.7%	94.6%	82.4%	96.5%	59.7%	93.9%
4-Aminobiphenyl	500	52*	56.0%	87.2%	58.5%	104.9%	46.1%	58.3%	42.3%	87.7%
Pentachlorophenol	500	53	93.2%	112.7%	77.0%	88.1%	84.0%	107.4%	83.0%	113.1%
2-sec-Butyl-4,6-dinitrophenol	500	54*	86.9%	101.8%	99.6%	102.2%	97.8%	106.5%	74.9%	97.4%
Di-n-butylphthalate	500	55	78.2%	95.3%	91.8%	95.9%	89.9%	96.6%	83.5%	95.0%
Methapyrilene HCL	500	56*	0.0%	1.9%	0.0%	7.1%	0.2%	9.2%	0.0%	2.1%
Benzidine	500	57*	Not Added	Not Added	0.0%	35.4%	Not Added	Not Added	Not Added	Not Added
p-Dimethylaminoazobenzene	500	58*	79.8%	90.8%	88.2%	96.9%	88.4%	96.0%	71.6%	90.3%
Butylbenzylphthalate	500	59	76.9%	95.6%	91.9%	95.6%	87.6%	95.4%	63.7%	95.4%
2-Acetylaminofluorene	500	60*	83.8%	102.8%	100.4%	104.0%	102.9%	105.3%	77.1%	96.9%
3,3'-Dichlorobenzidine	500	61	Not Added	Not Added	91.5%	88.0%	Not Added	Not Added	Not Added	Not Added
bis(2-ethylhexyl)phthalate	500	62	74.4%	96.8%	90.1%	95.7%	90.1%	96.0%	62.5%	96.5%
Di-n-octyl phthalate	500	63	70.6%	93.7%	88.1%	91.4%	84.0%	91.7%	59.6%	95.8%
7,12-Dimethylbenz(a)anthrace	500	64*	61.2%	83.7%	105.1%	108.9%	92.2%	105.6%	53.6%	86.7%

* Compounds are not on CLP target list.

DETERMINATION OF POLY(ETHYLENE GLYCOL)-600 FROM THE PHARMACEUTICAL MANUFACTURING INDUSTRY BY DERIVATIZATION AND LIQUID CHROMATOGRAPHY

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ABSTRACT

Section 304(h) of the Clean Water Act directs EPA to promulgate guidelines establishing test procedures (analytical methods) for analyzing pollutants. These test procedures are used for filing applications for compliance monitoring under the National Pollutant Discharge Elimination System (NPDES) found at 40 *CFR* Parts 122.41(j)(4) and 122.21(g)(7), and for the pretreatment program found at 40 *CFR* 403.7(d). Promulgation of these methods is intended to standardize analytical methods within specified industrial categories and across industries.

EPA has promulgated analytical methods for monitoring pollutant discharges at 40 *CFR* Part 136, and has promulgated methods for analytes specific to given industrial categories at 40 *CFR* Parts 400 to 480. EPA has published proposed regulations (60 FR 21654, May 2, 1995) establishing discharge limitations for the Pharmaceutical Manufacturing Industry (PMI). Wastewaters from the PMI contain a complex mixture of conventional pollutants, toxic (priority) pollutants, and non-conventional pollutants. Among the non-conventional pollutants identified from the PMI is poly(ethylene glycol)-600 (PEG-600).

PEG-600 is commonly used in the PMI as a non-ionic surfactant and thickening agent and has been identified as a constituent of PMI waste streams. In addition, PEGs have been implicated in the formation of toxic alkoxy acetic acid metabolites (Flam, 1994). PEG-600 is composed of 12 to 15 oligomers with a molecular weight centered around 600 Da. Methods for determination of PEGs found in the literature generally call for hydrohalic acid cleavage followed by gas chromatography or turbidimetric determination of the native analytes. Neither of these methods provide results that identify PEGs in specific molecular weight ranges. For this reason, we have developed a method for the quantitative determination of PEG-600, based on the work of Kinahan and Smyth (1991), using derivatization followed by high pressure liquid chromatography. Detection limits of around 300 parts-per-billion in water can be achieved with a quantitation limit of one part-per-million.

INTRODUCTION

Section 304(h) of the Clean Water Act directs EPA to promulgate guidelines establishing test procedures (analytical methods) for analyzing

pollutants. These test procedures are used for filing applications and for compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). Promulgation of these methods is intended to standardize analytical methods within specific industrial categories and across industries. EPA has promulgated analytical methods for monitoring pollutant discharges at 40 *CFR* Part 136, and has promulgated methods for analytes specific to given industrial categories at 40 *CFR* Parts 400 to 480. EPA has published regulations (60 FR 21654, May 2, 1995) establishing discharge limitations for the Pharmaceutical Manufacturing Industry (PMI). The Agency acquired data on the presence and concentration of approximately 400 analytes from the PMI during 18 sampling episodes and pilot studies conducted during a 10-year period from May of 1983 to October of 1993. The data collected during these studies and information acquired from a detailed questionnaire sent to all domestic pharmaceutical manufacturers form the basis for regulation of about sixty analytes from the PMI.

Wastewaters from the PMI contain a complex mixture of conventional pollutants, toxic (priority) pollutants, and non-conventional pollutants. Analytical methods exist for the determination of all of the conventional and priority pollutants from the PMI, but many of the non-conventional pollutants were without promulgated analytical methods. Among the non-conventional pollutants identified from the PMI without a promulgated analytical method is poly(ethylene glycol)-600 (PEG-600).

PEG-600 is commonly used in the PMI as a non-ionic surfactant and thickening agent and has been identified as a constituent of PMI waste streams. In addition, PEGs have been implicated in the formation of toxic alkoxy acetic acid metabolites (Flam, 1994). PEG-600 is composed of 12 to 15 oligomers with a molecular weight centered around 600 Da. Methods for determination of PEGs found in the literature generally call for hydrohalic acid cleavage followed by gas chromatography or turbidimetric determination of the native analytes. Neither of these methods provide results that identify PEGs in specific molecular weight ranges. For this reason, we have developed a method for the quantitative determination of PEG-600, based on the work of Kinahan and Smyth (1991), using derivatization followed by high pressure liquid chromatography.

EXPERIMENTAL

Sample Extraction and Derivatization

Place one liter of sample and one mL of surrogate standard (10 mg/mL of di(ethylene glycol)monohexyl ether in tetrahydrofuran) in a liquid-liquid extractor and extract with pesticide grade dichloromethane for 18 hours. Dry the dichloromethane solution over anhydrous sodium sulfate and evaporate off the solvent using the Kuderna-Danish procedure. Dry again over anhydrous sodium sulfate when the volume reaches 10 - 25 mL and use a gentle stream of dry nitrogen to remove most of the remaining solvent. Quantitatively transfer the residue to a V-shaped reaction vial using

anhydrous dichloromethane or anhydrous tetrahydrofuran and remove the last of the solvent with a stream of dry nitrogen.

After ensuring that the extract is free of water, add 5 mL of derivatization solution (10 mg/mL 3,5-dinitrobenzoyl chloride in tetrahydrofuran) and 2 drops of anhydrous pyridine. Seal and heat the vial and contents in a sand bath at 60°C (±5°C) for 1 hour. Cool the vial and quantitatively transfer the contents to a 125-mL separatory funnel. Add 50 mL of diethyl ether (ether) and sequentially extract with two 25-mL portions of dilute hydrochloric acid, then two 25-mL portions of water, then two 25-mL portions of sodium bicarbonate solution, and finally with two 25-mL portions of saturated sodium chloride solution. Take care not to lose any ether solution during the extraction procedure. Place a small plug of glass wool in a funnel and add approximately 10 g of anhydrous sodium sulfate. Drain the ether solution through the sodium sulfate in the funnel, then rinse the separatory funnel with two 10-mL portions of ether and drain through the anhydrous sodium sulfate in the funnel. Quantitatively transfer the ether solution to a clean Kuderna-Danish apparatus and evaporate the solvent. Perform a solvent exchange with 40% acetonitrile/water, adjust the volume to 2 mL and filter, if necessary, for analysis.

High Pressure Liquid Chromatography (HPLC)

Chromatographic conditions.

Column: Betasil C_{18}, 250 mm by 4.6 mm, 5-μm particle size (Keystone 255-701, or equivalent).

Mobile Phase: 40% acetonitrile/water to 100% acetonitrile over a period of 20 minutes.

Flow Rate: 2.0 mL/min.

UV Detector: 254 nm.

Injection Volume: 50 μL.

The retention time of the PEG-600 derivative relative to the surrogate derivative is centered about 0.63. Because PEG-600 is a mixture of poly(ethylene glycol) oligomers, the exact nature of PEG-600 samples from various manufacturers and different batches from a single manufacturer, may vary. For this reason, concentrations of PEG-600 in a specific waste stream are best determined when standards are prepared using the same batch of PEG-600 in use by the pharmaceutical manufacturer at the time of discharge of the waste stream under analysis. Where it is not possible to obtain such a sample, adequate results can be obtained by use of a PEG-600 product as a standard that is unrelated to the one in use by the pharmaceutical manufacturer, and careful definition of an "elution range" for derivatized PEG-600 in both the external standards and the samples. An "elution range" or retention time window is defined as a characteristic

period of time during which the derivatized PEG-600 elutes from the chromatographic column. This range should encompass at least 90 percent of the PEG-600 derivative in both the standard and the sample. The width of the retention time window used for quantitation should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of the retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

Calculations

Calculate each response factor (RF) as follows (mean value based on 5 points):

$$RF = \frac{concentration\ of\ standard}{area\ of\ the\ signal}$$

$$mean\ RF = \overline{RF} = \frac{\sum_{i=1}^{5} RF_i}{5}$$

Calculate the concentration of PEG-600 as follows:

$$\mu g/L = \overline{RF} \times area\ of\ signal \times concentration\ factor$$

where:

$$concentration\ factor = \frac{final\ volume\ of\ extract}{Initial\ sample\ volume}$$

CONCLUSIONS

Using this method it is possible to routinely detect PEG-600 at about 300 parts-per-billion and to quantitate at one part-per-million. The method is simple to apply and can be performed by any laboratory equipped with HPLC equipment. Caution must be exercised in the extraction and concentration steps to minimize loss of material. Extraction efficiencies are around 60 percent. While it is best to use standards derived from the feed stock used at the time of waste generation, adequate results can be achieved from standards that are unrelated to the feed stock.

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DETERMINATION OF NON-PURGEABLE, WATER-SOLUBLE ANALYTES FROM THE PHARMACEUTICAL MANUFACTURING INDUSTRY BY GC/MS AND GC/FID

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ABSTRACT

Section 304(h) of the Clean Water Act directs EPA to promulgate guidelines establishing test procedures (analytical methods) for analyzing pollutants. These test procedures are used for filing applications for compliance monitoring under the National Pollutant Discharge Elimination System (NPDES) found at 40 *CFR* Parts 122.41(j)(4) and 122.21(g)(7), and for the pretreatment program found at 40 *CFR* 403.7(d). Promulgation of these methods is intended to standardize analytical methods within specified industrial categories and across industries.

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INTRODUCTION

Section 304(h) of the Clean Water Act directs EPA to promulgate guidelines establishing test procedures (analytical methods) for analyzing pollutants. These test procedures are used for filing applications and for compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). Promulgation of these methods is intended to standardize analytical methods within specific industrial categories and across industries. EPA has promulgated analytical methods for monitoring pollutant discharges at 40 *CFR* Part 136, and has promulgated methods for analytes specific to given industrial categories at 40 *CFR* Parts 400 to 480. EPA has published regulations (60 FR 21654, May 2, 1995)

establishing discharge limitations for the Pharmaceutical Manufacturing Industry (PMI). The Agency acquired data on the presence and concentration of approximately 400 analytes from the PMI during 18 sampling episodes and pilot studies conducted during a 10-year period from May of 1983 to October of 1993. The data collected during these studies and information acquired from a detailed questionnaire sent to all domestic pharmaceutical manufacturers form the basis for regulation of about sixty analytes from the PMI.

Wastewaters from the PMI contain a complex mixture of conventional pollutants, toxic (priority) pollutants, and non-conventional pollutants. Analytical methods exist for the determination of all of the conventional and priority pollutants from the PMI, but many of the non-conventional pollutants were without promulgated analytical methods. Among the non-conventional pollutants identified from the PMI are a series of non-purgeable, water-soluble analytes that provide unique challenges to analysis by GC/MS and GC/FID. These pollutants are listed with their Chemical Abstracts Service Registry Numbers (CASRNs) in Table 1.

Table 1 - Non-Purgeable, Water-Soluble Analytes from the PMI

PMI Analyte	CASRN
Acetonitrile	75-05-8
Diethylamine	109-89-7
Dimethylamine	124-40-3
Dimethylsulfoxide	67-68-5
Ethanol	64-17-5
Ethylene glycol	107-21-1
Formamide	75-12-7
Methanol	67-56-1
Methylamine	74-89-5
Methyl cellosolve (2-methoxyethanol)	109-86-4
n-Propanol	71-23-8
Triethylamine	121-44-8

These analytes present a unique challenge to simultaneous analysis by gas chromatography because they are miscible with water and cannot be efficiently extracted from the aqueous waste streams in which they are found. In addition, they cannot be efficiently purged from water, even at

elevated temperatures, and trapped for GC analysis. One alternative for analysis is direct aqueous injection into a gas chromatograph equipped with a capillary column and either a mass spectrometric detector or a flame ionization detector. Because it was not known at the outset which might provide the most sensitivity for the simultaneous determination of these analytes, both column/detector combinations were investigated.

EXPERIMENTAL

The experimental section is divided in two subsections: GC/MS and GC/FID. Experimental conditions for each column/detector combination and column/detector specific information is found in each subsection. Method Detection Limits (MDLs) and Minimum Levels (MLs) for both approaches are provided in the results section and they are compared and contrasted in the conclusions section.

Gas Chromatography/Mass Spectrometry - Analyses were performed using a VG Trio-1 GC/MS system. The capillary column used was a Restek Rtx Amine (30 meter, 0.32mm i.d., 1.5 μm film thickness). The GC was programmed such that sufficient separation of target analytes was achieved while minimizing run times. The GC was held at 40°C for 4 minutes, ramped to 100°C at 8°C per minute, with no hold at 100°C, then rapidly heated to 220°C at 25°C per minute with a 3 minute hold at 220°C. A 30:1 pre-column split and 2 μL injections were used to achieve acceptable chromatographic peak shape. Helium carrier gas was introduced at 1.5 mL/min. The mass spectrometer was tuned using p-bromofluorobenzene at 50 nanograms. The mass spectrometer scan range was 20 to 200 atomic mass units. Table 2 provides absolute retention times, relative retention times, and quantitation masses for each analyte, their labeled analogs (where used), and the internal standard.

Some target analytes were not quantitated using isotope dilution techniques. These included the amines, ethylene glycol, and formamide. Labeled analogs of the amine free bases were not available. Ethylene glycol-d_5 and formamide-^{15}N could not be used because of their significant spectral contributions to the native analyte. In these cases, tetrahydrofuran-d_8 was used as an internal standard.

Gas Chromatography/Flame Ionization Detector - Analyses were performed using an HP 5880 GC/FID system. The capillary column used was an SPB-1 Sulfur (30 meter, 0.32mm i.d., 4.0 μm film thickness). The GC was programmed such that sufficient separation of target analytes was achieved while minimizing run times. The GC was held at 40°C for 2 minutes, ramped to 180°C at 10°C per minute. The injection port was set at 200°C and the FID at 300°C. A 30:1 pre-column split and 2 μL injections were used to achieve acceptable chromatographic peak shape. Hydrogen carrier gas was introduced at a head pressure of 10 psi. Table 3 provides absolute retention times and relative retention times for each analyte and the internal standard.

Table 2 - Retention Times and Quantitation Masses for the PMI Analytes by GC/MS

PMI Analyte	Absolute Retention Time (sec)	Relative Retention Time (sec)	Quantitation Mass (Da)
Methylamine	81	0.308	30
Methyl alcohol-d_3	85	0.323	35
Methyl alcohol	85.5	1.006	32
Dimethylamine	93	0.354	44
Ethyl alcohol-d_5	103	0.394	49
Ethyl alcohol	104	1.010	45
Acetonitrile-d_3	119	0.452	44
Acetonitrile	121	1.017	41
n-Propanol-1-d_1	170	0.464	32
n-Propanol	170.5	1.003	31
Diethylamine	188	0.717	58
Tetrahydrofuran-d_8 (internal standard)	263	1.000	80
Methyl cellosolve (2-Methoxyethanol)	290	1.103	45
Triethylamine	372	1.414	58
Ethylene glycol	398	1.513	31
Formamide	400	1.521	45
Dimethyl sulfoxide-d_6	639	2.431	66
Dimethyl sulfoxide	643	1.006	63

RESULTS

Minimum detection limits (MDLs) for each analyte were determined by the method described in 40 *CFR* Part 136, Appendix B. Minimum levels (MLs) were calculated from MDLs by multiplying by a factor of 3.18 and rounding to the nearest multiple of 1, 2, or 5 x 10^n, where n is a positive or negative integer, or zero. Table 4 provides MDLs and MLs for each native analyte and for each GC/Detector combination. Analytes have been arranged in groups with similar functionality and with the amines first, alcohols second, and miscellaneous compounds last.

Table 3 - Retention Times for PMI Analytes by GC/FID

PMI Analyte	Absolute Retention Time (sec)	Relative Retention Time (sec)
Methylamine	128	0.307
Methanol	139	0.334
Dimethylamine	165	0.396
Ethanol	188	0.452
Acetonitrile	203	0.488
n-Propanol	307	0.737
Diethylamine	341	0.819
Tetrahydrofuran (internal standard)	416	1.000
Methyl cellosolve (2-Methoxyethanol)	429	1.030
Formamide	473	1.136
Ethylene Glycol	495	1.189
Triethylamine	518	1.244
Dimethyl sulfoxide	676	1.624

CONCLUSIONS

The results provide no clear indication whether use of a GC/MS combination or a GC/FID combination is superior for all analytes. Choice of a column/detector combination will hinge on the identity of the analytes most important to the analyst, industry, permit writer, or regulator. It is apparent that amines are best analyzed by GC/FID; the MDLs for GC/FID range from about one-third to about one-fifth of those for GC/MS. MLs for the amines by GC/FID are consistently one-fourth of those for GC/MS.

MDLs for methanol by GC/MS and GC/FID are about the same, while MDLs for ethanol and n-propanol are lower by GC/MS. Due to rounding, MLs for methanol by the two methods are the same, while MLs for ethanol and n-propanol are lower when analyzed by GC/MS. Methyl cellosolve and ethylene glycol are apparently better analyzed by GC/FID because their MDLs are about one-fourth and one-half those achieved by GC/MS, respectively.

Of the remaining three compounds, acetonitrile is best analyzed by GC/MS while formamide and dimethyl sulfoxide are best analyzed by GC/FID. Results for formamide by GC/MS showed a high degree of variability. For

unknown reasons, the mass spectrometer response for formamide was both very low and inconsistent.

Table 4 - MDLs and MLs for PMI Analytes by GC/MS and GC/FID

PMI Analyte	GC/MS		GC/FID	
	MDL (mg/L)	ML (mg/L)	MDL (mg/L)	ML (mg/L)
Methylamine	83.8	200	19.2	50
Dimethylamine	68.8	200	22.8	50
Diethylamine	72.6	200	15.9	50
Triethylamine	55.4	200	20.4	50
Methanol	21.4	50	13.4	50
Ethanol	5.0	20	14.8	50
n-Propanol	9.0	20	15.8	50
Methyl cellosolve (2-Methoxyethanol)	21.5	50	5.4	20
Ethylene glycol	72.7	200	35.4	100
Acetonitrile	1.7	5	16.5	50
Formamide	407.5	1000	27.9	100
Dimethyl sulfoxide	36.8	100	5.2	20

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EVALUATION OF A ROBOTIC AUTOSAMPLER FOR THE ANALYSIS OF VOC'S

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INTRODUCTION

In the fast paced world we live in there is always an emphasis on reliable answers in a minimum amount of time. Laboratories have these same demands. The analyst is under increasing pressure to provide maximum productivity. By coupling automation and versatility laboratories can meet this goal. Automation allows a large number of samples to run virtually unattended. Versatility prevents costly down time while an instrument is moved or reconfigured.

The Precept is a vial autosampler that combines both automation and versatility. It analyzes up to 48 aqueous or solid samples unattended. The aqueous samples are typically drinking or waste water samples. The most common environmental solid samples are soil (e.g. clay, humus, and sand). The Precept accommodates up to two different sampling modules. The vials are moved to the sampling modules using a robotic arm. This allows the vials to remain in an upright position. A syringe is used to measure the sample volume. Up to two different standard solutions can be automatically added to the sample prior to purging.

There are three sampling modes available for the Precept. The modes are aqueous, solid S1, and solid S2. The aqueous module transfers the sample from a standard 40ml vial to the sampling syringe. The aliquot is then transferred to the glassware of the concentrator where the sample is purged. If automatic standard addition is used, it is transferred to the glassware with the sample.

The solid S1 module purges the sample directly in a standard 40ml vial. The dry sample is placed in a vial. A long concentric needle is inserted through the septum. Water is measured into the syringe and transferred to the vial. The standard is automatically transferred into the vial with the water. The purge gas enters the vial through holes at the base of the needle. The purged analytes are swept away from the vial and onto the trap through a hole near the top of the needle.

The solid S2 module also purges the sample directly in special 40ml vial. The vial used is threaded on both ends for septa and caps. There is also a frit inside the vial to increase purge efficiency of the solid sample. The dry solid placed on top of the frit and water is added to the vial. If automatic standard addition is used, it is transferred to the vial with the water. The analytes are purged from the vial by two short needles piercing the top and bottom septa. The bottom needle introduces purge gas up through the frit. The analytes are then swept onto the trap through the top needle.

The work in this paper focuses on the evaluation of the aqueous module of the Precept. Compounds from the USEPA Method 8260 and 524.2 were chosen for this assessment. Linearity of the system was examined utilizing two different configurations.

EXPERIMENTAL

Table 1: Parameters for the Method 8260 configuration

Tekmar Precept/3000 Parameters	
Line Temp	150°C
Valve Temp	150°C
MCS Line Temp	150°C

Sweep Needle Time	1min
Syringe Fill Volume	25ml
TransLine Sweep Time	0.5min
Syringe Rinse Volume	25ml
# of Syringe Rinses	2
Backflush Filter Time	1min
Flush Needle Time	0.5min
Sweep Lines Time	3.0min
Purge Ready Temp	30°C
Purge Temp	0°C
Sample Fill	1.5min
Purge Time	11min
Dry Purge Time	0min
Transfer Line Type	0.53mm Fused Silica
MCS Desorb Temp	50°C
Trap Type	Vocarb 3000
Desorb Preheat	245°C
Desorb Temp	250°C
Desorb Time	6min
Sample Drain	On
Glassware Rinse	On
Glassware Rinse Time	3min
Glassware Purge Time	1min
Bake Temp	260°C
Bake Time	4min
BGB	Off
MCS Bake Temp	300°C
TPC Setting	4psi
Purge Flow	40ml/min

HP 5890/Glass Jet Separator Parameters

Carrier Gas	Helium
Flow Rate	10ml/min
Detector A (Jet Separator)	150°C
Detector B (GC/MS Interface)	280°C
Makeup Flow	20ml/min
Transfer Line interfaced to the column via zero dead union	
Column	DB-624 75M 0.53mm 3µm
Temperature Program	40°C hold 1min; 20°C/min to 50°C; 7°C/min to 150°C; 20°C/min to 220°C hold 6min

HP 5970 Mass Selective Detector Parameters

Solvent Delay	2min
EM Voltage	1700
Scan Range	35-260
A/D	3

Table 2: Parameters for the Method 524.2 configuration

Tekmar Precept/3000 Parameters

Line Temp	150°C
Valve Temp	150°C

MCS Line Temp	150°C
Sweep Needle Time	1min
Syringe Fill Volume	5ml
Sample Std 1 Transfer	2.5ml
Sample Std 2 Transfer	2.5ml
TransLine Sweep Time	0.5min
Syringe Rinse Volume	25ml
# of Syringe Rinses	2
Backflush Filter Time	1min
Flush Needle Time	0.5min
Sweep Lines Time	3min
Purge Ready Temp	30°C
Purge Temp	0°C
Sample Fill	1.5min
Purge Time	11min
Dry Purge Time	0min
Transfer Line Type	0.32mm Fused Silica
Cryofocuser	On
Cryo Standby	150°C
Cryofocus Temp	-180°C
Cryo Inject Time	1.0min
Cryo Inject Temp	180°C
MCS Desorb Temp	50°C
Trap Type	Tenax/Silica Gel/Charcoal
Desorb Preheat	220°C
Desorb Time	225°C
Sample Drain	On
Glassware Rinse	On
Glassware Rinse Time	3min
Glassware Purge Time	1min
Bake Temp	230°C
Bake Time	12min
BGB	Off
MCS Bake Temp	300°C
TPC Setting	4.5psi
Purge Flow	40ml/min

HP 5890 Series II/ Plus Parameters

Carrier Gas	Helium
Column Head Pressure	15psi
Transfer Line interfaced to the column via zero dead union	
Detector A (Jet Separator)	150°C
Detector B (GC/MS Interface)	280°C
Column	DB-VRX 60m 0.25mm 1.4µm
Temperature Program	35°C hold 5min; 10°C/min to 200°C hold 5min; 20°C/min to 220°C hold 5min

HP 5970 Mass Selective Detector Parameters

Solvent Delay	2.0min
EM Voltage	1600
Scan Range	35-260amu
A/D	4

RESULTS AND DISCUSSION

The Precept was evaluated under two configurations. The first configuration utilized a wide bore column and jet separator for Method 8260 (Table 1). The linearity of the system from 1 to 100ppb was excellent.

The second configuration used Method 524.2 compounds on a narrow bore column (Table 2). a short 0.53mm precolumn was used in the Cryofocusing module to increase capacity of the column during desorb. The linearity of this configuration from 0.5 to 30ppb is shown in Table 4. Also listed are the Method Detection Limits (MDL) obtained by using seven replicates of 0.5ppb.

TABLE 3 RRF'S AND RSD'S FOR 8260 ANALYTES

Compounds	RRF	RSD (%)
1. dichlorodifluoromethane	0.4	2.8
2. chloromethane	0.2	2.4
3. vinyl chloride	0.3	2.3
4. bromomethane	0.3	5.1
5. chloroethane	0.2	8.8
6. trichlorofluoromethane	0.6	2.0
7. 1,1-dichloroethene	0.3	2.6
8. methylene chloride	0.3	24.9
9. trans-1,2-dichloroethane	0.3	2.9
10. 1,1-dichloroethane	0.6	2.7
11. cis-1,2-dichloroethane	0.3	3.2
12. 2,2-dichloropropane	0.5	3.6
13. bromochloromethane	0.1	4.2
14. chloroform	0.6	3.3
15. dibromofluoromethane	0.6	1.5
16. 1,1,1-trichlorethane	0.5	2.2
17. 1,1-dichloropropene	0.5	3.3
18. carbon tetrachloride	0.5	2.3
19. 1,2-dichloroethane	0.2	4.8
20. benzene	0.8	3.0
21. flurorobenzene	1.0	0.7
22. trichloroethene	0.4	1.8
23. 1,2-dichloropropane	0.3	3.2
24. dibromoethane	0.2	4.2
25. bromodichloromethane	0.4	2.7
26. cis-1,3-dichloropropane	0.4	10.8
27. toluene-d8	5.3	2.8
28. toluene	3.1	5.2
29. trans-1,3-dichloropropene	1.4	4.4
30. 1,1,2-trichloroethane	0.8	4.9
31. tetrachlorethene	2.9	12.9
32. 1,3-dichloroproane	1.4	9.0
33. dibromochloromethane	1.8	4.7
34. 1,2-dibromoethane	1.2	4.5
35. chlorobenzene	3.6	4.0
36. 1,1,1,2-tetrachloroethane	1.7	5.3
37. ethylbenzene	6.1	4.6
38. m,p-xylene	2.2	5.3
39. bromofluorobenzene	2.1	4.5
40. o-xylene	2.1	5.4

41. styrene	3.3	4.9
42. bromoform	1.0	4.5
43. isopropylbenzene	6.1	4.3
44. 1,1,2,2-tetrachloroethane	1.1	6.8
45. bromobenzene	1.7	4.4
46. 1,2,3-trichloropropane	0.3	17.6
47. n-propylbenzene	1.6	3.0
48. 2-chlorotoluene	1.4	3.4
49. 1,3,5-trimethylbenzene	2.4	4.9
50. 4-chlorotoluene	1.4	4.2
51. tert-butylbenzene	5.6	5.5
52. 1,2,4-trimethylbenzene	2.6	5.1
53. sec-butylbenzene	1.4	4.2
54. 1,3-dichlorobenzene	2.9	4.8
55. 4-isopropyltoluene	5.6	5.5
56. 1,4-dichlorobenzene	1.4	2.9
57. 1,2-dichlorobenzene	0.8	1.7
58. n-butylbenzene	2.6	2.5
59. 1,2-dichlorobenzene	1.1	3.1
60. 1,2-dibromo-3-chloropropane	0.1	11.2
61. 1,2,4-trichlorobenzene	0.8	3.6
62. hexachlorobutadiene	0.8	2.9
63. naphthalene	0.7	7.5
64. 1,2,3-trichlorobenzene	0.7	2.0

The internal standards used were pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5, and1,4-dichlorbenzene-d2.

TABLE 4 RRF'S, RSD'S AND MDL'S OF THE 524.2 ANALYTES

Compounds	RRF	%RSD	MDL(ppt)
1. dichlorodifluoromethane	0.056	18.75	3.7
2. chloromethane	0.070	6.98	24.9
3. vinyl chloride	0.025	4.79	5.5
4. bromomethane	0.114	6.34	9.8
5. chloroethane	0.083	4.41	8.5
6. trichlorofluoromethane	0.165	4.05	11.5
7. diethyl ether	0.142	2.89	7.1
8. methylene chloride	0.176	6.34	7.1
9. trans-1,2-dichloroethene	0.142	2.50	6.4
10. 1,1-dichloroethane	0.342	3.81	13.7
11. cis-1,2-dichloroethene	0.198	1.69	8.1
12. bromochloromethane	0.096	3.50	2.6
13. chloroform	0.352	24.04	20.5
14. 2,2-dichloropropane	0.176	4.43	18.7
15. 1,2-dichloroetane	0.268	3.88	9.6
16. 1,1,1-trichloroethane	0.222	2.55	7.9
17. 1,1-dichloropropene	0.238	1.62	15.2
18. carbon tetrachloride	0.191	3.32	8.8
19. benzene	0.686	1.00	16.0
20. dibromomethane	0.120	2.89	4.5
21. 1,2-dichloropropane	0.218	1.48	10.3
22. trichloroethene	0.194	3.81	14.3
23. bromodichloromethane	0.257	11.76	9.4

24. cis-1,3-dichloropropene	0.292	4.43	11.1
25. trans-1,3-dichloropropene	0.264	4.83	12.8
26. 1,1,2-trichloroethane	0.142	2.81	6.1
27. toluene	0.388	1.55	16.4
28. 1,3-dichloropropane	0.298	1.54	5.3
29. 1,2-dibromoethane	0.162	4.06	5.7
30. dibromochloromethane	0.174	6.45	9.1
31. tetrachloroethene	0.252	9.06	75.5
32. 1,1,1,2-tetrachloroethane	0.161	5.96	4.6
33. chlorobenzene	0.431	3.16	14.2
34. ethylbenzene	0.751	0.97	37.8
35. m,p-xylene	0.270	0.96	26.2
36. bromoform	0.112	15.20	7.6
37. styrene	0.446	3.93	27.9
38. o-xylene	0.274	1.98	12.1
39. 1,1,2,2-tetrachloroethane	0.178	4.38	28.6
40. 1,2,3-trichloropropane	0.258	6.31	14.6
41. isopropylbenzene	0.703	1.20	36.0
42. 4-bromofluorobenzene (surr)	0.393	4.29	128.4
43. bromobenzene	0.177	5.38	5.7
44. n-propylbenzene	0.866	1.37	56.1
45. 2-chlorotoluene	0.548	1.44	35.6
46. 4-chlorotoluene	0.554	1.39	43.3
47. 1,3,5-trimethylbenzene	0.571	1.34	26.7
48. tert-butylbenzene	0.123	5.10	9.7
49. 1,2,4-trimethylbenzene	0.593	1.21	31.0
50. sec-butylbenzene	0.735	1.13	43.5
51. 1,3-dichlorobenzene	0.337	4.08	14.1
52. 1,4-dichlorobenzene	0.355	3.83	30.6
53. p-isopropyltoluene	0.605	1.54	46.3
54. d4-1,2-dichlorobenzene (surr)	0.358	5.86	122.1
55. 1,2-dichlorobenzene	0.339	3.12	14.1
56. n-butylbenzene	0.599	1.28	48.4
57. 1,2-dibromo-3-chloropropane	0.041	4.36	5.4
58. 1,2,4-trichlorbenzene	0209	8.27	25.4
59. hexachlorobutadiene	0.096	4.12	9.9
60. naphthalene	0.512	11.13	73.0
61. 1,2,3-trichlorobenzene	0.188	9.87	21.2

The Internal Standard used for this work was Fluorobenzene.

CONCLUSIONS

Laboratories can increase productivity through automation. The automation chosen should be reliable and versatile. The Precept aqueous module was evaluated using two different configurations and it performed well in both cases. The calibration curves at both ranges were linear. The MDL's were also good for the 524.2 analytes. Because the autosampler can also be equipped with a solid module, the precept provides maximum productivity.

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EXAMINATION OF GC/FID FOR THE ANALYSIS OF MODIFIED METHOD TO-14 FOR VOCS IN AMBIENT AIR

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INTRODUCTION

Toxic organic compounds in ambient air are often analyzed by gas chromatography/mass spectrometry(GC/MS.)[1] While this approach offers both sensitivity and selectivity, it can be more complicated and expensive than necessary. A simpler analytical method was evaluated for screening and quantitation of volatile organic compounds(VOCs) from ambient air samples in SUMMA® canisters. In this case, a gas chromatograph, equipped with a flame ionization detector, was utilized to determine the applicability for an air toxics monitoring laboratory.

The sensitivity, accuracy, and precision are presented for polar and non-polar analytes. This is represented by method detection limits, calibration curve linearity, and evaluation of reference standard samples

EXPERIMENTAL

The calibration standard was prepared from a commercially available TO-14 mixture and from two standards made in 2 liter static dilution bottles (SDB.) The stock TO-14 standard has a concentration of 2.0 ppmv (Alphagasz - Morrisville, PA). The two SDBs were made by injecting neat liquids into the SDB for vaporizatrion. Two microliters each of three trihalomethanes (bromoform, bromodichloromethane, chlorodibromomethane) were injected into the SDB to yield a concentration of 2 ng/L. The polar standard (acetone, acrylonitrile, 2-butanone, methyl methacrylate, methyl isobutyl ketone) was prepared in a separate SDB by adding 2.9 µL of each component, resulting in a concentration of 3 ng/L. The calibration standard was made by injecting 1.0 mL of the brominated trihalomethane, 0.5 mL of the polar, and 150 mL of the TO-14 standard into an evacuated eight liter canister. After the standards were added, the canister was pressurized to 22 psig and simultaneously humidified to 35% relative humidity by adding 150 µL of water. The resulting concentrations were: 15 ppbv for the TO-14 components, 12 to 15 ppbv for the trihalomethanes mixture, and 7 to 14 ppbv for the polar analytes.

The concentrator, cryofocusing module, and canister interface were connected to the GC. The flow rates were adjusted to the conditions listed below. The system was leak checked with the instrument's control software. The trap in the system was baked and standards were analyzed. The system was calibrated using external standard quantitation.

A six point calibration curve was run on June 29, 1994 from a 15 ppbv standard. The points of the calibration were obtained by using six different volumes of this standard. The volumes for

the calibration (50, 100, 250, 500, 750, and 1000mL) were metered onto the trap using an electronic mass flow controller (MFC.) The integrated chromatograms were used to calculate response factors (RF) for each level and the percent relative standard deviation of the response factors. This was then repeated on July 31, 1994 to determine the reproducibility of calibration.

Once the calibration curve was built, the sensitivity of the system was determined. For this test, seven 20 mL aliquots of 10 ppbv calibration standard were analyzed. These seven aliquots were quantitated to determine the concentration. The standard deviation of the calculated concentration was determined and multiplied by the student t-value for the 99% confidence limits (3.143) to determine the method detection limit (MDL.)

The system performance was then verified against a National Institute of Standards and Technology (NIST) audit sample to determine accuracy of the results. Six samples were analyzed, three at 500 mL and three at 1000 mL, and the percent difference was determined between the actual and calculated concentrations.

CONDITIONS

Tekmar 6000/AEROCan

Line/Valve Temp	200°C
Standby Flow	10 mL/min
Trap Standby Temp	100°C
Sweep Gas(Nitrogen)	
Flow Rate	100 mL/min
Sweep/Flush time	1 min
Glass Bead Packed Trap Setpoints	
Cooldown	-165°C
Desorb Preheat	195°C
Desorb	5 min @ 200°C
Bake	10 min @ 225°C
Bake Flow	100 mL/min
Moisture Control System	
Standby Temp	200°C
Desorb Temp	50°C
Bake Temp	320°C
Cryofocusing Module	
Standby	100°C
Cooldown	-175°C
Inject	100°C
Injection port bypassed	

Hewlett Packard 5890

Column	HP-5
ID	0.32 mm
Film Thickness	1 µm
Length	50 m
Carrier Gas	Helium
Flow Rate	2.65 mL/min @35°C
Oven Profile	
Initial Temp	5°C for 4 min
Ramp	7°C/min to 220°C
FID Temperature	250°C
Hydrogen Flow Rate	30 ml/min
Air Flow Rate	300 ml/min

RESULTS

Calibration

The system was first calibrated on June 29, 1994 and again on July 31, 1994. The results for all 50 compounds are listed in Table 2. Both calibration curves meet precision requirements of less than 30% RSD stated in EPA Method TO-14, including three polar analytes. There are five sets of coeluting analytes including:

3-chloro-1-propene/methylene chloride, benzene/carbon tetrachloride,
1,2-dichloropropene/trichloroethylene,
meta & para-xylene,

one month period as evidenced by the similarities of the precision and response factors from the two calibration curves. This also gives a good indication of the precision at which the standards were diluted over this same period. The data from July exhibits a value slightly higher than expected for the precision of dichlorodifluoromethane and is probably due to interfering hydrocarbons from the dilution gas.

The method detection limits are similar to those expected from a TO-14 analysis by GC/MS. Some holes in the data appear in the permanent gases, peaks one through six, and are attributed to the sensitivity of the FID to these halogenated C1 and C2 compounds.

The NIST standard was evaluated on the system to determine accuracy of the system to a reference. The determined oncentration agreed well with this standard. Of the fifteen analytes in the mixture, eleven analytes were well within the true concentration range provided with this standard, dated July 1991.

CONCLUSION

The system is a reliable and rugged mechanism for screening air toxics samples prior to analysis. This can also be used as a final analysis tool in well characterized sampling sites. This technique shows impressive sensitivity for the TO-14 compounds, the additional three brominated trihalomethanes, and the five polar analytes.

There are two drawbacks with this system. The three sets of coeluting peaks could limit final analysis on this system unless a conformational column is used. In addition, the sensitivity to C1 and C2 hydrocarbons to FID can also be prohibitive. The addition of an electron capture detector to the system could partially resolve this issue. Overall, the system exceeded expectations for sensitivity and linearity for the analytes tested.

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TABLE 1- Calibration Curve Linearity for June and July 1994

Peak #	Analyte	50 ml RF	100 ml RF	250 ml RF	500 ml RF	750 ml RF	1000 ml RF	June 1994 % RSD RF	July 1994 % RSD RF
1	Dichlorodifluoromethane	0.0336	0.0665	0.0378	0.0382	0.0382	0.0384	28.66%	10.28%
2	Chloromethane	0.0099	0.0105	0.0110	0.0113	0.0112	0.0114	5.28%	11.71%
3	1,2-Dichlorotetrafluoroethane	0.0129	0.0135	0.0135	0.0135	0.0135	0.0134	1.78%	11.43%
4	Vinyl Chloride	0.0072	0.0075	0.0080	0.0081	0.0081	0.0083	5.32%	12.13%
5	Bromomethane	0.0123	0.0155	0.0160	0.0161	0.0162	0.0162	10.02%	15.62%
6	Chloroethane	0.0072	0.0075	0.0073	0.0077	0.0077	0.0077	2.75%	7.83%
7	Trichlorofluoromethane		0.0426	0.0441	0.0445	0.0437	0.0441	1.67%	7.18%
P1	Acetone	0.0059	0.0070	0.0070	0.0064	0.0071	0.0074	7.85%	12.21%
8	1,1-Dichloroethene	0.0073	0.0075	0.0078	0.0077	0.0077	0.0078	2.60%	8.63%
P2	Acrylonitrile	0.0070	0.0074	0.0076	0.0076	0.0076	0.0077	3.48%	11.43%
9	1,1,2-Trichloro-trifluoroethane	0.0087	0.0089	0.0091	0.0091	0.0092	0.0094	2.63%	14.27%
10&11	3-Cl-1-Propene & Meth Cl	0.0077	0.0080	0.0081	0.0081	0.0081	0.0080	1.84%	7.36%
12	1,1-Dichloroethane	0.0075	0.0079	0.0082	0.0081	0.0082	0.0082	3.48%	8.97%
P3	2-Butanone (MEK)	0.0061	0.0061	0.0063	0.0063	0.0064	0.0055	5.35%	9.35%
13	cis-1,2-Dichloroethene	0.0074	0.0077	0.0079	0.0078	0.0079	0.0079	2.46%	8.14%
14	Chloroform	0.0165	0.0170	0.0176	0.0175	0.0177	0.0179	3.04%	8.34%
15	1,1,1-Trichloroethane	0.0076	0.0079	0.0081	0.0081	0.0082	0.0082	3.16%	7.96%
16	1,2-Dichloroethane	0.0076	0.0079	0.0082	0.0082	0.0082	0.0084	3.40%	8.98%
17&18	Benzene & Carbon Tetrachloride	0.0044	0.0046	0.0047	0.0047	0.0047	0.0048	2.92%	11.78%
19&20	1,2-DCP & TCE	0.0059	0.0061	0.0063	0.0063	0.0064	0.0064	3.32%	8.59%
Br1	Bromodichloromethane	0.0368	0.0381	0.0388	0.0387	0.0388	0.0391	2.25%	8.19%
P4	Methyl Methacrylate	0.0055	0.0058	0.0057	0.0056	0.0056	0.0057	1.37%	6.69%
P5	MIBK	0.0039	0.0040	0.0041	0.0040	0.0041	0.0041	1.74%	8.65%
21	cis-1,3-Dichloropropene	0.0059	0.0062	0.0062	0.0064	0.0064	0.0064	2.92%	7.86%
22	trans-1,3-Dichloropropene	0.0103	0.0105	0.0100	0.0103	0.0099	0.0099	2.32%	4.67%
23	Toluene	0.0022	0.0023	0.0024	0.0024	0.0024	0.0024	3.15%	9.41%
24	1,1,2-Trichloroethane	0.0075	0.0078	0.0080	0.0081	0.0081	0.0082	2.99%	8.81%
Br2	Dibromochloromethane	0.0248	0.0237	0.0254	0.0248	0.0245	0.0261	3.28%	14.54%
25	1,2-Dibromoethane	0.0077	0.0081	0.0083	0.0083	0.0083	0.0084	2.88%	8.52%
26	Tetrachloroethene	0.0036	0.0037	0.0037	0.0036	0.0035	0.0035	2.07%	7.38%
27	Chlorobenzene	0.0025	0.0026	0.0027	0.0027	0.0027	0.0028	3.18%	9.22%
28	Ethylbenzene	0.0019	0.0020	0.0021	0.0021	0.0021	0.0021	3.26%	9.33%
29&30	m-Xylene & p-Xylene	0.0019	0.0021	0.0021	0.0021	0.0022	0.0022	4.54%	9.26%
Br3	Bromoform		0.0498	0.0495	0.0496	0.0482	0.0482	1.60%	7.25%
31	Styrene	0.0033	0.0034	0.0035	0.0035	0.0036	0.0036	3.20%	8.98%
32	o-Xylene	0.0021	0.0021	0.0022	0.0022	0.0022	0.0023	3.46%	9.63%
33	1,1,2,2-Tetrachloroethane	0.0082	0.0085	0.0087	0.0087	0.0087	0.0088	2.66%	9.15%
34	4-Ethyltoluene	0.0018	0.0019	0.0020	0.0020	0.0021	0.0021	5.14%	9.90%
35	1,3,5-Trimethylbenzene	0.0018	0.0019	0.0020	0.0020	0.0020	0.0020	3.69%	9.41%
36	1,2,4-Trimethylbenzene	0.0019	0.0020	0.0020	0.0020	0.0021	0.0021	3.59%	8.74%
37	1,3-Dichlorobenzene	0.0027	0.0028	0.0029	0.0029	0.0029	0.0030	3.24%	8.94%
38&39	1,4-DCB & Benzyl Chloride	0.0040	0.0042	0.0043	0.0042	0.0042	0.0042	2.08%	7.71%
40	1,2-Dichlorobenzene	0.0027	0.0028	0.0029	0.0029	0.0029	0.0030	3.39%	9.16%
41	1,2,4-Trichlorobenzene	0.0035	0.0039	0.0039	0.0038	0.0038	0.0039	4.20%	6.43%
42	Hexachloro-1,3-butadiene	0.0046	0.0048	0.0050	0.0050	0.0051	0.0053	4.91%	8.51%

Method Detection Limits

The method detection limits are displayed from seven 20 mL aliquots of the calibration standard. The MDLs are listed below in Table 2. In this table the concentration values calculated from these samples, the standard deviation, and the method detection limits are outlined.

TABLE 2- Method Detection Limits for Seven Replicate Analyses

Peak #	Analyte	7 Replicate Analyses using 20 mL of a 10 ppbv Standard							Avg Conc (ppbv)	Standard Deviation	MDL (pptv)
		20mL-1	20mL-2	20mL-3	20mL-4	20mL-5	20mL-6	20mL-7			
1	Dichlorodifluoromethane	0.9392		0.9274	0.7959	0.3662		0.9741	0.8005	0.2520	944
2	Chloromethane	0.2147	0.2225		0.1825	0.1951	0.1995	0.0252	0.1732	0.0739	249
3	1,2-Dichlorotetrafluoroethane	0.3103	0.3160		0.3076	0.3478	0.3229	0.2563	0.3102	0.0301	101
4	Vinyl Chloride					0.1699			0.1699		
5	Bromomethane		0.1865			0.1628	0.1707		0.1733	0.0121	84
6	Chloroethane	0.1879	0.1925			0.1691	0.1729		0.1806	0.0113	51
7	Trichlorofluoromethane	0.2862	0.2821	0.3026	0.2711	0.2670	0.3161	0.2954	0.2886	0.0174	55
P1	Acetone	0.2884	0.3051	0.2765	0.4287	0.2779	0.3004	0.8099	0.3838	0.1952	614
8	1,1-Dichloroethene	0.2051	0.2122	0.2014	0.1668	0.1890	0.1979	0.1834	0.1937	0.0153	48
P2	Acrylonitrile	0.1933	0.2010	0.1768	0.1515	0.1665	0.1749	0.1663	0.1758	0.0169	53
9	1,1,2-Trichloro-trifluoroethane	0.2105	0.2148	0.1944	0.2251	0.1892	0.1991	0.1920	0.2036	0.0134	42
10&11	3-Cl-1-propene & Meth Cl	0.6027	0.6286	0.5828	0.4849	0.5331	0.5603	0.5222	0.5592	0.0497	156
12	1,1-Dichloroethane	0.1736	0.1903	0.1759	0.1417	0.1657	0.1705	0.1723	0.1700	0.0146	46
P3	2-Butanone (MEK)	0.4273	0.4168	0.4425	0.3614	0.3633	0.3852	0.4017	0.3997	0.0313	98
13	cis-1,2-Dichloroethene	0.2042	0.2080	0.1853	0.1553	0.1782	0.1868	0.1739	0.1845	0.0180	57
14	Chloroform	0.1875	0.1802	0.1692	0.1453	0.1656	0.1745	0.1577	0.1686	0.0141	44
15	1,1,1-Trichloroethane	0.1943	0.1998	0.1857	0.1592	0.1741	0.1880	0.1691	0.1814	0.0145	46
16	1,2-Dichloroethane	0.2070	0.2144	0.1990	0.1700	0.1880	0.1981	0.1787	0.1936	0.0157	49
17&18	Benzene & Carbon Tetrachloride	0.4821	0.4884	0.4566	0.3452	0.3892	0.4834	0.4728	0.4454	0.0559	176
19&20	1,2-DCP & TCE	0.2967	0.3019	0.2777	0.2306	0.2548	0.2755	0.2471	0.2692	0.0262	82
Br1	Bromodichloromethane	0.2061	0.2039	0.1798	0.1626	0.1786	0.2117	0.1755	0.1883	0.0187	59
P4	Methyl Methacrylate	0.1053	0.1099	0.0991	0.0828	0.0936	0.0973	0.0909	0.0970	0.0091	28
P5	MIBK	0.0886	0.0892	0.0830	0.0702	0.0794	0.0835	0.0764	0.0815	0.0068	21
21	cis-1,3-Dichloropropene	0.2049	0.2123	0.1938	0.1616	0.1818	0.1912	0.1633	0.1870	0.0194	61
22	trans-1,3-Dichloropropene	0.1957	0.1988	0.1823	0.1602	0.1747	0.1752	0.1634	0.1786	0.0148	46
23	Toluene	0.2091	0.2124	0.1983	0.1660	0.1870	0.1959	0.1779	0.1923	0.0166	52
24	1,1,2-Trichloroethane	0.1942	0.1959	0.1850	0.1557	0.1755	0.1823	0.1678	0.1795	0.0144	45
Br2	Dibromochloromethane	0.3194	0.3306	0.3227	0.2834	0.3148	0.3257	0.3553	0.3217	0.0214	67
25	1,2-Dibromoethane	0.1945	0.1995	0.1842	0.1510	0.1712	0.1837	0.1605	0.1778	0.0177	56
26	Tetrachloroethene	0.2327	0.2373	0.2217	0.1900	0.2163	0.2280	0.0953	0.2031	0.0500	157
27	Chlorobenzene	0.1947	0.1960	0.1816	0.1532	0.1722	0.1787	0.1616	0.1768	0.0159	50
28	Ethylbenzene	0.1935	0.1979	0.1822	0.1511	0.1723	0.1803	0.1643	0.1774	0.0163	51
29&30	m-Xylene & p-Xylene	0.3600	0.3674	0.3403	0.2824	0.3208	0.3392	0.3009	0.3301	0.0308	97
Br3	Bromoform	0.2061	0.2198	0.1998	0.1677	0.1876	0.2091	0.2051	0.1993	0.0170	53
31	Styrene	0.0992	0.1014	0.0940	0.0768	0.0877	0.0931	0.0908	0.0918	0.0081	26
32	o-Xylene	0.1887	0.1921	0.1798	0.1496	0.1686	0.1775	0.1625	0.1741	0.0150	47
33	1,1,2,2-Tetrachloroethane	0.1902	0.1947	0.1798	0.1507	0.1705	0.1833	0.1634	0.1761	0.0155	49
34	4-Ethyltoluene	0.1800	0.1854	0.1721	0.1415	0.1612	0.1683	0.1554	0.1663	0.0150	47
35	1,3,5-Trimethylbenzene	0.1703	0.1746	0.1620	0.1347	0.1528	0.1610	0.1597	0.1593	0.0130	41
36	1,2,4-Trimethylbenzene	0.1577	0.1608	0.1496	0.1211	0.1392	0.1468	0.1346	0.1443	0.0138	43
37	1,3-Dichlorobenzene	0.1751	0.1806	0.1698	0.1301	0.1550	0.1642	0.1497	0.1607	0.0173	54
38&39	1,4-DCB & Benzyl Chloride	0.2845	0.2935	0.2737	0.2182	0.2493	0.2707	0.2461	0.2623	0.0260	82
40	1,2-Dichlorobenzene	0.1706	0.1777	0.1633	0.1296	0.1508	0.1615	0.1506	0.1577	0.0158	50
41	1,2,4-Trichlorobenzene	0.0652	0.0940	0.0880	0.0645	0.0821	0.0786	0.0722	0.0778	0.0112	35
42	Hexachloro-1,3-butadiene	0.1299	0.1407	0.1305	0.1486	0.1078	0.1251	0.1172	0.1285	0.0137	43

NIST-traceable Audit Samples

Once the sensitivity and the linearity of the system were determined, the NIST audit sample, cylinder No. AAL-21390, was analyzed. The resulting concentrations from the three aliquots each at 500 and 1000 mL are listed. These values were averaged and compared to the true concentration in Table 3 and an example chromatogram is shown in Figure 2.

1,4-dichlorobenzene/benzyl chloride.
An example of 500 mL of the calibration mixture is illustrated below in Figure 1.

FIGURE 1- *500 ml of a 15 ppbv TO-14 Standard*

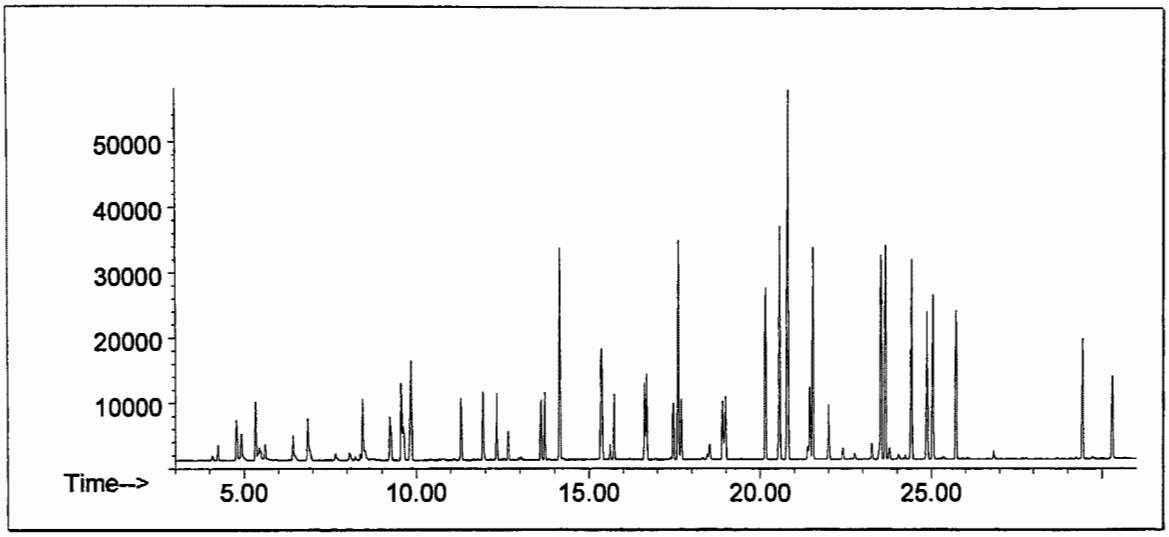

FIGURE 2- *500 mL of a NIST-traceable reference mixture*

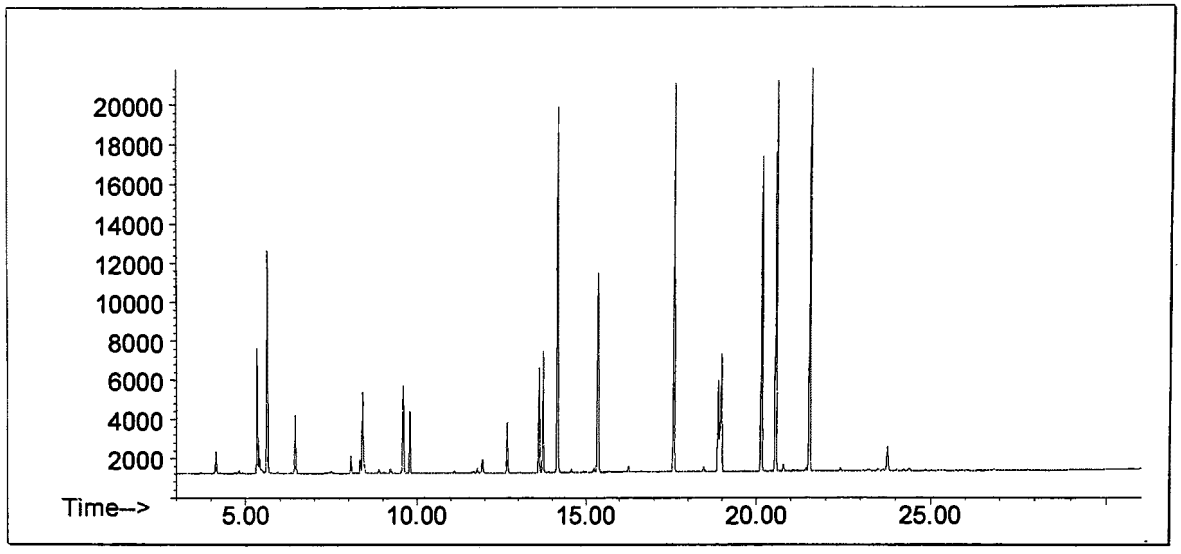

TABLE 3- System Accuracy as compared to NIST-traceable audit mixture

Peak #	Analyte	500 ml #1	500 ml #2	500 ml #3	1000 ml #1	1000 ml #2	1000 ml #3	True Conc.	Average Exp Conc.	% Diff. from true
4	Vinyl Chloride	5.43	5.39	7.19	6.63	5.44	5.50	4.91	5.93	20.77%
5	Bromomethane	5.44	5.41	5.37	5.71	5.67	5.66	5.27	5.54	5.18%
7	Trichlorofluoromethane	4.84	4.71	4.63	4.83	4.70	4.67	5.02	4.73	-5.78%
10&11	3-Cl-1-propene & Methylene Chloride	2.24	2.23	2.22	2.27	2.25	2.26	4.56	2.24	-50.79%
14	Chloroform	4.60	4.58	4.53	4.67	4.66	4.65	4.91	4.62	-6.00%
15	1,1,1-Trichloroethane	4.77	4.73	4.72	4.86	4.85	4.85	5.45	4.80	-12.00%
16	1,2-Dichloroethane	5.13	5.08	5.07	5.22	5.20	5.17	4.87	5.15	5.66%
17&18	Benzene & Carbon Tetrachloride	9.49	9.35	9.32	9.67	9.64	9.58	9.01	9.51	5.52%
19&20	1,2-Dichloropropane & Trichloroethene	11.09	11.00	10.95	11.27	11.23	11.21	9.82	11.12	13.29%
23	Toluene	4.87	4.82	4.81	4.97	4.96	4.93	5.05	4.89	-3.11%
25	1,2-Dibromoethane	4.14	4.10	4.10	4.23	4.20	4.19	4.84	4.16	-14.04%
26	Tetrachloroethene	5.55	5.54	5.50	5.68	5.61	5.60	5.01	5.58	11.39%
27	Chlorobenzene	4.88	4.84	4.83	4.99	4.98	4.97	5.10	4.92	-3.60%
28	Ethylbenzene	4.43	4.40	4.37	4.52	4.51	4.50	4.89	4.45	-8.92%
32	o-Xylene	4.89	4.85	4.82	5.01	4.98	4.97	5.30	4.92	-7.18%

DISCUSSION

The results from the calibration show excellent linearity and precision for the 6 sample volumes taken during calibration. This also illustrates the wide sample volume which can be loaded onto the glass bead-packed, cryogenic trap (50 mL to 1000 mL.) This system was stable over the

THE SUITABILITY OF POLYMERIC TUBINGS FOR SAMPLING WELL WATER TO BE ANALYZED FOR TRACE-LEVEL ORGANICS

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ABSTRACT

There is concern in the groundwater monitoring industry that polymeric tubings used to sample groundwater can affect contaminant concentrations. Results from a recent study that looked for sorption and leaching of organic contaminants by twenty polymeric tubings will be presented. The flexible and rigid tubings that were tested included several polyethylene and polypropylene formulations, several different fluoropolymers, as well as polyurethane, polyamide, and flexible PVC.

In this study, the tubings were exposed to a solution containing a mixture of eight organic compounds (nitrobenzene, trans-1,2-dichloroethylene, m-nitrotoluene, trichloroethylene, chlorobenzene, o- and p- dichlorobenzene, and tetrachloroethylene), each at a concentration of 10 to 16 mg/L. Our results indicate that three rigid fluoropolymers [fluorinated ethylene propylene (FEP), FEP-lined polyethylene, and polyvinylidene fluoride (PVDF)] were the least sorptive of the tubings tested. During this study, we observed that the reversed-phase HPLC chromatograms for samples exposed to some of the tubings had spurious peaks. This indicates that several of the tubings leached contaminants into the test solution. Only the polyethylene tubings, the rigid fluoropolymer tubings, and one plasticized polypropylene tubing did not appear to leach any contaminants.

Based on the findings from this study and relative cost, we tentatively recommend PVDF when a rigid tubing can be used and a copolymer of vinylidene fluoride and hexafluoropropylene [P(VDF-HFP)] when a more flexible tubing is required. However, since this study was conducted under static conditions, and sampling usually involves continual replenishment of the contacting solution, we are currently conducting studies under dynamic conditions.

INTRODUCTION

It is important that the reported concentrations of contaminants in samples taken from groundwater monitoring wells reflect the true in-situ values. One concern about sampling methods that in-

Table 1. Polymeric tubings used for sampling trace-level organics.

	Tubing material	Rigidity*	Cost†/ft² ($)	Dimensions (cm) I.D.	O.D.	Wall	Length (cm)	$Area_{sur}$ to vol_{sol} (cm^{-1})
1	polyethylene, low density (LDPE)	R	0.19	0.64	0.95	0.16	20	6.3
2	polyethylene, cross-linked high density (XLPE)	R	0.43	0.64	0.95	0.16	20	6.3
3	polyethylene liner in ethyl vinyl acetate shell	R	0.57	0.64	0.95	0.16	20	6.3
4	polyethylene liner cross-linked to ethyl vinyl acetate shell	R	1.08	0.64	0.95	0.16	20	6.3
5	co-extruded polyester lining in polyvinylchloride shell	R	0.77	0.64	0.95	0.16	20	6.3
6	polypropylene (PP)	R	0.27	0.64	0.95	0.16	20	6.3
7	polytetrafluoroethylene (PTFE)	R	4.27	0.75	0.95	0.10	17	5.3
8	perfluoroalkoxy (PFA)	R	5.58	0.64	0.95	0.16	20	6.3
9	polyurethane, ether-grade	F	0.64	0.64	0.95	0.16	20	6.3
10	ethylenetetrafluoroethylene (ETFE)	R	5.50	0.48	0.64	0.08	27	8.4
11	polyproplyene-based material with plasticizer, type I	F	0.58	0.64	0.95	0.16	20	6.3
12	polyamide (nylon)	R	0.71	0.71	0.95	0.12	18	5.6
13	linear copolymer of vinylidene fluoride and hexafluoropropylene P(VDF-HFP)	F	1.99	0.64	0.80	0.08	20	6.3
14	flexible PVC	F	0.89	0.64	0.95	0.16	20	6.3
15	silicone-modified thermoplastic elastomer (TPE)	F	0.96	0.64	0.95	0.16	20	6.3
16	polypropylene-based material with plasticizer, type II	F	2.48	0.64	0.95	0.16	20	6.3
17	polyvinylidene fluoride (PVDF)	R	1.80	0.64	0.95	0.16	20	6.3
18	fluoroelastomer	F	8.70	0.64	0.95	0.16	20	6.3
19	FEP-lined polyethylene	R	3.00	0.64	0.80	0.08	20	6.3
20	fluorinated ethylene polypropylene (FEP)	R	3.90	0.64	0.95	0.16	20	6.3

* R-can be stepped on without collapsing the tubing; F-finger pressure can collapse tubing.
† Cost varies with quantity, dimensions and supplier.

volve pumping groundwater samples to the surface is that there may be interactions between the tubing and the sample as it is pumped. The tubing could leach or sorb inorganic or organic contaminants to or from the sample. Also, if a pump and its tubing are not dedicated to a particular well, it is possible that tubing used previously to sample a well with high concentrations of contaminants could subsequently desorb previously sorbed contaminants into samples. In a recent review of the literature on decontamination, Parker (1) found there has been very little study of desorption of organic contaminants from tubings and very little study of how to decontaminate these tubings.

The purpose of this study was to compare sorption of organic solutes by twenty commercially available sampling tubings and to look for signs of contaminants leaching from these products. Table 1 lists the tubing materials used in this study and their abbreviations, tubing dimensions, costs, and flexibilities. The flexibility of the products we tested varied from non-rigid (i.e., easy to collapse with only finger pressure) and thus very flexible, to rigid (i.e., standing on the tubing failed to collapse it) with only slight flexiblity (i.e., coilable). Cost of the tubings used in this study ranged from $19 (LDPE) to $870 (fluoroelastomer) per 100 ft.

MATERIALS AND METHODS

First sorption study

The twenty tubings were cut to different lengths so that they would all have the same internal surface area, 40 cm^2 (Table 1). This was necessary because three types of tubing (PTFE, ETFE, and polyamide) had different internal diameters from the rest. As a result, the tubing surface-area-to-solution-volume ratios differed for these three materials.

The cut tubing sections were rinsed with several volumes of deionized water and left to air dry. One end of each of the tubings was plugged with a glass rod whose diameter matched the internal diameter of the tubing. The glass rod was inserted in the tubing to a depth of 1 cm, and the outside of the tubing was clamped with a plastic tubing clamp.

The test solution was prepared by adding eight neat organic compounds directly to well water in a 2-L glass bottle to give mg/L concentrations of nitrobenzene (NB), trans-1,2-dichloroethylene (TDCE), m-nitrotoluene (MNT), trichloroethylene (TCE), chlorobenzene (CLB), o-dichlorobenzene (ODCB), p-dichlorobenzene (PDCB), and tetrachloroethylene (PCE). Mercuric chloride was added to the

solution (40 mg/L) to prevent losses due to biological activity. After adding all of the analytes, the bottle was topped off with well water so there was no headspace, capped with a glass stopper, tightly wrapped with Parafilm, and stirred with a magnetic stirrer for two days. The initial concentrations of the organic solutes varied from 10 to 16 mg/L.

For each type of tubing, there were five sampling times (1, 8, 24, 48, and 72 hours) and two replicates for each sampling time. For each sampling time, the tubings were filled in random order using a glass re-pipettor. The open end of each tubing was then sealed by inserting another piece of glass rod so there was no head space, and clamped with a plastic tubing clamp. The tubings were stored in the dark at room temperature. At the beginning and end of filling each set of tubings, three HPLC autosampler vials were filled with the test solution, capped with Teflon-lined plastic caps, and stored in the dark in a refrigerator. These solutions served as controls.

When it was time to take a sample from one of the tubings, one of the plugged ends of the tubing was cut off and a Pasteur pipet was used to transfer an aliquot of the test solution to an HPLC auto-sampler vial.

Analytical determinations were performed using reversed-phase HPLC (RP-HPLC). A modular system was employed consisting of a Spectra-Physics SP8875 autosampler with a 100-µL injection loop, a Spectra-Physics SP8810 isocratic pump, a Spectra-Physics SP8490 variable-wavelength detector set at 215 nm, and a Hewlett-Packard 3396 series II digital integrator. Separations were obtained on a Supelco LC-18 25-cm x 0.46-cm (5-µm) column eluted with 65/35 (V/V) methanol/water at a flow rate of 2.0 mL/min. The detector response was obtained from the digital integrator operating in the peak-height mode.

Primary and working standards were made as described by Parker and Ranney (2). The working-standard solutions were made fresh on each sampling day and run in triplicate. The method detection limit (MDL) for PDCB was 8.6 µg/L and 3.5 µg/L for PCE. The MDLs for these analytes were obtained according to the EPA protocol described elsewhere (3).

Second Sorption Study

Since three of the tubings used in this study (PTFE, ETFE, and polyamide) had different surface-area-to-solution-volume ratios than the other tubings, this study was conducted so that we could compare sorption of organic solutes by these tubings with the other seventeen tubings.

Five-centimeter pieces of the three tubing types were placed in three different-sized glass vials (9, 25 and 40 mL). The test solution contained the same organic compounds and was made in the same manner as in the previous study. The solution was poured into the vials so there was no headspace, and the vials were capped with Teflon-lined plastic caps. The surface-area-to-solution-volume ratios were: for PTFE, 0.70, 1.15, 3.55; for ETFE, 0.45, 0.74, and 2.15; and for polyamide, 0.69, 1.14, and 3.59. Same-sized vials, filled with test solution but no tubing, served as controls; there were two controls for each vial size and sampling time. All samples were kept in the dark at room temperature. Duplicate samples were taken after 1 hour, 8 hours, and 24 hours. With a Pasteur pipet, an aliquot of each sample was transfered from each of the test vials to an autosampler vial.

Analyses were done as described previously in the first sorption study.

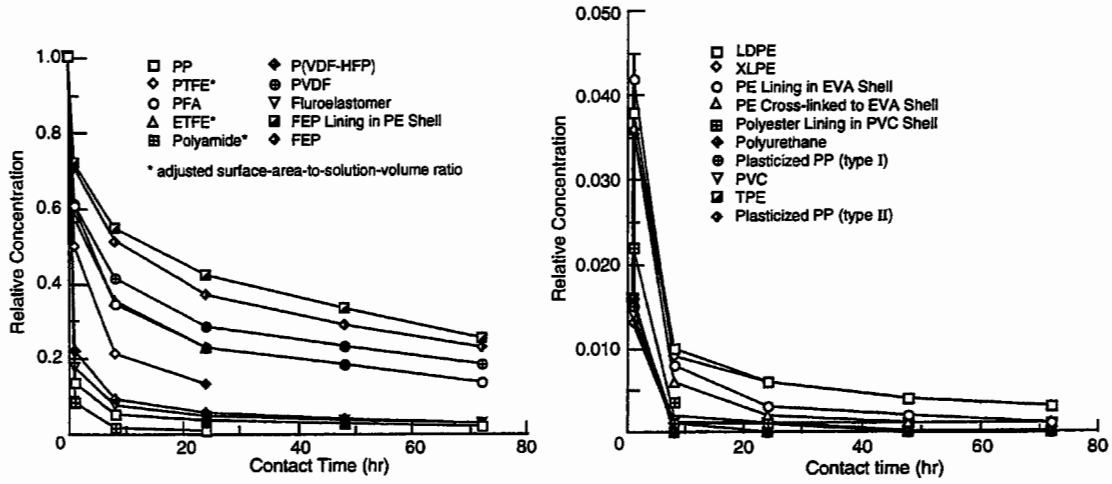
RESULTS AND DISCUSSION

Sorption Of Organic Solutes

Figures 1 and 2 show mean normalized concentrations of PCE and PDCB the solutions exposed to the twenty polymeric tubings. These two analytes and ODCB were sorbed the most rapidly and to the greatest extent of all the analytes tested in this study (2). Mean normalized concentration was calculated by dividing the mean concentration of an analyte exposed to a given tubing for a given time by the mean concentration of the same analyte in the control samples at the same time. Thus, a mean normalized value of 1.00 represents no loss of analyte.

The figures also show the adjusted mean normalized concentrations for the three materials that had different surface area to volume ratios (PTFE, ETFE, and polyamide). These were found by taking the best-fit equation for the data from the second experiment (2) for each material, analyte and time, and using it to determine what the adjusted normalized values would be for these three materials if the surface-area-to-solution-volume ratios were the same as the other seventeen tubings.

For PDCB, the least sorptive tubings (both in rate and extent of sorption) were FEP-lined PE, FEP, and PVDF (Figure 1a). Fisher's Protected Least Significant Difference tests showed that FEP-lined PE generally performed significantly better than FEP, which performed significantly better than PVDF, which in turn performed significantly better than PFA (2). The most sorptive tubings were flexible tubings that were not fluoropolymers (polyurethane, silicone-modified thermoplastic elastomer [TPE], the plasticized

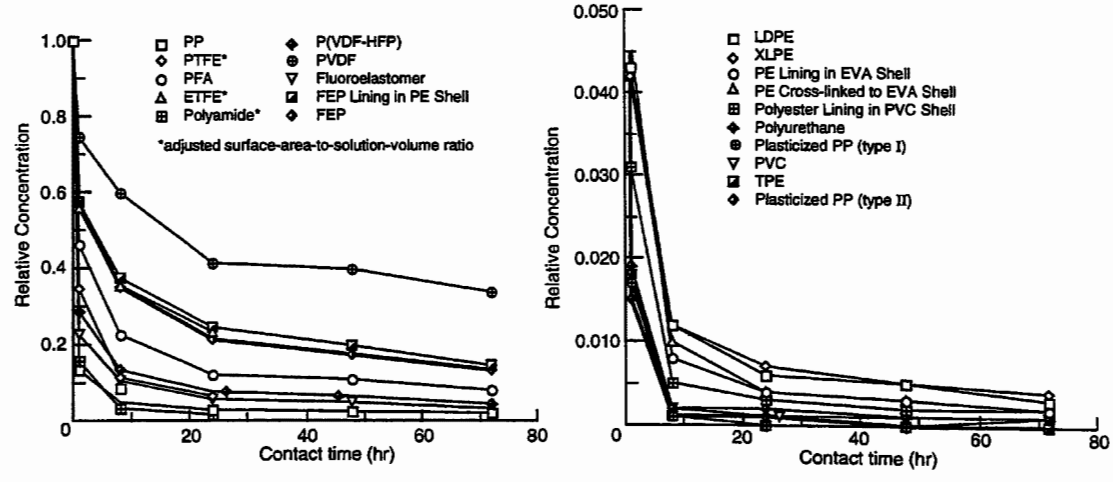


a. Least sorptive tubings. b. Most sorptive tubings.

Figure 1. Sorption of PDCB.

polypropylenes, and flexible PVC) (Figure 1b). These tubings sorbed more than 98% of the analytes in the first hour. The various polyethylene tubings were the next most sorptive group of tubings (Figure 1b).

Figure 2a shows that for PCE, PVDF was the least sorptive tubing. FEP-lined PE, FEP, and ETFE were the next least sorptive tubings. Generally there was no significant difference in the concentrations of solutions exposed to FEP and FEP-lined PE (2). The six tubings that were the most sorptive of PDCB were also the most sorptive tubings of PCE (Figure 2b). Again, the polyethylene tubings were the next most sorptive tubings.



a. Least sorptive tubings. b. Most sorptive tubings.

Figure 2. Sorption of PCE.

These results are typical for the other six analytes (2). We found that PVDF was also the least sorptive material for TDCE and TCE, and that FEP and FEP-lined PE were the least sorptive materials for the other four analytes (NB, MNT, CLB, ODCB).

The results from this study appear to agree well with the results from a number of similar studies (4-10). These studies compared sorption of organic solutes by a few polymeric tubing materials. Generally, these studies found that flexible materials like silicone rubber and flexible PVC were the most sorptive materials, and that PTFE and other fluoropolymers and rigid PVC were the least sorptive.

Leaching of Contaminants

When we compared the chromatograms of solutions exposed to the tubings with those of the control solutions, we saw additional peaks in solutions exposed to some of the tubings. By the end of the experiment (72 hr), solutions exposed to nine of the tubings had extra peaks (Table 2). The polyurethane, polyamide, and PVC tubing leached at least eight compounds (as indicated by spurious peaks), with polyurethane leaching the most (twelve). Of the rigid polymers, only the fluoropolymers and polyethylenes did not

Table 2. Number of spurious HPLC peaks found during tubing material study.

	Contact time (hr)	
Tubing material	1	72
LDPE	0	0
XLPE	0	0
PE in a EVA shell	0	0
PE cross-linked to EVA shell	0	0
Polyester lining in a PVC shell	1	4
PP	1	1
PTFE	0	0
PFA	0	0
Polyurethane	5	12
ETFE	0	0
Plasticized PP (type I)	1	1
Polyamide	2	9
P(VDF-HFP)	1	1
PVC	3	8
TPE	1	4
Plasticized PP (type II)	0	0
PVDF	0	0
Fluoroelastomer	1	1
FEP-lined PE	0	0
FEP	0	0

leach any contaminants. Of the flexible polymers, only one of the plasticized polypropylene tubings (type II) did not leach any contaminants. However, several of the flexible tubings leached only one contaminant [P(VDF-HFP), the fluoroelastomer, and the other plasticized polypropylene].

These results agree well with the few studies that looked for leaching of contaminants from polymeric tubing materials (4, 6, 11, 12). Generally, these studies found that fluoropolymers (especially PTFE) did not appear to leach contaminants (6, 12).

Based on these findings, we would tentatively recommend not using the following tubing materials since each of them leached several contaminants: polyurethane, polyamide, flexible PVC, polyester-lined PVC, and silicone-modified thermoplastic elastomer. In addition, polypropylene, plasticized polypropylene (type I), P(VDF-HFP), and the fluoroelastomer tubings each leached one contaminant and thus may also be less desirable than those tubings that did not leach any contaminants (the polyethylene and rigid fluoropolymer tubings).

CONCLUSIONS

Based on this study, the rigid fluoropolymers appear to be the best materials for sampling groundwater since they were the least sorptive of organic solutes and do not appear to leach any contaminants. Among the fluoropolymers, FEP, FEP-lined PE, and PVDF were the least sorptive materials tested. If one also considers cost, PVDF becomes the most desirable choice; it's price was less than one-half that of the FEP tubing and approximately 60% of the FEP-lined PE tubing. In fact, PVDF was the least expensive of all the rigid fluoropolymers tested.

In some instances a more flexible tubing may be required (e.g., in the head of a peristaltic pump). Among the flexible (non-rigid) tubings, the two fluorinated tubings [the fluoroelastomer and P(VDF-HFP)] were much less sorptive of organic solutes than the others. In addition, these two tubings and the two plasticized polypropylenes were the best products with respect to leaching of contaminants. Thus, among the flexible tubings we tested, we would tentatively recommend using the fluoroelastomer or P(VDF-HFP) tubings. However, if we also consider cost, we see that the fluoroelastomer was the most expensive of all the tubings tested ($870/100 ft). Since the price of the P(VDF-HFP) tubing was less than 1/4 of that of the fluoroelastomer tubing, we would tentatively recommend using P(VDF-HFP) when flexible tubing is required.

If under dynamic conditions these tubings reach equilibrium prior

to sampling, then loss of organic solutes should no longer be an issue, unless transfer through the tubing to the atmosphere is significant. It is also possible that leaching of components from rigid polymers is a surface phenomenon that decreases with time, as several researchers (13-16) have observed for rigid PVC. On the other hand, if higher flow rates increase leaching, as Junk et al. (17) found with flexible PVC, then leaching may be more problematic than sorption when sampling a well. Since the costs of the materials we found to be the most inert are still quite high (around $200/100 ft), it would be desireable to use a less expensive alternative (e.g., LDPE is only $19/100 ft) if the water samples are not affected. We are currently conducting studies to determine if the behaviors we discovered in this study remain the same, increase, or disappear under dynamic conditions.

ACKNOWLEDGMENTS

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THE ANALYSIS OF HEXACHLOROPHENE BY SW846 8151

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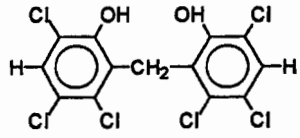
ABSTRACT

In response to the Resource Conservation and Recovery Act, hazardous waste generators are frequently required to monitor waste streams for target compounds known as the Appendix IX list. Included in this list are volatiles, semi-volatiles, pesticides, and herbicides. Hexachlorophene, also known as 2,2'-Methylene-bis(3,4,6-trichlorophenol), is listed as a target analyte with poor and erratic chromatographic performance in SW846 8270, the GC/MS method for the semi-volatile fraction. Since many of the organic fractions are required most of the time, it is practical to analyze hexachlorophene as a target analyte in the herbicide fraction using SW846 8151 and obtain much better performance than that observed when using 8270. Since hexachlorophene is a phenolic compound, it is readily derivatized by the methylating reagents used in the 8151 preparation. Results indicate the potential for much improved method detection limits, improved chromatographic performance, and acceptable precision when hexachlorophene is analyzed by 8151 as opposed to 8270.

Introduction

The passage of the Resource Conservation and Recovery Act (RCRA) in 1976 set the stage for the passage of a series of amendments that defines hazardous waste and regulates its disposal. The definition of a waste as hazardous or not hazardous can require extensive analytical testing. The methods for testing are described in a series of methods known as SW-846, which is now in the third update of its third edition. The target analytes for RCRA testing are compiled in several lists in the regulations, one of which is known as the Ground-Water Monitoring List (40 CFR Part 264 Appendix IX). This list includes the names of the target compounds of interest, the CAS number of each, suggested methods, and the PQL for each target compound. One of the compounds on the Appendix IX list is hexachlorophene and the suggested method for this compound is SW846 8270. Upon examination of the list of compounds in the method, it is evident that hexachlorophene does not perform well by 8270. Adsorption to walls of glassware during extraction and storage, and non-reproducible chromatographic performance is likely to occur. No QC acceptance criteria were given in Table 6 of 8270.

Hexachlorophene (2,2'-Methylene-bis[3,4,6-trichlorophenol]) is an anti-infective agent that is used chiefly in the manufacture of germicidal soaps. It is regulated primarily because of its potential neurotoxicity in humans.



Hexachlorophene

$C_{13}H_6Cl_6O_2$ Formula Weight 406.92

Analytical Approach

The first approach to the analysis of hexachlorophene at our laboratory was to use SW846 8270. The recoveries observed using this method were erratic and detection limits were variable. It appeared that some form of chemical degradation or reaction was occurring during the gas chromatographic analysis. Figure 1 illustrates a typical chromatogram of a hexachlorophene standard under the conditions of the 8270 analysis. Not only was the chromatographic peak badly tailing, but the mass spectrum of the peak was not consistent (Figure 2 and Figure 3) with the expected mass spectrum of hexachlorophene. Elevated quantitation limits are often the result of chemical instability and poor chromatography. These limitations of 8270 indicate that an alternative method could lead to better performance.

Figure 1
Total Ion Chromatogram of 494 mg/L Hexachlorophene

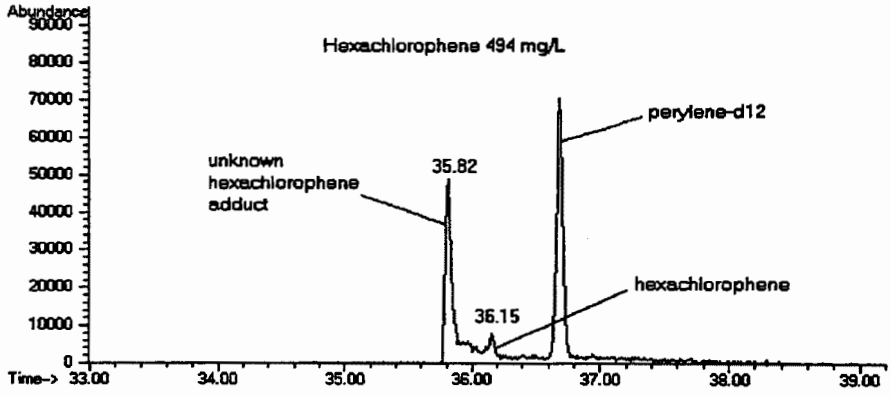


Figure 2
Mass Spectrum of Unknown Adduct

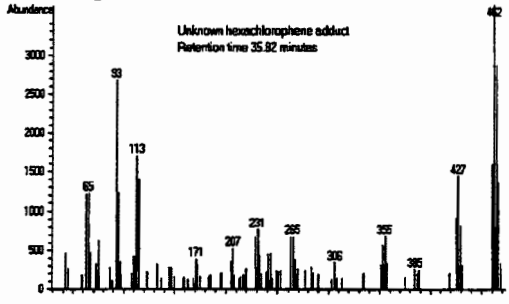
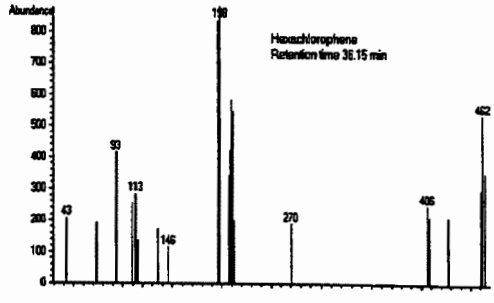


Figure 3
Mass spectrum of Hexachlorophene



The structure of hexachlorophene indicates that it is a chlorinated phenolic compound that might behave in a similar manner to other

phenolic compounds such as pentachlorophenol (PCP). PCP is a target compound listed in SW846 8151 Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization: Capillary Column Technique. The SW846 8151 method could potentially be applied to the analysis of hexachlorophene. Preliminary mass spectral data (Figure 4 and Figure 5) indicated that complete derivatization was observed when hexachlorophene was methylated with diazomethane.

Figure 4
Total Ion Chromatogram of
Methylated Hexachlorophene

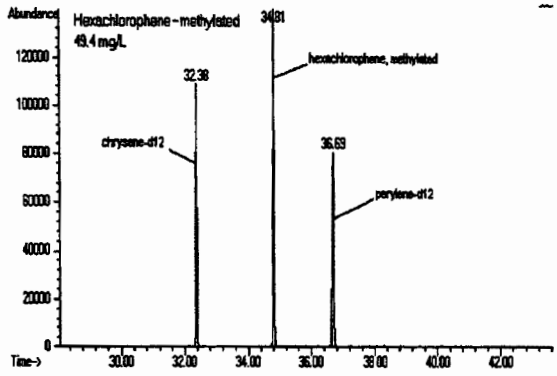
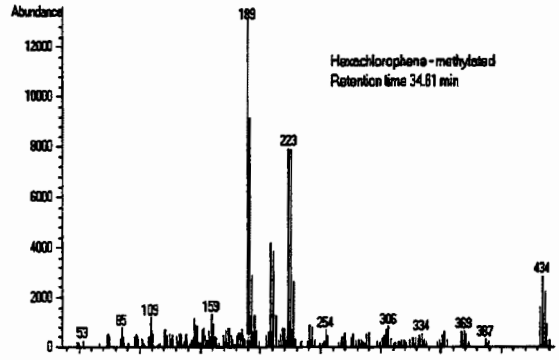


Figure 5
Mass Spectrum of Methylated
Hexachlorophene



Experimental Design

The first step was to determine the gas chromatographic conditions for the analysis of methylated hexachlorophene. This derivative was not readily available from commercial vendors and so a stock solution of hexachlorophene was derivatized with diazomethane according to the bubbler method described in SW846-8151. From this stock, five levels of calibration standards were prepared at 17.06, 34.11, 68.30, 170.60, and 341.10 ug/l.

The standards were then used to calibrate the gas chromatographic system. The analysis was performed on a HP5890 Series II GC equipped with Electronic Pressure Control and two columns installed into one injection port.

The columns chosen for this analysis were:
Analytical columns:
DB-608, 30 meters, 0.53 mm ID, 0.83 micron film (J&W P/N 125-1730)
DB-1701, 30 meters, 0.53 mm ID, 1.0 micron film (J&W P/N 125-0732)
Guard column:
RTX-5, 3 meters, 0.53 mm ID, 3.0 micron film (Restek Cat # 10282)

The following chromatographic conditions were used:
Injection port- 260 C; Detector- 300 C; Helium carrier at 3.5 PSI; Temperature program- 80 C for 3 min, 5 C/min to 180 C, then 20 C/min to 260 C. Figures 6, 7, 8, and 9 illustrate the chromatographic results and calibration curves that were obtained.

Figure 6
Chromatogram of Herbicide Methyl Esters and Hexachlorophene on DB-608

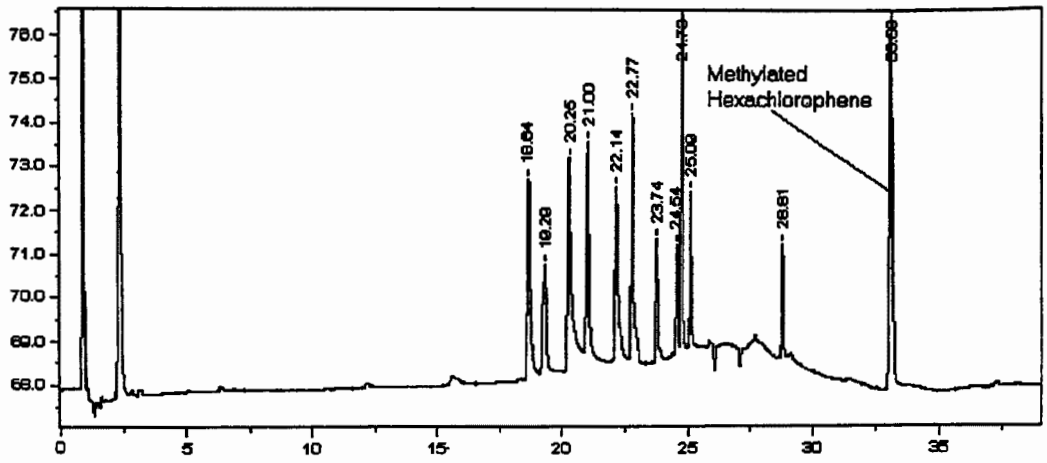


Figure 7
Chromatogram of Herbicide Methyl Esters and Hexachlorophene on DB-1701

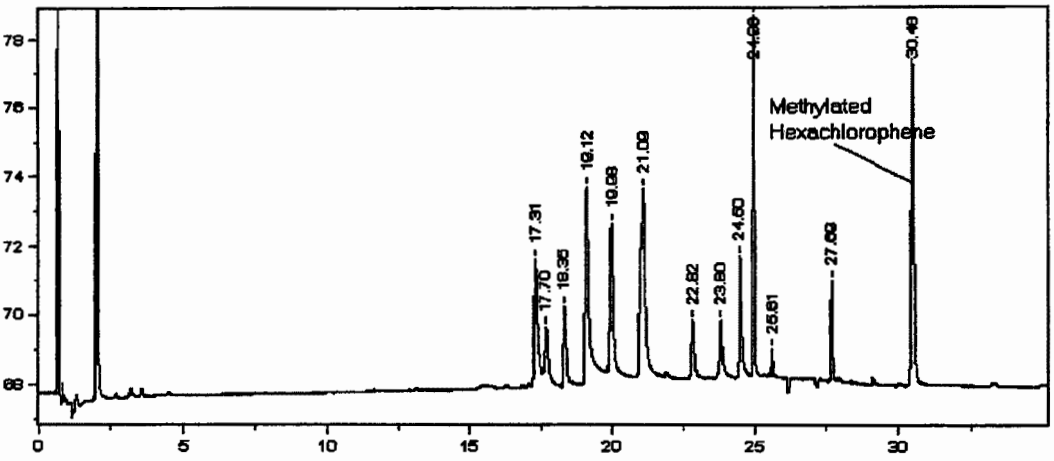


Figure 7
Calibration Curve on DB-608
Hexachlorophene Methyl Esters

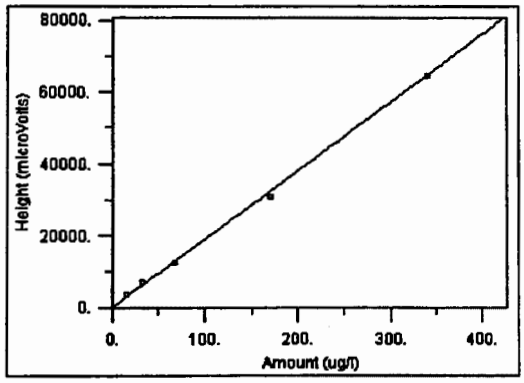
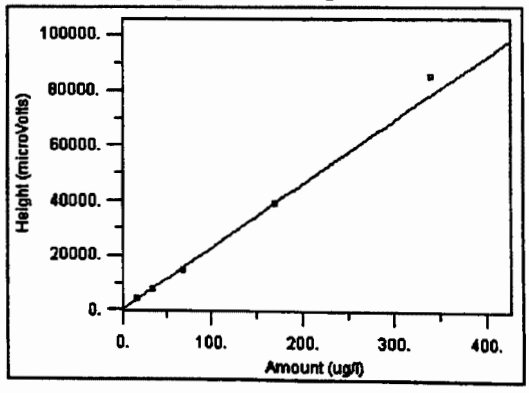


Figure 8
Calibration Curve on DB-1701
Hexachlorophene Methyl Esters



The samples were prepared according to the September 1994 revision of SW846-8151 Section 7.0.

The following steps summarize the preparation for waters:
- Add NaCl to 1 liter of sample
- Adjust pH of sample to greater than 12
- Extract with methylene chloride
- Adjust pH of sample to less than 2
- Extract with diethyl ether and dry with sodium sulfate
- Derivatize the extract with diazomethane using the bubbler method

The steps required in the preparation of soils include:
- Adjust pH of sample to less than 2
- Add sodium sulfate
- Extract with methylene chloride/acetone
- Hydrolyze the extract with KOH
- Extract with methylene chloride
- Adjust pH to less than 2
- Extract with diethyl ether and dry with sodium sulfate
- Derivatize the extract with diazomethane using the bubbler method

Preliminary extraction data indicated 40-50% recovery of hexachlorophene through this procedure, and that a significant amount of hexachlorophene was lost in the methylene chloride step. It appears that the pK of the second hydroxyl group is quite high and that even at a pH above 12, the hydrogen is not fully dissociated.

To address the low recovery of the hexachlorophene, the methylene chloride wash step was not performed, but instead, an additional florisil cartridge cleanup was used that was modified from the florisil cleanup described SW846 3620. Preliminary data from real-world soil samples indicate that the florisil cleanup is effective in reducing some types of chromatographic interferences.

A spiked water sample and a spiked soil sample were analyzed in triplicate.

Analytical Results

The results of the recovery study are illustrated in Figure 10.

Figure 10
Recovery Results for Hexachlorophene by SW846-8151
on DB-608

Sample	Spike amount	Spike found	% Recovery	%RSD
Water 1	9.7 ug/l	7.7 ug/l	79.	
Water 2	9.7 ug/l	8.1 ug/l	84.	
Water 3	9.7 ug/l	9.8 ug/l	101.	
				13.1
Soil 1	320. ug/Kg	240. ug/Kg	76.	
Soil 2	320. ug/Kg	310. ug/Kg	97.	
Soil 3	320. ug/Kg	230. ug/Kg	72.	
Soil 4	320. ug/Kg	270. ug/Kg	84.	
				13.4

Figure 11
Recovery Results for Hexachlorophene by SW846-8151
on DB-1701

Sample	Spike amount	Spike found	% Recovery	%RSD
Water 1	9.7 ug/l	9.0 ug/l	93.	
Water 2	9.7 ug/l	11.2 ug/l	115.	
Water 3	9.7 ug/l	12.3 ug/l	127.	
				15.4
Soil 1	320. ug/Kg	280. ug/Kg	87.	
Soil 2	320. ug/Kg	360. ug/Kg	114.	
Soil 3	320. ug/Kg	270. ug/Kg	85.	
Soil 4	320. ug/Kg	300. ug/Kg	95.	
				13.4

Conclusion

Recovery data indicate that SW846 8151 can successfully be applied to the analysis of hexachlorophene in soils and waters. This approach results in much improved chromatographic performance. The GC-ECD method provides for more reproducible and reliable detection and quantitation of hexachlorophene than does SW846 8270.

Some work remains to demonstrate the utility of this method and validate its performance. The conditions of the florisil cartridge cleanup need to be finalized. A quad study and method detection limit study need to be performed. The resulting Method Detection Limit and Practical Quantitation Limit obtained using SW846 8151 are expected to be two to three orders of magnitude lower than those obtained using SW846 8270.

SOLVENT RECOVERY IN THE PESTICIDE EXTRACTION LABORATORY UTILIZING STANDARD LABORATORY GLASSWARE

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ABSTRACT

With the enactment of the Clean Air Act, there is an increased interest in recovery of solvents used in the extraction of soil, water, and waste samples as prescribed by the U. S. Environmental Protection Agency's 500 series Drinking Water methods, 600 series Waste Water methods, and the SW-846 Solid Waste methods. Until promulgated methodology allows for the application of other techniques to pesticide trace residue analysis, such as supercritical fluid extraction (SFE) and solid phase extraction (SPE), the use of solvents such as methylene chloride, acetone, hexane, and diethyl ether are required. Following the extraction of the sample, aliquots of the solvent extract are combined in a Kuderna Danish concentrator. During a typical concentration process, the solvent is vented by a fume hood into the atmosphere. Our environmental laboratory began capturing some solvents several years ago. Our current goal is to capture more than 80% of the solvents we use, including those solvents used in the pesticides sample preparation laboratory. Commercially available solvent recovery products were reviewed on the basis of cost, ruggedness, and ease of use. Based on this review, it was determined that a more cost effective solution could be custom designed. Several vendor's systems and the performance of the custom designed system are reviewed.

INTRODUCTION

Air quality has been a major concern for the Environmental Protection Agency since the passage of the Clean Air Act in 1970. The list of compounds of interest has continued to expand through the 1980s which led to the passage of the Clean Air Act Amendments in 1990. These Amendments place more responsibility on industry and local, state, and federal agencies to keep the public informed about the health effects of the hazardous air pollutants (HAPs) emissions and levels of exposure to these pollutants.[1]

Although the Clean Air Act is seen by many forecasters of the environmental market as a driving force in the creation of an expanded market segment for analytical services, its focus is to hold industry accountable for emissions of HAPs. Many companies are concerned about environmental issues and are creatively seeking ways to minimize or eliminate the generation of hazardous waste through pollution prevention programs. In addition to concern for the environment, environmental and industrial laboratories that use solvents (many are listed as HAPs) in sample preparation should be aware of their potential liability under the provisions of Title I or Title III of the Clean Air Act Amendments. For the environmental laboratory, a perplexing paradox exists: The solvents that are regulated by the Clean Air Act are the same solvents that are required by current approved analytical methods. Table 1 summarizes the solvent requirements for several approved EPA methods.

Solvent reclaimation could contribute in a significant way to the minimization of solvent emissions from the pesticide sample preparation laboratory. In an effort to implement an effective solution, a study was conducted to compare several solvent reclaimation methods.

REVIEW OF LABORATORY OPERATIONS

Many of the current methods of sample extraction in the pesticide laboratory have similar approaches to the separation and concentration of target analytes from the sample matrix. First, a sample of soil or water is extracted with several hundred milliliters of a solvent such as methylene chloride using standard extraction techniques such as sonication, shake out in a separatory funnel, continuous liquid-liquid extraction, or soxhlet extraction. Secondly, the extract is concentrated in a Kuderna-Danish concentrator on a steam bath. A solvent exchange step to a non-halogenated solvent is required depending on which instrumental analysis method will be employed. Thirdly, the extract is subjected to various cleanup techniques such as gel permeation and solid phase cartridge cleanup. Re-concentration of the extract might be required after cleanup. And last of all, the extract is analyzed by gas chromatography (GC) using an electron capture detector (ECD), a nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), or flame ionization detector (FID). A solvent recovery system would be most effective during the Kuderna-Danish concentration step.

SOLVENT RECOVERY SYSTEM REQUIREMENTS

Several performance requirements and hardware specifications for our solvent recovery system were identified:

- The system needs to recover greater than 90% of the solvent during extract concentration.
- Negative impacts on the efficiency of laboratory operations need to be minimized.
- The hardware needs to be reasonably rugged to endure daily wear and tear.
- The initial cost of the hardware needs to be minimized.
- The operational cost of the system needs to be minimized.
- The safety of operators cannot be compromised.

COMMERCIALLY AVAILABLE SOLVENT RECOVERY SYSTEMS

Several vendors have developed solvent recovery systems that are based on different approaches to the recovery problem.

Some automated hardware is available that concentrates sample extracts and recovers the solvent one extract at a time. In our operation, several units would be required to obtain enough capacity to meet the demands of our laboratory. This approach did not meet our requirement of minimal initial cost.

Another approach is to connect some type of condenser to the Kuderna-Danish concentrator to collect the solvent vapors. Two vendors were considered that took this approach. The system design from one vendor included a specially designed Snyder/Condenser unit. The glassware appeared to be especially susceptable to breakage. There was no convenient way to perform the solvent exchange step. The size and dimensions of the unit made it difficult to use in the laboratory fume hood. The design from the other vendor reflected more closely the design of the glassware used in the normal operation of our laboratory. Some of the components appeared to be a special design, and these components were connected using rigid ball and socket clamp joints. There was a provision for solvent exchange. The potential for breakage appeared to be high which could lead to significant operational costs.

After a review of commercially available systems, it became evident that an effective solvent reclaimation system could be developed in house that would meet the system requirements of cost minimization, ruggedness, and operational efficiency. Table 2 summarizes the comparison of the various approaches that were considered in this study.

CUSTOM SOLVENT RECOVERY SYSTEM

The solvent recovery system designed at Lancaster Laboratories took advantage of the glassware and hardware that was already purchased. This included much of the glassware, including the Kuderna-Danish apparatus and the steam bath heater.

The solvent extract is placed in the Kuderna-Danish flask with its concentrator tube. A standard three-ball Synder column is attached to the flask. At this point, the Kuderna-Danish apparatus is placed on a steam bath located inside a fume hood. An aluminum rack supports the Kuderna-Danish apparatus as sample concentration occurs. A standard vacuum adapter is attached to the Snyder column. Flexible corrugated TEFLON tubing is attached to the vacuum adapter which provides a flow path for the solvent vapors to an Allihn condenser. A recirculating cooler provides the coolant to the condensers. The condensate collects in a gently sloping TEFLON tubing manifold and then flows through a drain line to a 10 liter collection vessel.

Figure 1 illustrates the setup of the custom solvent recovery system. The components used to construct the system are summarized in Table 3.

Hardware was assembled in two hoods to accomodate the simultaneous concentration of 24 sample extracts.

THE FUTURE OF SOLVENT RECOVERY

One reason that it was particularly appropriate to minimize capital expenditures is that approval of new methodologies utilizing alternative isolation and concentration techniques has been given by the EPA or the approval is imminent. Many of the 500 Series Drinking Water methods already allow for solid phase isolation techniques to be used. Immunoassay techniques are increasingly being applied to pesticide analyses. New methods are scheduled to be released with the Proposed Update III to the SW-846 collection of RCRA methods.[2] These methods include Method 3530(c) - Pesticides and PCBs by Open-Tubular Solid Phase Extraction; Method 3535 - Solid Phase Extraction Disk Method (SPE); Method 3545(c) - Automated Solvent Extraction (ASE); and many immunoassay methods specifically for pesticides - Methods 4015, 4020, 4040, 4041, and 4042. These new methods require much less solvent than conventional extraction techniques. This is very good news for the extraction laboratory. Lower levels of solvent usage translate to lower costs for solvent purchase and disposal, and more importantly, lower potential risks associated with worker exposure to these solvents.

In sample preparations where significant amounts of solvents are required, the recovery of those solvents will allow for the purfication and recycling of those solvents. This minimizes expenses associated with the purchase of new solvent and the disposal of the spent solvent. Recycling of solvents in the pesticide laboratory is especially challenging because of the range of solvents that are used. The broad scope of extraction techniques employed in the analysis of pesticides,

herbicides, and PCBs leads to mixtures of solvent that have similar boiling points that are difficult to separate for re-use.

CONCLUSION

The custom designed system meets the requirements of minimal initial cost, ruggedness, ease of use, and throughput. The system has been functioning well for several months. By designing and building our own system, a savings in initial capital investment of $10,000 - $12,000 was realized.

Figure 1
Custom Solvent Capture System

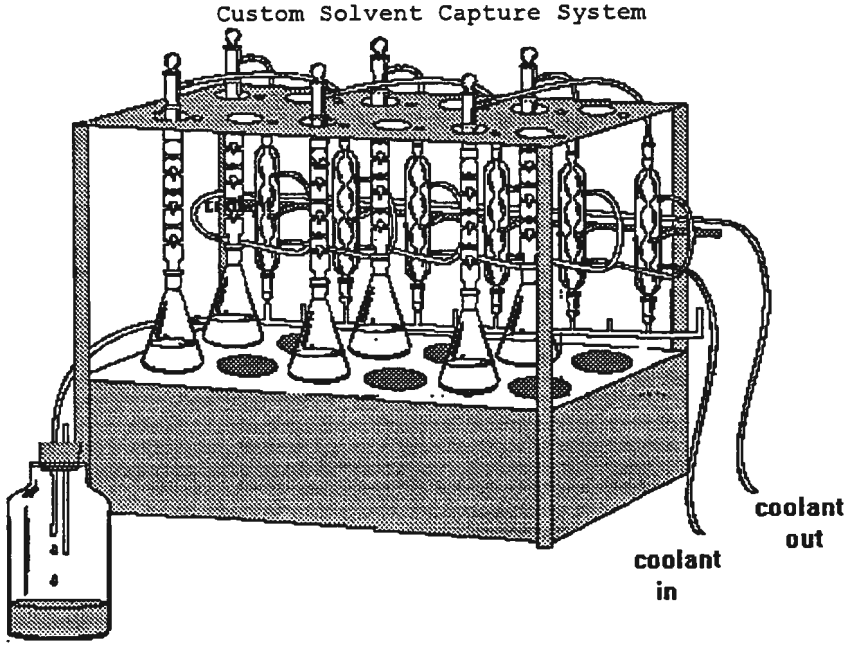

Table 2
Comparison of Approaches to Solvent Recovery

Vendor	Technique	Cost per Sample Position	Ruggedness	Ease of Use	Throughput (estimate)
Number 1	heating with fan action	>$2500.	unknown	unknown	serial process with 1 hour per sample
Number 2	heating with special K-D and condenser	$633.	possibly suseptible to breakage	somewhat cumbersome	estimate at 8 samples per 1/2 hour/unit
Number 3	heating with standard K-D	$695.	possible breakage from rigid connections	acceptable	estimate at 6 samples per 1/2 hour per unit
Custom	heating with standard K-D	$205.*	little breakage during 1st 4 months	acceptable	estimate at 12 samples per 1/2 hour per unit

* assumes use of already purchased steam bath and K-D units.

TABLE 1
Volumes of Solvent used in Sample Preparation
using Various EPA Methods

EPA Method	hexane (ml)	petroleum ether (ml)	methylene chloride (ml)	acetone (ml)	MTBE (ml)	aceto-nitrile (ml)	diethyl ether (ml)	Total (ml)
507/508	0	0	200	0	150	0	0	350
515	0	0	180	60	20	0	263	523
600/4-81-045	255	10	0	0	0	0	0	265
SW846-3640	0	0	100	0	0	0	0	100
SW846-8080-sw	135	0	195	285	0	0	0	615
SW846-8080-w	105	0	225	0	0	0	0	330
SW846-8150-sw	100	0	252	300	0	0	200	852
SW846-8150-w	0	0	0	30	0	0	512	542
SW846-8310-sw	0	0	195	285	0	0	0	480
SW846-8310-w	0	0	225	0	0	0	0	225

Table 3
Items for Custom Solvent Recovery System

Item	Vendor	Part Number	Cost	Number	Subtotal
Steam bath (12 pos)*	Lindberg/Blue M	MW-1130A-1	$2,000.00	1	$2,000.00
Teflon tubing (3/8")	Cole Parmer	G-06407-40	$64.30	1	$64.30
Teflon Tees (3/8")	Cole Parmer	G-06361-90	$38.53	12	$462.36
Teflon Elbow (3/8")	Cole Parmer	G-06361-60	$22.00	1	$22.00
Corrugated Teflon tubing (3/8")	Cole Parmer	G-06407-52	$70.00	5	$350.00
Extension Clamp	VWR	05-769-3	$9.72	12	$116.64
Clamp Holder	VWR	05-754	$5.53	12	$66.36
Pyrexplus 9500 ml bottle	VWR	B7579-9LS	$216.93	1	$216.93
Allihn Condenser	Perpetual Sys	PS500-03	$43.00	12	$516.00
Glass Stopper 24/40	Perpetual Sys	PS1300-05	$7.60	12	$91.20
Inlet/Outlet Adpt 24/40	Perpetual Sys	PS162-01	$8.43	12	$101.16
Inlet/Outlet Adpt 24/40	Perpetual Sys	PS164-01	$9.71	12	$116.52
Vacuum Adapter 24/40	Perpetual Sys	PS202-01	$24.51	12	$294.12
Green Plastic Clips	Perpetual Sys	05-880E	$1.68	12	$20.16
Tygon tubing (3/8")	VWR		$2.34	12	$28.08
			Total		$2,465.83

*NOTE: Steam bath was already in place so was considered sunk cost.

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2. Lesnik, B. and Ollie Fordham, "SW-846:The Current Status", *Environmental Lab*, December/January 1994/95, p. 25-33.

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DETERMINATION OF TNT IN SOIL AND WATER BY A MAGNETIC PARTICLE-BASED ENZYME IMMUNOASSAY SYSTEM.

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ABSTRACT

Use of immunoassays as field-screening methods to detect environmental contaminants has increased dramatically in recent years. Immunochemical assays are sensitive, rapid, reliable, cost-effective and can be used for lab or field analysis. A magnetic particle-based immunoassay system has been developed for the quantitation of TNT in soil and water. Paramagnetic particles used as the solid-phase allow for the precise addition of antibody and non-diffusion limited reaction kinetics. The magnetic particle-based immunoassay is ideally suited for on-site investigation and remediation processes to delineate TNT contamination. This system includes easy-to-use materials for collection, extraction, filtration and dilution of soil samples prior to analysis by immunoassay. The method detects TNT, and various nitroaromatic compounds such as Tetryl, and 1,3-5-Trinitrobenzene at less than 0.25 parts-per-million (ppm) levels in soil and at less than 1 part-per-billion (ppb) in water. The typical precision of the assay (within assay) in soil and water is less than 12% and 8%, respectively. Recovery studies averaged 106% from soil, and 103% from water. The analysis of soil samples by this ELISA correlates well with Method 8330, yielding a correlation coefficient (r) of 0.970; when water samples were compared to SW-846 Method 8330, a correlation (r) of 0.951 was obtained. The application of this ELISA method permits the cost-effective evaluation of samples with minimal solvent disposal and can result in savings of time and money. The system's flexibility allows the analysis of TNT in many other sample matrices with minimum sample preparation.

INTRODUCTION

TNT is the common name for 2,4,6-trinitrotoluene, the most widely used military high-explosive, it is used widely in shells, bombs, grenades, demolition and propellant compositions. Trinitrotoluene is produced at Army Ammunitions Plants (AAPs), its production from 1969 to 1971 was reported as 85 million pounds per month (Ryon et al., 1984). During that period, as much as one half million gallons of TNT wastewater were generated per day by a single TNT production facility (Hartley et al., 1981). The wastewater generated was collected in lagoons which after evaporation has resulted in localized areas of severe contamination. Storage and testing of explosives has also contributed to environmental contamination.

TNT is cosidered highly toxic, mutagenic and carcinogenic in bacterial and animal tests (U.S. EPA, 1989). The lifetime Health Advisory Level for TNT in drinking water has been set at 2 ppb (U.S. EPA, 1989). As military bases throughout the United States and Europe are decommissioned and turnovered for other uses, contaminated sites on these bases need to be remediated. To define the extent of contamination and monitor the progress of the cleanup, samples are initially screened on site, or sent for laboratory analysis. The analysis of TNT contamination in environmental samples is typically performed by HPLC, such as SW-846 Method 8330 (U.S. EPA, 1992), this method is accurate and precise but can be time-consuming and expensive. This poster describes a magnetic-particle solid-phase immunoassay method for TNT in water and soil samples. Immunoassays have the advantage of being rapid and less expensive than GC/MS or HPLC, as well as field-portable.

The principles of enzyme linked immunosorbent assays (ELISA) have been described (Hammock and Mumma, 1980). Magnetic particle-based ELISAs have previously been described and applied to the detection of pesticide residues (Itak et al, 1992, 1993; Lawruk et al, 1992, 1993; Rubio et al, 1991). These ELISAs eliminate the imprecision problems that may be associated with antibody coated plates and tubes (Harrison et al, 1989; Engvall, 1980) through the covalent coupling of antibody to the magnetic particle solid-phase. The uniform dispersion of particles throughout the reaction mixture allows for rapid reaction kinetics and precise addition of antibody. The TNT magnetic-based ELISA described in this paper combines antibodies specific for TNT with enzyme labeled TNT. The presence of TNT in a sample is visualized through a colorimetric enzymatic reaction and results are obtained by comparing the color in sample tubes to those of calibrators.

MATERIALS AND METHODS

Amine terminated superparamagnetic particles of approximately 1 um diameter were obtained from Perseptive Diagnostics, Inc. (Cambridge, MA). Glutaraldehyde (Sigma Chemical, St. Louis, MO). Rabbit anti-TNT serum and TNT-HRP conjugate (Ohmicron, Newtown, PA). Hydrogen peroxide and TMB (Kirkegaard & Perry Labs, Gaithersburg, MD). TNT, its metabolites, and non-related cross-reactants (Chem Service, West Chester, PA). Other explosives (U.S. Army Environmental Center, Aberdeen, MD).

The anti-TNT coupled magnetic particles were prepared by glutaraldehyde activation (Rubio et al, 1991). The unbound glutaraldehyde was removed from the particles by magnetic separation and washing four times with 2-(N-morpholino) ethane sulfonic acid (MES) buffer. The TNT antiserum and the activated particles were incubated overnight at room temperature with agitation. The unreacted glutaraldehyde was quenched with glycine buffer and the covalently coupled anti-TNT particles were washed and diluted with a Tris-saline/BSA preserved buffer.

TNT was dried using phosphorous pentoxide overnight under vacuum. TNT and TNT related compounds used during cross-reactivity studies were diluted in methanol to obtain

a stock concentration of 1000 ppb. The stocks were further diluted in TNT diluent to obtain concentrations of 10, 5, 1, 0.25, and 0.1 ppb. After dilution, the diluted compounds were analyzed as samples in the assay.

Soil samples (TNT free) were fortified with TNT in acetone to obtain concentrations of 1, 5 and 10 ppm, the samples were then air dried and analyzed promptly to minimize degradation. When analyzing soil samples, a simple extraction was performed prior to analysis: 10 g of soil and 20 mL of a methanolic solution are added to a soil collector (Figure 1). The collector was shaken vigorously for 1 minute and the mixture allowed to sit at least five minutes. The cap of the soil collector was then replaced with a filter cap and the extract collected in a small glass vial. The filtered extract was then diluted 1:500 in TNT zero standard and assayed. Water samples were collected in glass vessels with teflon lined caps before analyzing in the assay.

Diluted soil extract or water samples (100 uL) and horseradish peroxidase (HRP) labeled TNT (250 uL) were incubated for 15 minutes with the antibody coupled solid-phase (500 uL). A magnetic field was applied to the magnetic solid-phase to facilitate washing and removal of unbound TNT-HRP and eliminate any potential interfering substances. The enzyme substrate (hydrogen peroxide) and TMB chromogen (3,3',5,5'-tetramethyl benzidine) were then added and incubated for 20 minutes. The reaction was stopped with the addition of acid and the final colored product was analyzed using the RPA-I RaPID Analyzer™ by determining the absorbance at 450 nm. The observed absorbance results were compared to a linear regression line using a log-logit standard curve prepared from calibrators containing 0, 0.25, 1.0, and 5.0 ppb of TNT. If the assay is performed in the field (on-site), a battery powered photometer such as the RPA-III™ can be used.

RESULTS AND DISCUSSION

Figure 2 illustrates the mean standard curve for the TNT calibrators collected over 50 runs; error bars represent two standard deviations (SD). This figure shows the typical response of the assay and the reproducibility of the standard curve from run-to-run. The displacement at the 0.25 ppb level is significant (78.9 % B/Bo, where B/Bo is the absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard). The assay sensitivity in diluent based on 90% B/Bo (Midgley et al, 1969) is 0.07 ppb. When analyzing water samples, the assay has a range of 0.07 to 5.0 ppb. The assay range when analyzing soils in conjuction with the TNT Sample Extraction Kit is 0.25 to 5 ppm as a result of sample extraction and dilution.

A precision study was conducted in which four surface and groundwater samples were fortified with TNT at four concentrations, and assayed 5 times in singlicate per assay on five different days. The results are shown in Table 1. Coefficients of variation (%CV) within and between day (Bookbinder and Panosian, 1986) were less than 8% in both cases.

In another precision study, ten samples of two soils were weighed on a balance or measured by packed volume in the soil collector. The samples were then extracted and diluted (as described in the Methods Section), followed by assaying in duplicate in one assay. Results are shown in Table 2. The overall coefficient of variation for TNT measurement using components of the Soil Collection and the Soil Extraction Kit with analysis by the TNT RaPID Assay® was determined to be less than 12% in both cases.

Table 3 summarize the cross-reactivity data of the TNT RaPID Assay for various explosives and nitroaromatic compounds. The percent cross-reactivity was determined as the amount of analog required to achieve 50% B/Bo. The specificity of the antibody used, allows for the detection of TNT and various nitroaromatic compounds. Many non-structurally related organic compounds demonstrated no reactivity at concentrations up to 10,000 ppb (data not shown).

Table 4 summarize the accuracy of the TNT RaPID Assay in soil samples. Ten different soil types were fortified with TNT at 1, 5, and 10 ppm. The samples were extracted and diluted as described above, followed by analysis in the immunoassay. Soil recoveries obtained were: 97% at 1 ppm, 107% at 5 ppm, and 115% at 10 ppm, obtaining an average of 106% across the range tested.

Table 5 summarizes the accuracy of the TNT ELISA in water. Four ground water samples were spiked with TNT at the following levels: 0.25, 0.35, 0.50, 0.75, 1.50, 2.0, 3.0, and 4.0 ppb. TNT was recovered correctly in all cases with an average assay recovery of 103%.

Figure 3 illustrates the correlation of 30 water samples fortified with TNT, between the ELISA (y) and SW-846 Method 8330 (x) after correction for surrogate recovery. The regression analysis yields a correlation (r) of 0.951 and a slope of 0.98 between methods.

Correlation of nineteen field soil samples, analyzed by the ELISA method (y) and SW-846 Method 8330 (x) is illustrated in Figure 4. The regression analysis yields a correlation (r) of 0.970 and a slope of 0.93 between methods.

SUMMARY

This work describes a magnetic particle-based ELISA for the detection of TNT and its performance characteristics in soil and water samples. The assay compares favorably to SW-846 Method 8330, is faster, and eliminates the need for expensive instrumentation and solvent disposal. The ELISA exhibits good precision and accuracy which can provide consistent monitoring of environmental samples. Using this ELISA, forty (40) results from soil samples can be obtained in less than two hours without the variability encountered with antibody coated tubes and microtiter plates (e.g. coating variability, antibody leaching, etc.). This system is ideally suited for adaptation to on-site monitoring of TNT in water, soil, and solid waste samples.

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Table 1

Precision of TNT Measurement in Water

Source:	Surface	Municipal	Ground	Surface
Replicates	5	5	5	5
Days	5	5	5	5
N	25	25	25	25
Mean (ppb)	0.35	0.77	2.17	3.96
% CV (within)	7.8	4.3	2.9	3.4
% CV (between)	7.8	4.4	4.8	3.1

Table 2

Precision of TNT Measurement in Soil

Soil:	Manhatten, KS		Pleasant Hill, NC	
Sample Collection Method	weight	volume	weight	volume
Replicates	10	10	10	10
Mean (ppm)	0.55	0.53	0.41	0.41
% CV (total)	8.3	8.3	10.0	11.8

Table 3

Specificity (Cross-Reactivity)

Compound	90% B/Bo LDD (ppb)	50% B/Bo ED50 (ppb)	% Cross Reactivity
TNT	0.07	1.44	100
1,3,5-Trinitrobenzene	0.04	2.20	65.5
2,4-Dinitroaniline	0.10	22	6.5
Tetryl	0.10	30	4.8
2,4-Dinitrotoluene	1.0	35	4.1
2-Amino-4,6-dinitrotoluene	0.25	45	3.2
1,3-Dinitrobenzene	2.38	83	1.7
4-Amino-2,6-dinitrotoluene	0.10	98	1.5
2,6-Dinitrotoluene	100	3880	0.04
2,4-Dinitrotoluene	7.95	>10,000	<0.1
3-Nitrotoluene	155	>10,000	<0.1
RDX	702	>10,000	<0.1
1,2-Dinitrobenzene	1000	>10,000	<0.1
Dinoseb	1000	>10,000	<0.1
4-Nitrotoluene	1160	>10,000	<0.1
2-Nitrotoluene	2320	>10,000	<0.1
Nitrobenzene	3410	>10,000	<0.1
HMX	4520	>10,000	<0.1

B/Bo = Absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard.

% Cross Reactivity = Concentration of TNT exhibiting 50% inhibition (1.44 ppb) divided by the 50% inhibition of a compound x 100.

Table 4

Accuracy of the TNT RaPID Assay In Different Soil Types

TNT Added:	1 ppm TNT	5 ppm TNT	10 ppm TNT
Mean Observed (ppm)	0.97	5.34	10.2
n	10	10	10
%CV	11.1	8.1	8.1
% Recovery	97	107	102

Soil type analyzed: Beardon ,ND (clay loam); Churchville, PA (sandy loam); Glen Cove, NY (loam); Holland, PA (clay loam); Levittown, PA (silt loam); Munin (clay loam); Princeton, NJ (clay loam); Pt. Pleasant , NJ (sand); Tennessee (sandy loam); Wisconsin (loam).

Mean Observed = concentration obtained after fortification with the listed concentrations of TNT.

Table 5

Accuracy of The TNT RaPID Assay In Water

Added (ppb)	Observed (ppb)	SD (ppb)	Recovery (%)
+ 0.25	0.24	0.03	96
+ 0.35	0.35	0.04	100
+ 0.50	0.52	0.06	104
+ 0.75	0.79	0.05	105
+1.50	1.65	0.10	110
+2.00	2.11	0.11	105
+3.00	3.25	0.16	108
+4.00	3.95	0.16	99
Average			103

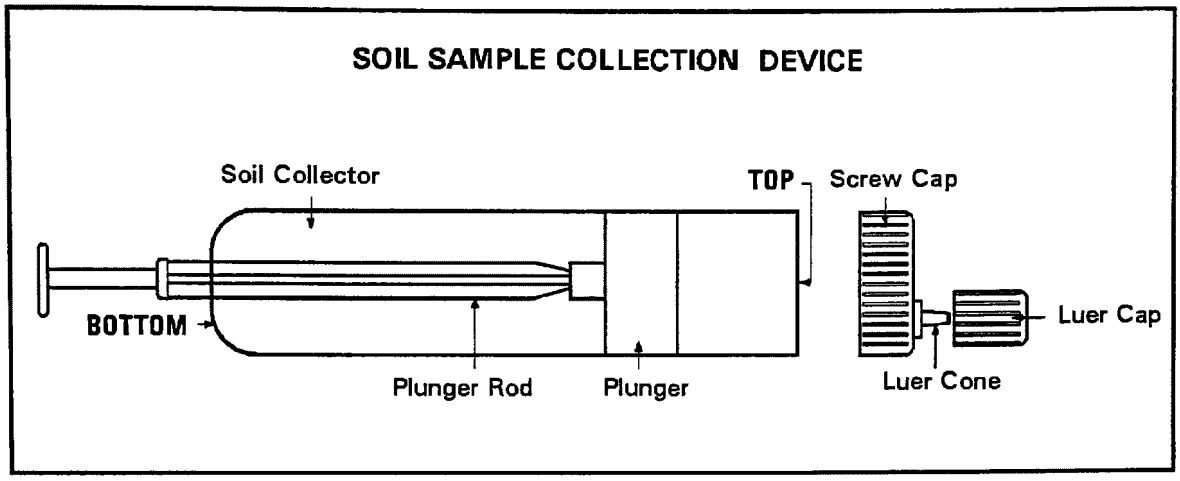

Figure 1. Diagram of soil collector used to collect and extract soil samples.

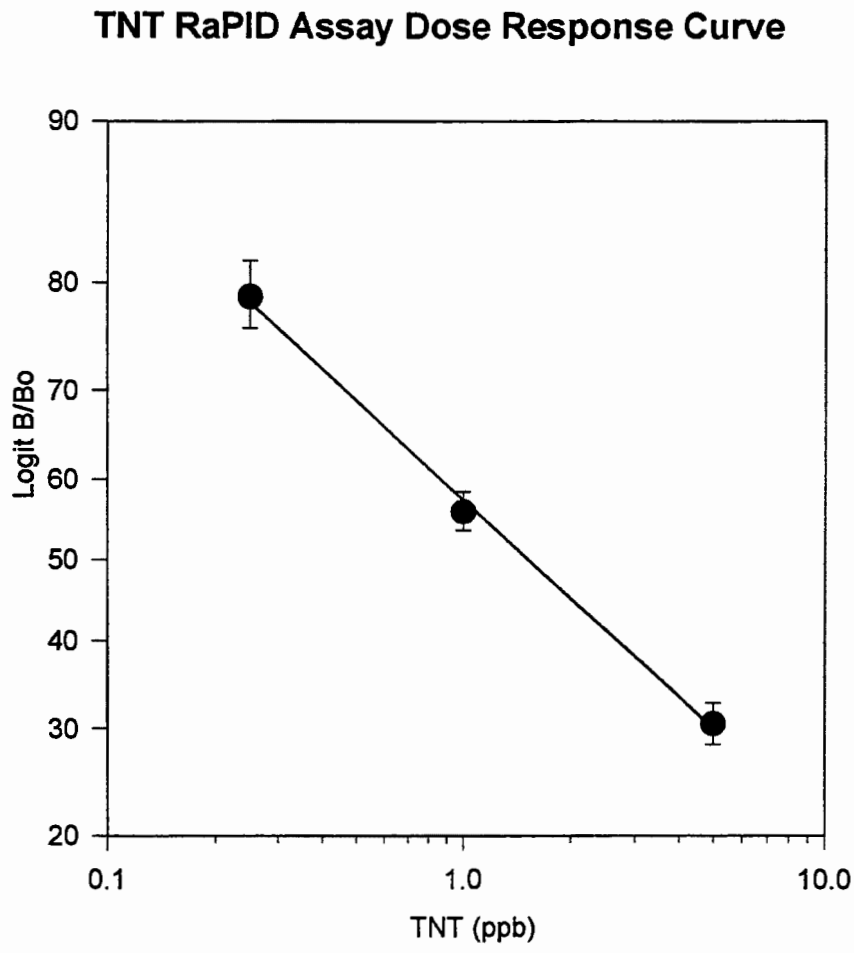

Figure 2. TNT RaPID Assay dose response curve. Each point represents the mean of 50 determinations. Vertical bars indicate +/- 2 SD about the mean.

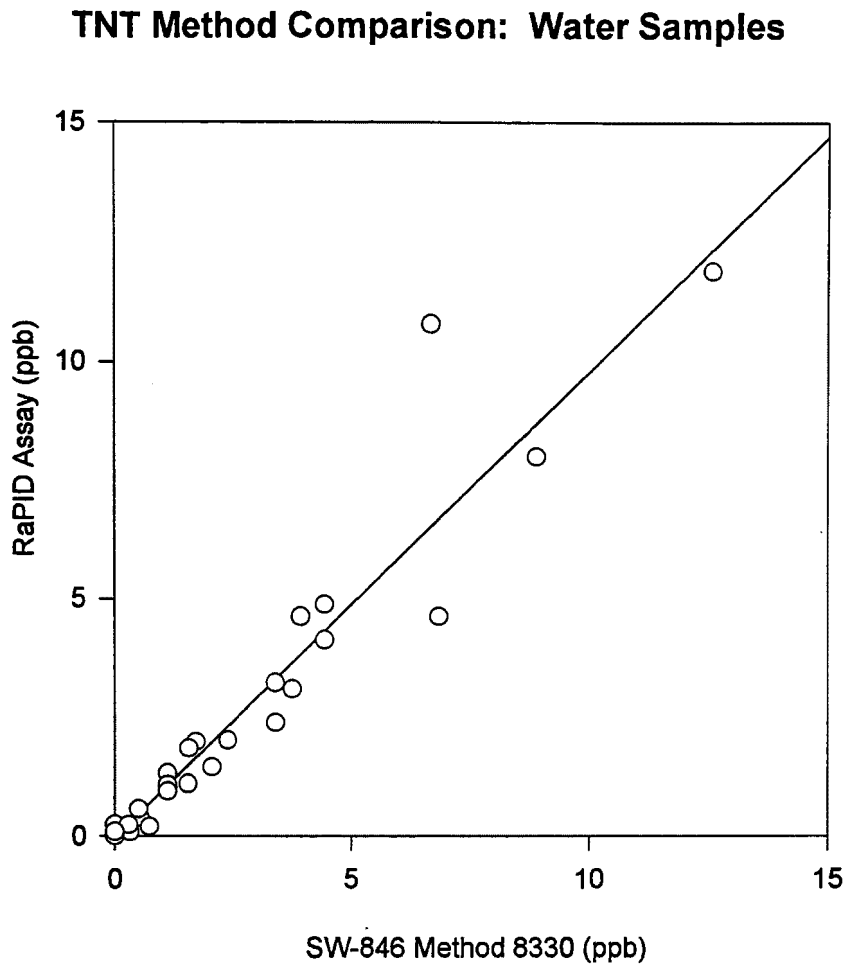

Figure 3. Correlation between TNT concentration as determined by the RaPID Assay and SW-846 Method 8330 (corrected for surrogate recovery) in water samples. n = 30, r = 0.951, y = 0.98x - 0.02.

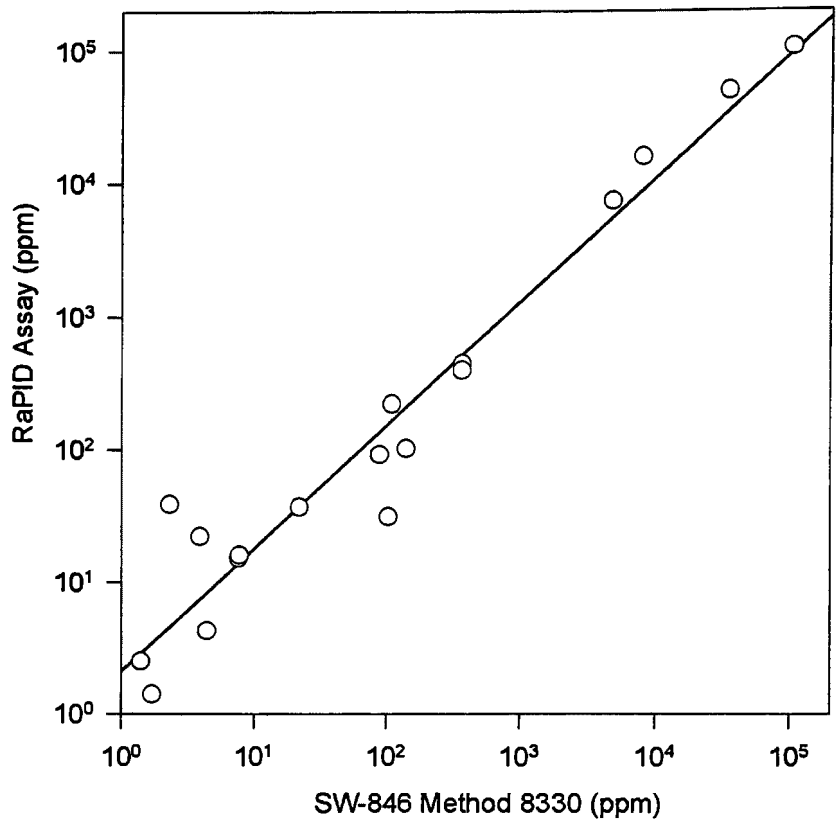

Figure 4. Correlation between TNT concentration as determined by the RaPID Assay and SW-846 Method 8330 in soil samples. n = 19, r = 0.970, y = 0.93x + 0.33.

An Immunoassay for 2,4,5-TP (Silvex) in Soil

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2-(2,4,5,-Trichlorophenoxy)propionic acid, known as 2,4,5-TP and Silvex, is a herbicide used for the control of trees and shrubs. 2,4,5-TP is a hormone type herbicide absorbed by leaves and translocated.

An Immunoassay has been developed that is sensitive to 2,4,5-TP in soil. The EnviroGard™ Silvex in Soil Kit uses clear plastic tubes coated on the inside with antibodies raised to 2,4,5-TP. Extracts from soil samples are added to the tubes along with a 2,4,5-Trichlorophenoxy-acetic acid (called 2,4,5-T)-enzyme conjugate competitor. This competitor is a 2,4,5-T molecule with an enzyme attached that competes with contaminates in the sample extract for a limited number of antibody binding sites. After a short incubation the competition is stopped by washing the tubes with tap water. The amount of antibody bound enzyme conjugate competitor remaining in the tube is inversely proportional to the amount of contamination in the soil. Next a clear solution of chromagenic (color producing) substrate is added to the tubes. The blue color that develops is also inversely proportional the contamination in the soil. The reaction is stopped after 5 minutes turning the product from blue to yellow and the tubes are read visually or in a portable photometer at 450 nm.

Soil extraction is accomplished by adding 10 mL of an extraction buffer to 5 grams of soil and shaking for 2 minutes. The extract is filtered and then used in the assay.

The assay is cross reactive to 2,4,5-T, a herbicide used post emergence and applied as a foliage spray. It is absorbed through roots, foliage and bark and along with 2,4-D was a major active ingredient in Agent Orange. Production of 2,4,5-T has been associated with significant levels of Dioxins as a by-product. Its production has been discontinued.

The detection limit of the assay for 2,4,5-TP is approximately 0.1 ppm and for 2,4,5-T approximately 0.02 ppm. Data will be presented on negative and fortified soil samples and cross-reactivity.

The Envirogard™ Silvex in Soil Kit provides a fast, convenient and field portable method of screening soils for contamination with 2,4,5-TP.

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DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOILS USING THERMAL EXTRACTION-GAS CHROMATOGRAPHY-PHOTOIONIZATION-ELECTROLYTIC CONDUCTIVITY DETECTION

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OI Analytical, P.O. Box 9010, College Station, Texas 77842

INTRODUCTION

Sample preparation is generally the most time consuming step in the analysis of semivolatile organic compounds. The extraction and concentration of the semivolatile organic compounds has traditionally been a complex, multistep procedure. The extraction of semivolatile organics from a solid sample matrix involves an initial estimate of concentration so that an appropriate mass of the sample is extracted. The sample is placed into the extraction apparatus and is then sonicated or Soxhlet extracted using an organic solvent or a mixture of organic solvents. The solid matrix is extracted for the amount of time specified in the extraction method, then the extracted liquid is collected and the volume is reduced. Any necessary sample cleanup procedures such as gel permeation chromatography or column chromatography are performed at this time. In many cases, the solvent is exchanged for hexane instead of the extracting solvent. The extract may now be injected into the gas chromatograph or other analytical instrument.

It can be seen that there are several disadvantages to using the above general procedure. The procedure is very labor intensive, and thus is quite expensive. Several of the most common and efficient extraction solvents are on the USEPA list of compounds whose use is to be minimized. Solvent use costs are steadily rising, with increased record keeping and disposal costs adding to the expense of using large volumes of solvents. One problem with the conventional extractions which is not generally recognized is the skill required to reproducibly extract samples. The least experienced personnel in the laboratory are generally assigned to this task. While extraction of large numbers of samples can be tedious, reproducible extractions are a key factor in reproducible final results.

Several methods can be used to modify the conventional extraction procedure to increase efficiency and reproducibility. One approach is to automate the current extraction process using robotics to increase the reproducibility of the mechanical phases of the process. This approach is very expensive and does not address the expenses in the use of large volumes of solvent. Automation of the current extraction process is not feasible for the majority of laboratories performing extractions for semivolatile analysis.

A more promising approach to the improvement of semivolatile organic analysis involves the use of alternative extraction technology. The most commonly used alternative to solvent extraction is extraction with a supercritical fluid, usually carbon dioxide or carbon dioxide with a small percentage of an organic solvent added as a modifier to increase extraction efficiency. Supercritical fluid extraction has suffered from matrix effects, and there is usually a lengthy method development process required before reproducible, efficient extraction parameters are determined.

Another technology which can replace conventional solvent extraction is thermal extraction. This technique involves heating the sample in a flow of an inert gas to volatilize the organics from the solid matrix. By controlling the temperature of the extraction cell, compounds of a specific volatility range may be selectively extracted from the sample matrix.

EXPERIMENTAL

The system used for this work was a Ruska Instrument Corporation ThermEx Inlet System interfaced to a Hewlett Packard 5890 Series II gas chromatograph. The gas chromatograph was fitted with an OI Analytical PID/ELCD tandem detector. The column used for this work was a J&W 30 m x 0.32 mm DB-5 with a 0.25 micron phase coating. The oven was held at 35°C for 6 minutes, ramped to 310°C at 8°C per minute, and held at 310°C for 2 minutes. The sample in the ThermEx Inlet System was held at 60°C for 1 minute, then ramped to 340°C at 35°C per minute, and held at 340°C for 2 minutes.

The samples for analysis were weighed into fused quartz crucibles before analysis. The crucibles had a quartz frit in the base and were fitted with a lid constructed from fused quartz frits. The sample size was approximately 50 milligrams for all samples.

The samples used in this work were clean soil which had been analyzed and was free of detectable semivolatile organic compounds, a subsample of this soil spiked with a standard mix of 14 polychlorinated biphenyl congeners, a subsample of the polychlorinated biphenyl soil spiked with diesel fuel, and a subsample of the clean soil spiked with a subset of the USEPA SW-846 Method 8270 analyte list. These samples were aliquots of mixtures used for the verification of thermal extraction technology for Draft Method 8275A, a gas chromatography-mass spectrometry method for the quantitative determination of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in soils and sediments.

RESULTS & DISCUSSION

Thermal extraction-gas chromatography-mass spectrometry has been accepted by the Organic Methods Work Group of the USEPA as a viable technique for the quantitative determination of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. Many analysts prefer to use detectors rather than mass spectrometers for a variety of reasons, including cost, complexity, and ruggedness. The issue of reliability becomes very important in mobile laboratory applications where it is often critical to have rapid sample turnaround. The use of selective detectors on a gas chromatograph interfaced to a thermal extraction unit eliminates many of the concerns analysts have regarding mass spectrometer use.

The samples described above were analyzed to determine the feasibility of using selective detectors instead of a mass spectrometer for semivolatile organic compound determination. Figures 1 and 2 are chromatograms of the PCB standard at a concentration of 5 PPM of each congener. Figure 1 is a photoionization detector trace of the standard spiked soil. The PCB congeners are in a retention

time window from 27 to 38 minutes. Even though the peaks are distinct for the congeners with retention time of approximately 30 minutes the signal is noisy and has a high baseline. The smaller peaks may be compounds other than PCBs which are present in concentrations too low to detect with a mass spectrometer.

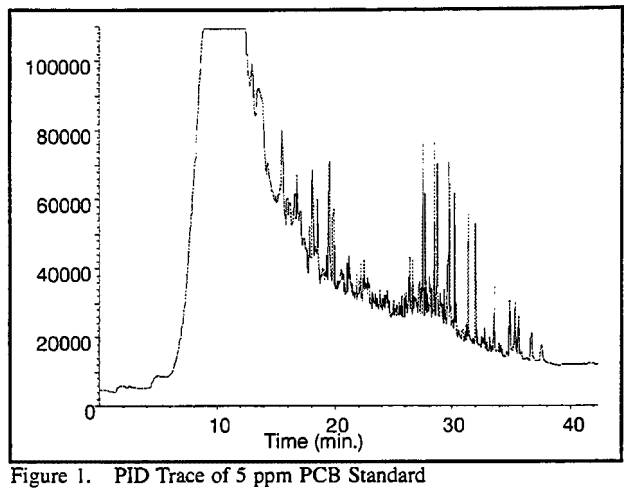

Figure 1. PID Trace of 5 ppm PCB Standard

Figure 2 is the electrolytic conductivity detector trace for the same sample run. The ELCD is very selective for halogenated compounds, and the trace shows responses only for the PCBs and any trace halogenated components which may be present in the soil. The chromatogram is much simpler with quantitation and congener identification using ELCD detection instead of PID detection.

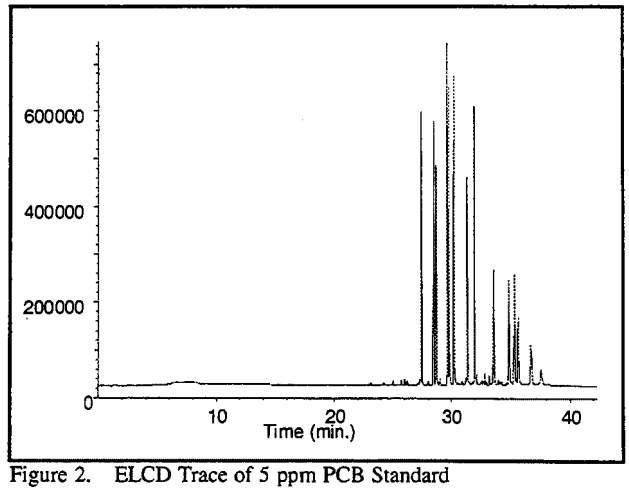

Figure 2. ELCD Trace of 5 ppm PCB Standard

Figure 3 illustrates the sensitivity of selective detectors interfaced to the thermal extraction inlet. The PCB congeners in this soil sample were present at a concentration of 0.5 ppm of each component. All fourteen congeners in the mixture are easily detected at this level, which is lower than the method detection limit specified in Method 8275A. The peak broadening seen in the late eluting peaks is due to the temperature limitations of the PID in the tandem configuration. A stand-alone ELCD will have a better peak shape, increased peak height, and improved detection limits.

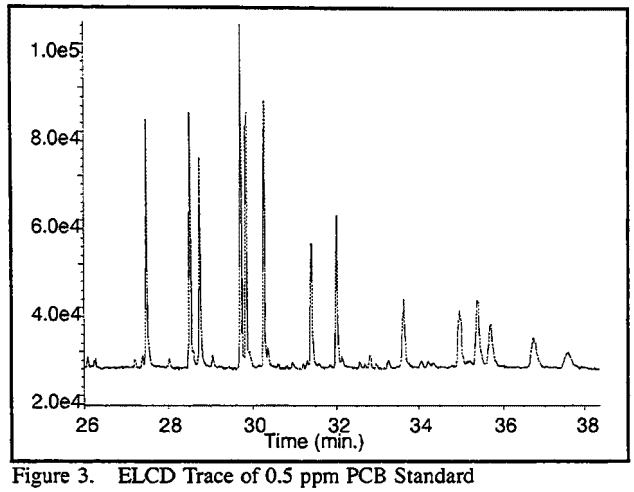

Figure 3. ELCD Trace of 0.5 ppm PCB Standard

Figures 4 and 5 show an analysis of a sample which is more representative of the types usually analyzed. The soil for this sample was spiked with a high concentration of diesel fuel, giving a high hydrocarbon background. The PID trace, Figure 4, is similar to the trace of a GC-MS run of the same type of sample. In both cases, the analyte peaks are masked by the high background signal. Extracted ion chromatograms from a mass spectrometer run should allow the integration and quantitation of the PCB congeners, but the high background level of hydrocarbons may affect ionization efficiency and cause inaccurate quantitation.

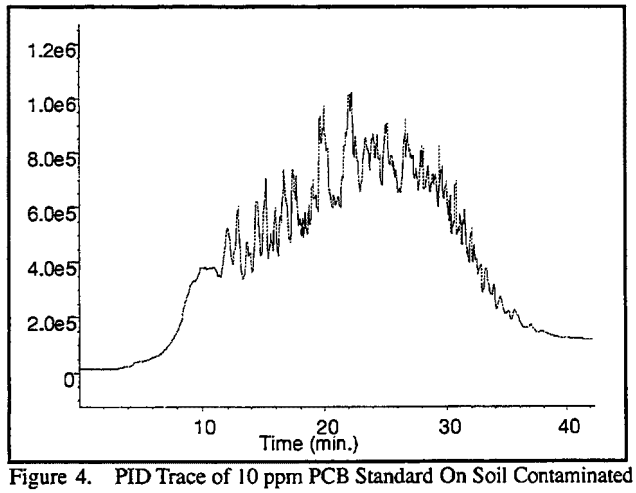

Figure 4. PID Trace of 10 ppm PCB Standard On Soil Contaminated With Diesel Fuel

Figure 5 illustrates the value of selective detectors in the analysis of a complex sample matrix. The high levels of hydrocarbon present in the sample are not detected by the ELCD, so the chromatogram shows only the PCB congeners. This chromatogram may easily be integrated and the compounds quantitated accurately. The use of a selective detector for the analysis of this sample eliminated the need for sample cleanup.

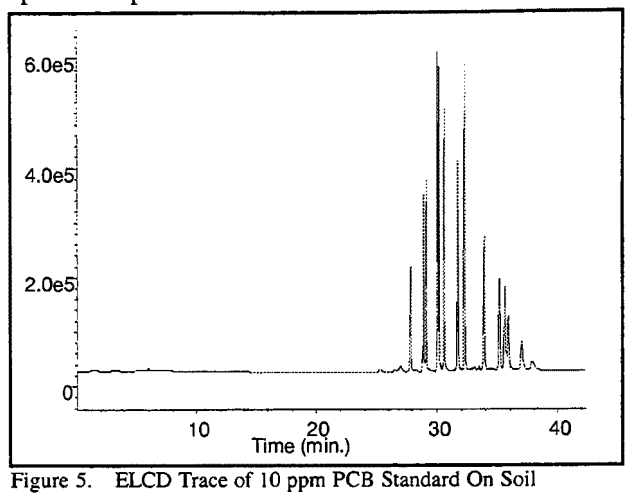

Figure 5. ELCD Trace of 10 ppm PCB Standard On Soil Contaminated With Diesel Fuel

An important point is the speed of the extraction and analysis of the PCB congeners when using the thermal extraction-gas chromatography-mass spectrometry system. The system is configured so that the extracted analytes are transferred directly to a gas chromatograph injection port, and the extraction and analysis are integrated. The total extraction and analysis time for the PCB congeners is approximately 40 minutes. In cases where rapid sample turnaround is essential, this system will provide quantitative data in a very short time.

The use of selective detectors improves detection limits for halogenated compounds compared to mass spectrometers. A mass spectrometer operates at low flow rates, but a thermal extraction unit requires a relatively high flow rate, generally 20 to 40 mL/min, for an efficient transfer of the semivolatile organic compounds to the gas chromatograph injection port. This leads to using a split ratio of approximately 30 to 1 for most thermal extraction-gas chromatography-mass spectrometry work. Selective detectors can handle much higher flow rates, and with the use of megabore columns can be operated in a splitless mode. Selective detectors can also have inherently lower detection limits for classes of organic compounds than mass spectrometers. These factors allow detection limits to be significantly lower for selective detectors than for mass spectrometers.

CONCLUSION

The use of selective detectors is a viable alternative to mass spectrometry when using a thermal extraction-gas chromatography system for the analysis of semivolatile organic compounds. When the sample matrix is complex the use of selective detectors may be preferable as only the compound classes of interest are detected. Selective detectors may also improve the detection limits for the analytes of interest. A thermal extraction system configured with selective detectors on the gas chromatographs addresses the issues of cost, reliability, and complexity while eliminating solvent extraction.

Congener-Specific Separations of PCBs- Extraction by SPME, Separation by Capillary GC, and Detection by ECD and MS

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Supelco, Inc., Supelco Park, Bellefonte, PA USA 16823-0048

ABSTRACT

A variety of capillary GC columns, along with a new column containing a bonded octylmethyl polysiloxane stationary phase (SPB-Octyl), were evaluated for their propensity to separate PCB congeners. The separation of all 209 PCB congeners on columns including: 5%, 20%, 35%, and 50% phenyl polysiloxane phases as well as polydimethylsiloxane were included in the study. Emphasis was placed on the separation of low-level toxic PCB congeners belonging to the classification of "coplanar PCBs". The elution order of PCB congeners was affected by the column polarity and polarizability.

Extracting PCB congeners from soil by using solid phase microextraction(SPME) proved to be successful. SPME is a solventless alternative to soxlet extractions. By exposing the 1cm-long polydimethylsiloxane-coated fiber at the tip of the SPME device to the headspace above the soil, PCB congeners were extracted and concentrated without using solvents. Extractions usually required 15-30 minutes and the SPME fibers were reused 50-200 times. The PCB congeners were then desorbed in the GC injection port, where they are transferred to the column.

INTRODUCTION

The analysis of PCB congeners is challenging in several respects. Synthetic PCB mixtures are commonly retained in soil, sludge, clay and airborne particles, but are quite insoluble in water. PCBs bioaccumulate in food chains. They can be traced from soil and air to plant life, from plants to herbivores, and from herbivores to various levels of carnivores. Both aquatic and terrestrial animals bioaccumulate PCBs, mainly in fat tissue and vital organs. The most toxic PCB congeners are in low abundance in synthetic PCB mixtures, but exist in higher concentrations in incinerator fly-ash. Escalating the analytical challenge is the large number of possible PCB congeners, 209, with as many as 10-15 congeners eluting per minute from a high resolution GC column. The sheer

complexity has resulted in quantitation often being reported for two or more coeluting congeners.

PCBs have received considerable regulatory attention because the high toxicities of a dozen individual PCB congeners are similar to the toxicities of several dioxins. The key to the toxicity of these PCB and dioxin congeners to mammals is found in their chemical structures (**Figure A**). The two structures on the left side of Figure A represent PCB congeners. Substitution of chloro-groups in the *ortho* positions has a marked affect on the free rotation of the coupled phenyl rings. PCB 77 (3,3',4,4'-TCB) is highly toxic and is found in low abundance in synthetic PCB mixtures, while PCB 110 (2,3,3',4',6-PCB) is quite abundant, but relatively non-toxic. The key to the difference in their toxicities is in their chemical structures (**Figure B**). The most toxic PCB congeners have chloro-groups in the 3,4,4' positions, with zero or one chloro-group in the 2 or *ortho* position. In PCB 77 there is unrestricted rotation of the bond that links the phenyl groups. Therefore, the phenyl rings of PCB 77 can achieve geometries that are essentially coplanar. The most toxic dioxins and furans contain the common 2,3,7,8-tetrachloro-substitution with aromatic rings that are coplanar. On the other hand, the phenyl rings of PCB 110 are restricted in rotation, due to the chloro-substitution in the two *ortho* positions. PCB 110 is limited to noncoplanar conformations.

EXPERIMENTAL

Five capillary GC columns were evaluated for PCB congener separations. The separation of all 209 PCB congeners was determined on polydimethylsiloxane (SPB-1) and on 5% (SPB-5), 20% (SPB-20), and 50% (SPB-50) phenyl polysiloxane bonded phases. A new capillary GC column, SPB-Octyl, containing 50% n-octyl groups on a polysiloxane backbone, was evaluated based on the previous positive results [1-4]. ECD and MSD detection with splitless injections (300°C) on HP-5890 were used in this work. The columns were run with helium carrier gas at 37.5cm/s at 40°C. Oven temperatures were programmed from 75°C (2 min) to 150°C at 15°C/min, then to 280°C at 2.5°C/min. The last congener, PCB 209, always eluted before 280°C during temperature programming. Mixtures of PCB congeners, at 40pg/µL per congener for ECD and 4ng/µL for MSD; as well as Aroclor mixtures at 400ppb for ECD and 40ppm for MSD were utilized. The limits of detection were approximately 0.5ppb/congener by ECD and 10ppb/congener for MSD.

RESULTS AND DISCUSSION

The ECD chromatogram in **Figure C** illustrates the complexity of PCB congener separations, with nearly 100 congeners eluting within 8 minutes. The brackets

below the chromatogram mark the elution ranges of PCB homologs: trichloro-, tetrachloro-, pentachloro-, hexachloro-, heptachloro- and octachlorobiphenyls. There are 30 possible tetrachloro-, 46 pentachloro- and 42 hexachlorobiphenyl congeners. This complexity leads to coelutions of PCB homologs and overlapping of elution ranges for PCBs of different homologs (e.g., pentachloro- and hexachlorobiphenyls).

With a mass selective detector (MS, MSD or ion trap), the congeners of each chloro-homolog can be extracted from the total ion chromatogram. In this slide, pentachlorobiphenyls (m/z 326) and hexachlorobiphenyls (m/z 360) are stacked separately (**Figure D**), thereby overcoming the overlapping of elution ranges. For instance, partially coeluting PCB 118 and PCB 132 can be correctly identified by retention time or retention index and accurately quantified by using extracted ion plots. ECD is more sensitive to PCB congeners, but mass spectrometric detection is more selective and enhances the chromatographic separation.

The effect of chloro-substitution in the *ortho* positions can be classified into six categories (**Figure E**). Non-*ortho* and mono-*ortho*-substituted PCB congeners can achieve coplanar conformations since the phenyl groups are free to rotate. Rotation about the common bond of di-*ortho*-substituted PCB congeners diminishes, due to steric hindrance. The number of conformations is limited further by tri-*ortho* and tetra-*ortho* substitution of chloro-groups. Achieving coplanarity with these congeners is impossible since two chloro groups repulse each other as the phenyl groups approach coplanarity. With no chloro-groups in the *ortho* positions, PCB 77 has unrestricted rotation and is capable of coplanar conformations. On the other hand, PCB 95 contains three chloro-substituents in *ortho* positions, thereby reducing rotational freedom and limiting phenyl group conformations to nearly perpendicular geometries. An interesting note is that the aromatic rings of the most toxic chloro-substituted aromatics (dibenzodioxins, dibenzofurans and naphthalenes) are rigid and planar (Figure A), whereas the most toxic PCB congeners are flexible and coplanar.

These classes of ortho-substituted PCBs overlap to differing degrees on the capillary columns we studied. With the 5% phenyl SPB-5 column (**Figure F**) there was some overlap of the di-*ortho* (2,6 and 2,2') with the tri-*ortho* (2,2',6)-substituted pentachlorobiphenyls. With SPB-20 the overlap increased, because the increased phenyl content of the column stationary phase widened the elution range of the *ortho*-substitution classes.

The overlap between *ortho*-substitution classes of PCBs increases with increasing phenyl-substitution in the column stationary phase. With the 50% phenyl SPB-50 column (**Figure G**), the elution zones are approximately twice as wide as those for SPB-5 column. The basis of the widening of the elution zones is the increased average dipole-induced dipole interactions between the

polarizable phenyl-containing phases (SPB-5, SPB-20, and SPB-50) and the moderately polar PCB congeners.

With SPB-Octyl columns, the elution zones for the *ortho*-substitution classes are narrower and well separated from each other (**Figure H**). The brackets help to show that the noncoplanar congeners (e.g., tetra-*ortho 2,2',6,6'*) elute first and the flexible coplanar congeners (e.g., non-*ortho*) elute last for each group of chloro-homologs. One of the most toxic PCB congeners, non-*ortho*-substituted, coplanar PCB 126 (3,3',4,4',5-PeCB), elutes well separated and last in the group of pentachlorobiphenyls.

The same pattern is evident for the hexachlorobiphenyls (**Figure I**) separated on the SPB-Octyl column. Another of the most toxic PCB congeners, PCB 169 (3,3',4,4',5,5'-HxCB), also a non-*ortho*-substituted, coplanar congener, elutes last among the hexachloro homologs.

The column stationary phase has a significant effect on the elution order of PCB congeners. The enlarged segments of the chromatographic separations of heptachlorobiphenyls 170 (2,2',3,3',4,4',5-HpCB) and 190 (2,3,3',4,4',5,6-HpCB) depicted in **Figure J** demonstrate the effect that increasing phenyl content in the column phase has on elution order. PCB 190 has 2 chloro-groups in the *ortho* positions, while PCB 170 contains only one. PCB 170 elutes first on the SPB-1 and SPB-5 columns, but is retained more on SPB-20 and SPB-50. SPB-Octyl has the same elution order as SPB-1, but provides resolution and retention times similar to SPB-50. As an illustration of the change in elution order, resolution values for 170/190 are positive for SPB-Octyl, SPB-1 and SPB-5, but negative for SPB-20 and SPB-50.

The resolution values for a number of closely eluting or coeluting congeners on SPB-5 are listed for the five column phases evaluated (**Figures K and L**). The sets of doublets shown in these figures have the same number of chloro-substitutions; Type A are classified by the same *ortho*-substitution class, while Type B correspond to different substitution classes. PCB 31 and PCB 28 separate on SPB-Octyl, but not on the other phases. Type A separations are the most difficult because the chemical structures and boiling points are very similar. Type B separations are more easily facilitated by the differences in *ortho* substitution.

Type C separations (Figure L) involve congeners from different chloro-homologs and different *ortho*-substitution classes. The changes in resolution values from SPB-1 up to SPB-50 were not higher than 3 units, while from SPB-1 to SPB-Octyl changes as high as 10-14 units were achieved. The accentuated resolution using the SPB-Octyl column indicates a unique selectivity of this column for PCB congeners.

Solid phase microextraction (SPME) is a means of rapidly extracting PCB congeners from soil. The process of microextracting and concentrating organic compounds from a sample of water, soil or sludge by SPME is shown in **Figure M**. By exposing the 1cm-long polysiloxane-coated fiber at the tip of the SPME device to the headspace above the soil, one can extract and concentrate PCB congeners without using solvents. Extractions usually require 15-30 minutes. The PCBs then are desorbed in the injection port, where they are transferred to the column.

The ECD chromatogram in **Figure N** depicts the SPME-extracted organics from a stream sediment collected downstream from a major industrial site where transformer oils accidentally leaked into the stream more than 10 years ago. The extracted PCB profile is nearly identical to that of Aroclor 1242, except for the increased abundance of several di- and trichlorobiphenyls. To give an idea of the extraction levels, the peak representing PCB 44/65 were at 700 parts per trillion and PCB 105 was at 50 parts per trillion. With SPME extraction a minimum extraction limit of less than 5 parts per trillion is detectable by ECD, with an extraction time of only 60 minutes.

CONCLUSIONS

From this work, one can conclude that the SPB-50 column phase exhibited the strongest dipole-induced dipole interactions with PCB congeners. The SPB-Octyl column was shown to have unique separation characteristics. The elution orders of PCB congeners that typically coelute on SPB-5 columns were opposite for the SPB-Octyl and SPB-50 columns. Congeners of the same chloro-homolog elute in discrete ranges, as a function of their chloro-substitution in the four *ortho* positions. The noncoplanar tetrachloro-*ortho* congeners eluted first and the non-*ortho* congeners eluted last for each series of chloro-homologs. SPB-Octyl and SPB-1 columns provide an excellent dual-column system for ECD, with the SPB-Octyl/SPB-50 combination also showing promise. Finally, PCB congeners can be extracted from soil by solid phase microextraction (SPME), down to parts per trillion, without the need for solvents.

Figure A. Chemical structure of toxic halogenated aromatics.

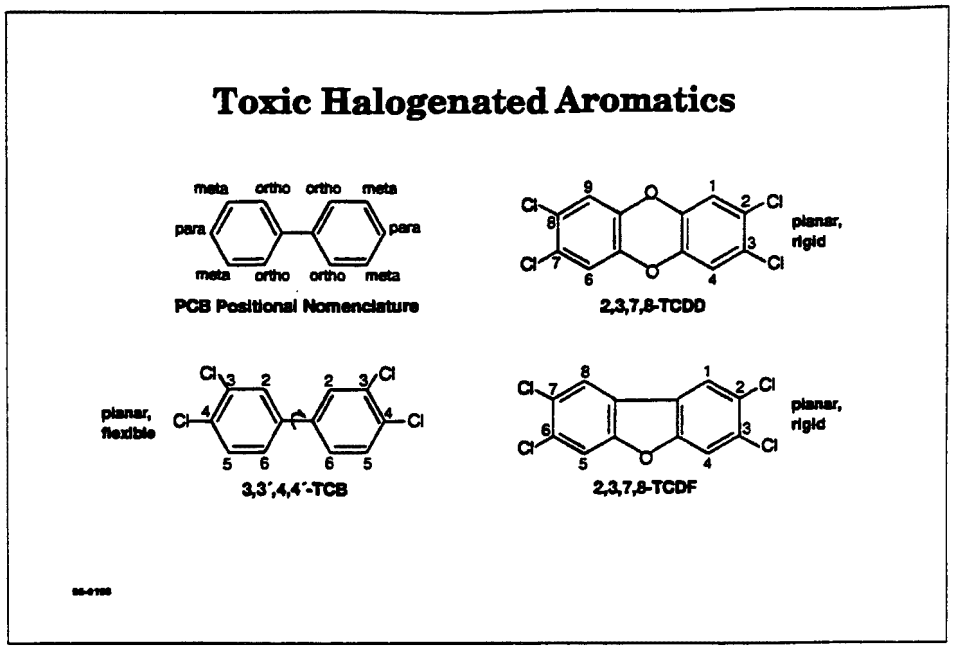


Figure B. List of toxic equivalence factors (TEF) for dioxin-like PCB congeners.

Toxic, Dioxin-Like PCBs

Type	PCB Congener IUPAC No.	PCB Congener Structure	Toxic Equivalency Factor (TEF)
Non-*ortho*	77	3,3',4,4'-TCB	0.0005
	126	3,3',4,4',5-PeCB	0.1
	169	3,3',4,4',5,5'-HxCB	0.01
Mono-*ortho*	105	2,3,3',4,4'-PeCB	0.0001
	114	2,3,4,4',5-PeCB	0.0005
	118	2,3',4,4',5-PeCB	0.0001
	123	2',3',4,4',5-PeCB	0.0001
	156	2',3,3',4,4',5-HxCB	0.0005
	157	2',3,3',4,4',5'-HxCB	0.0005
	167	2',3',4,4',5,5'-HxCB	0.00001
	189	2',3,3',4,4',5,5'-HpCB	0.0001
Di-*ortho*	170	2,2',3,3',4,4',5-HpCB	0.0001
	180	2,2',3,4,4',5,5'-HpCB	0.00001

U.G. Ahlborg, *et al.*, *Chemosphere* 25 (6):1049-1067 (1994).

Figure C. Capillary ECD chromatogram of Aroclor 1254.

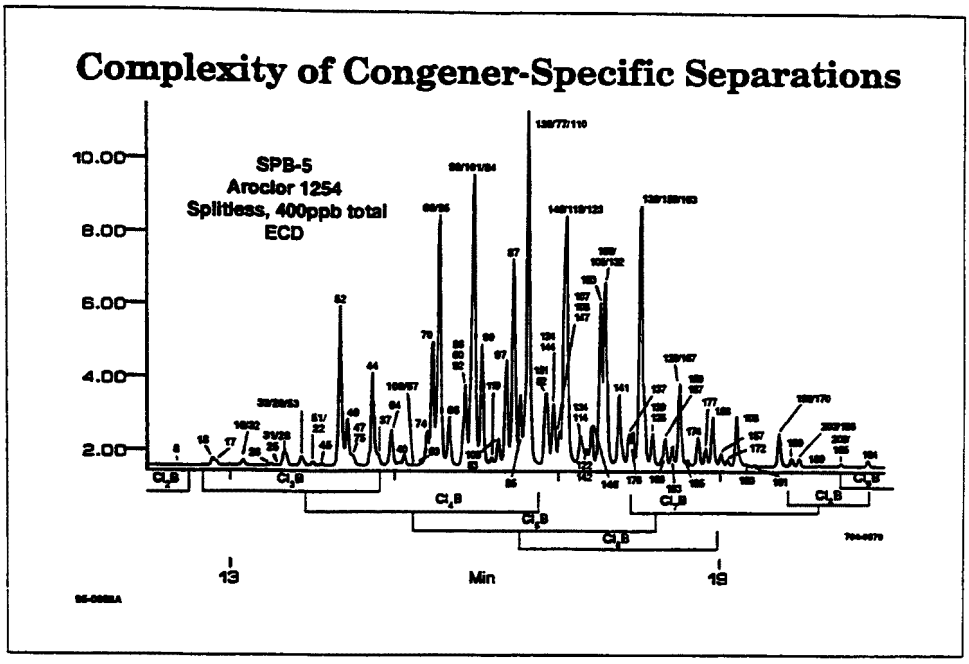


Figure D. Selected ion chromatograms for pentachlorobiphenyls and hexachlorobiphenyls.

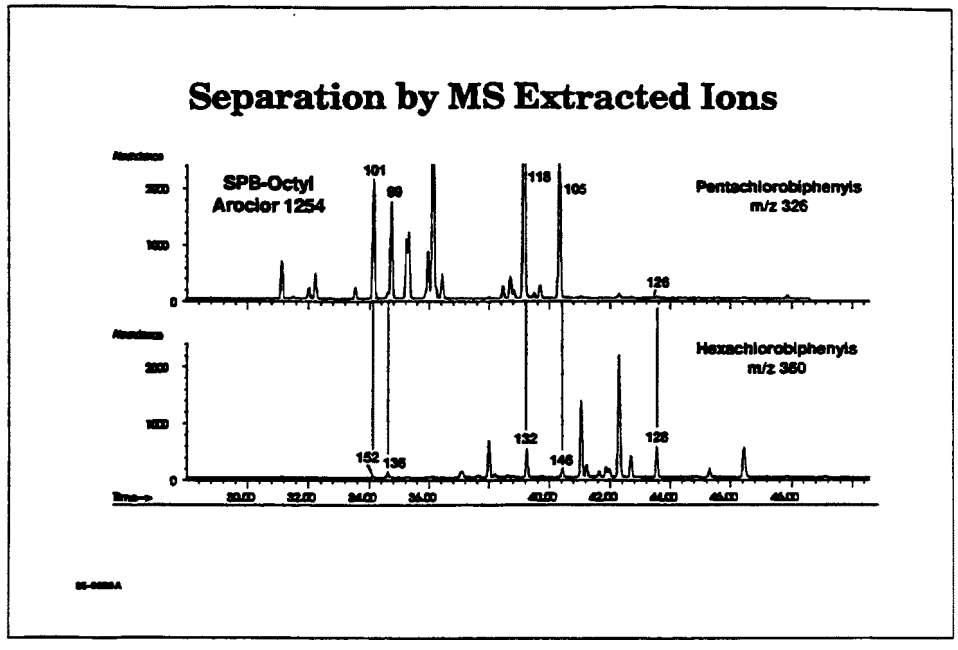


Figure E. Effect that chloro-substitution in the *ortho* positions has on the coplanarity of PCB congeners.

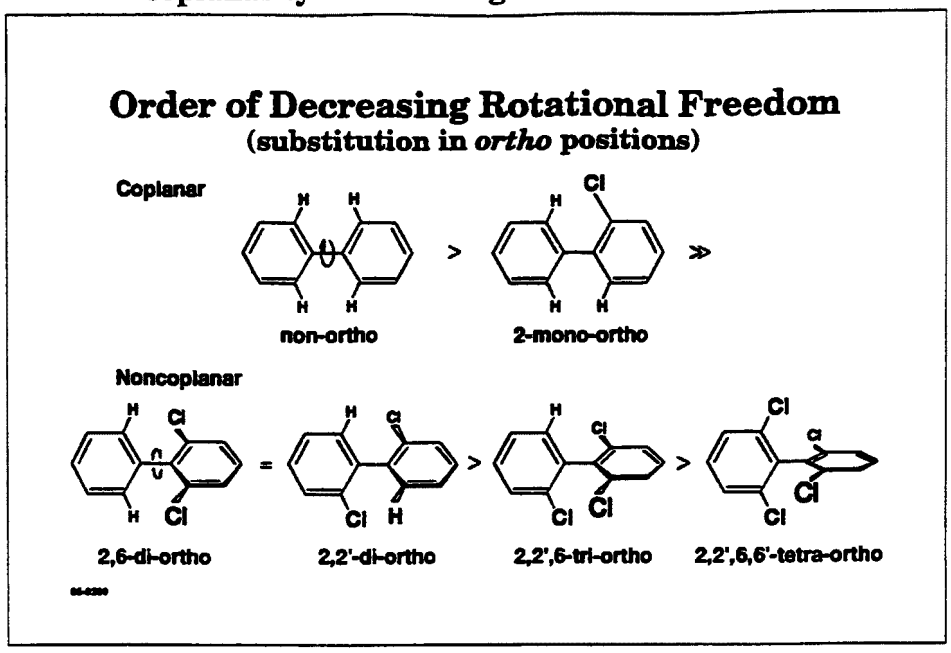


Figure F. Separation of *ortho*-substituted PCBs on the SPB-5 column.

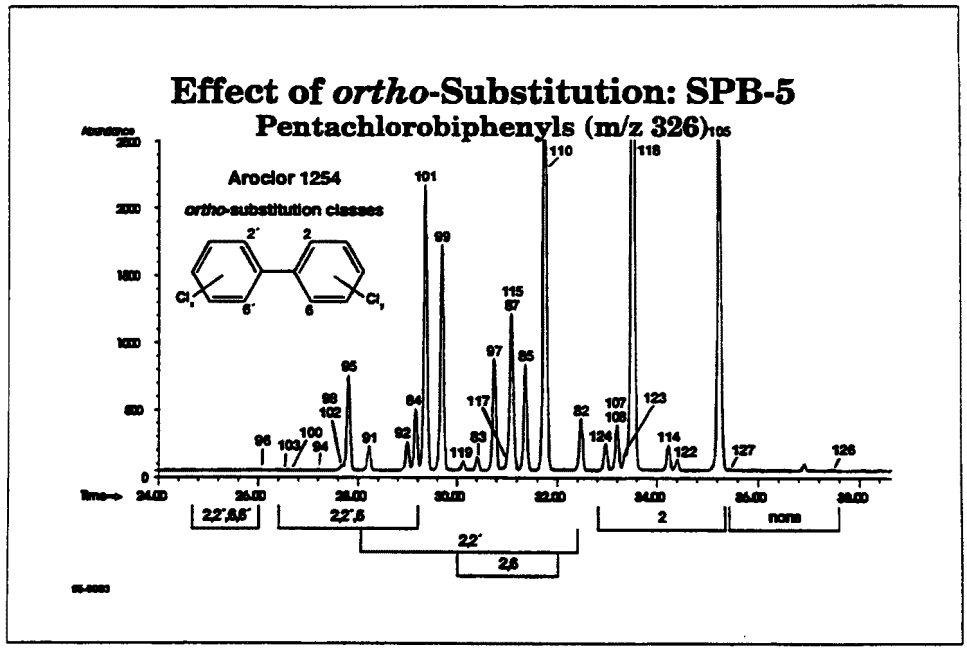


Figure G. Separation of *ortho*-substituted PCBs on the SPB-50 column.

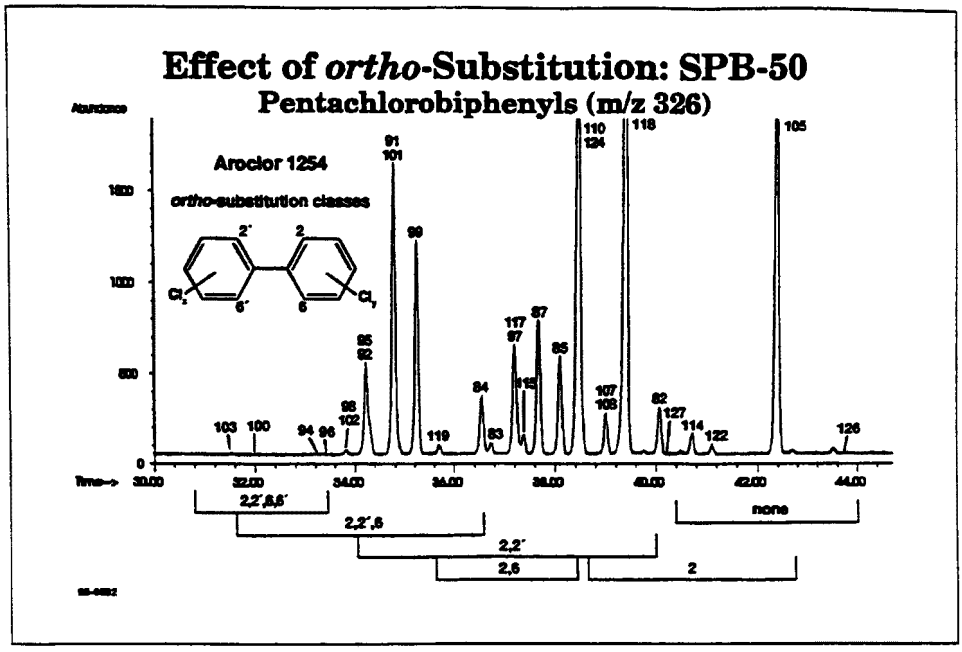


Figure H. Separation of *ortho*-substituted PCBs on the SPB-Octyl column.

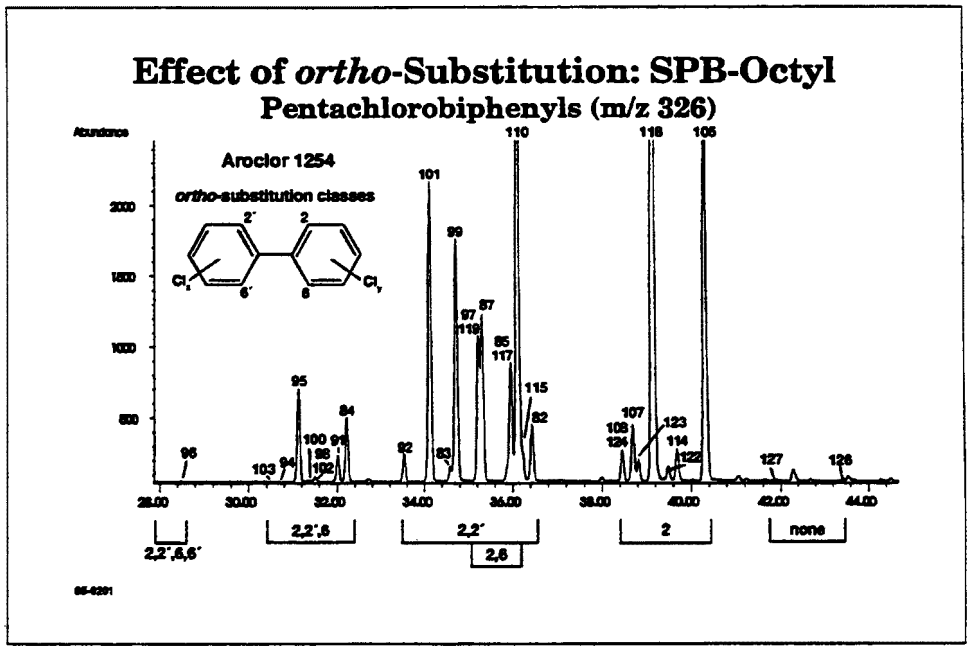


Figure I. Separation of *ortho*-substituted hexachlorobiphenyls on the SPB-Octyl column.

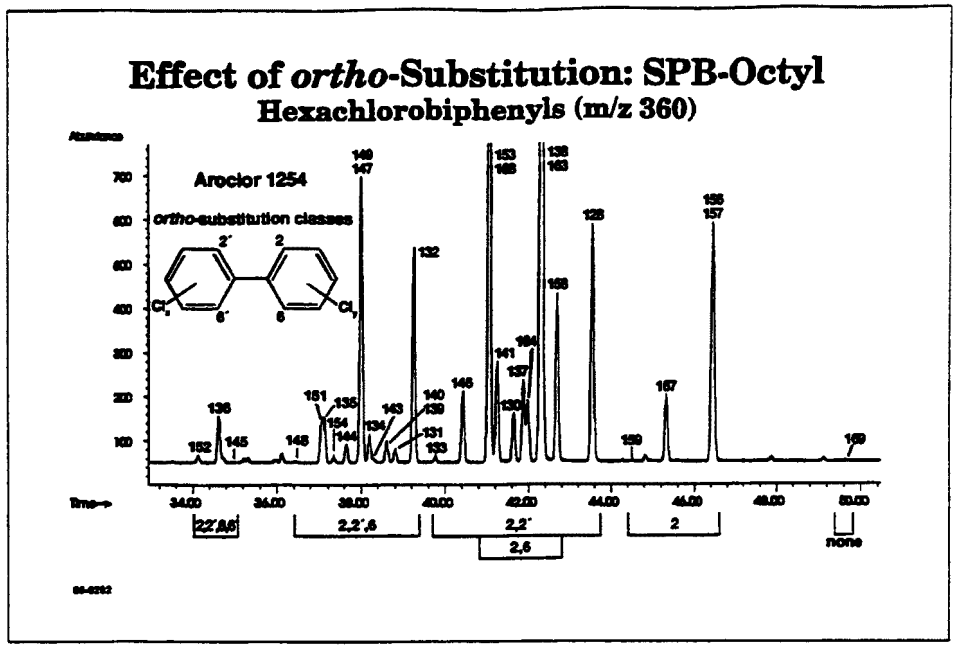


Figure J. Effect of column phase on elution order and resolution (Rs) of PCB congeners.

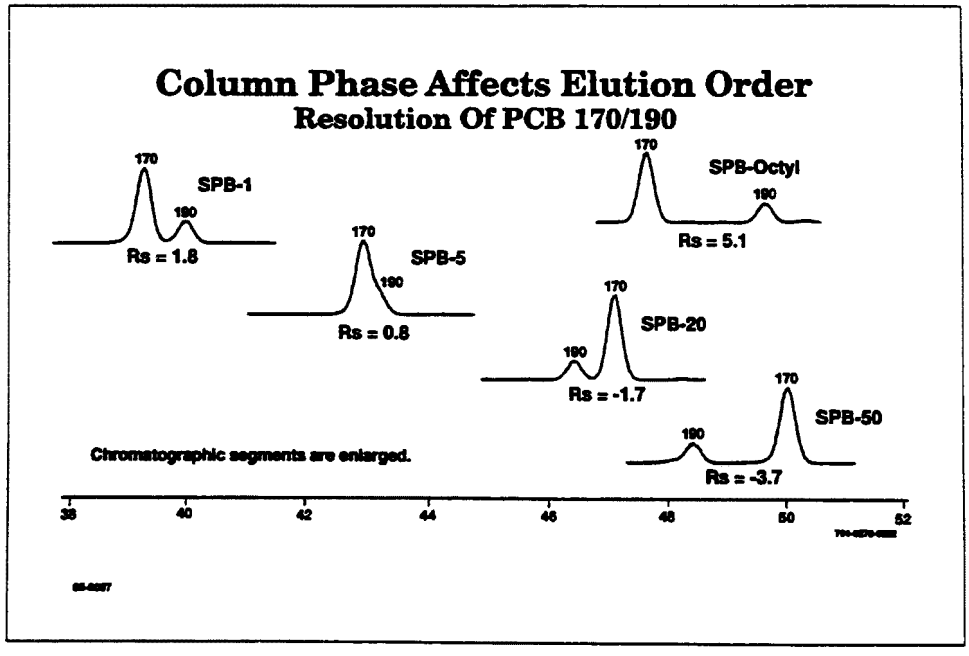


Figure K. Resolution of PCB congeners with the same number of chloro-substituents, but different *ortho*-substitution.

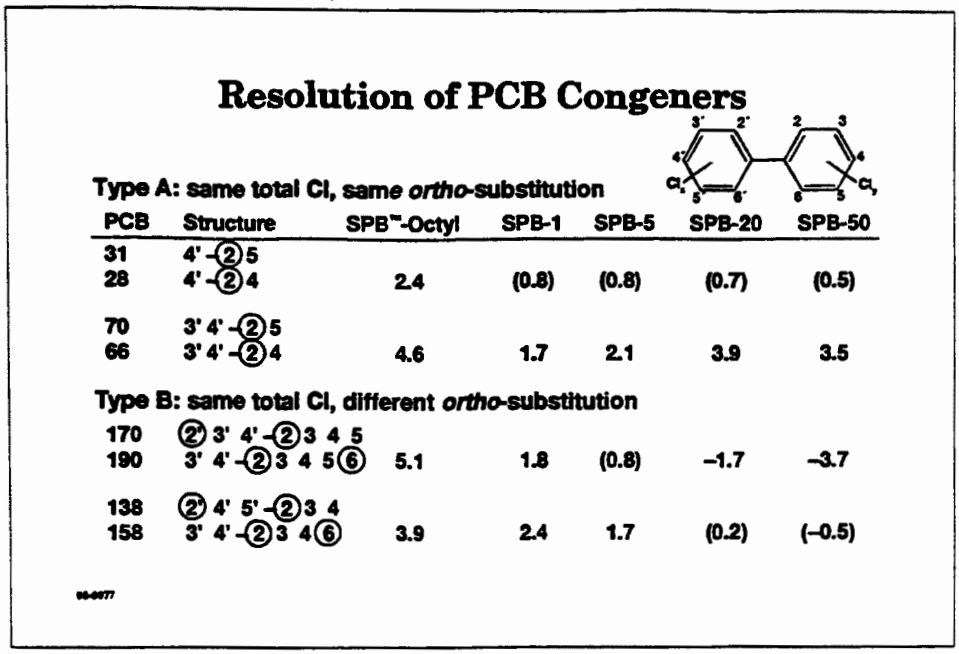


Figure L. Resolution of PCB congeners with differing number of chloro-substituents and different *ortho*-substitution.

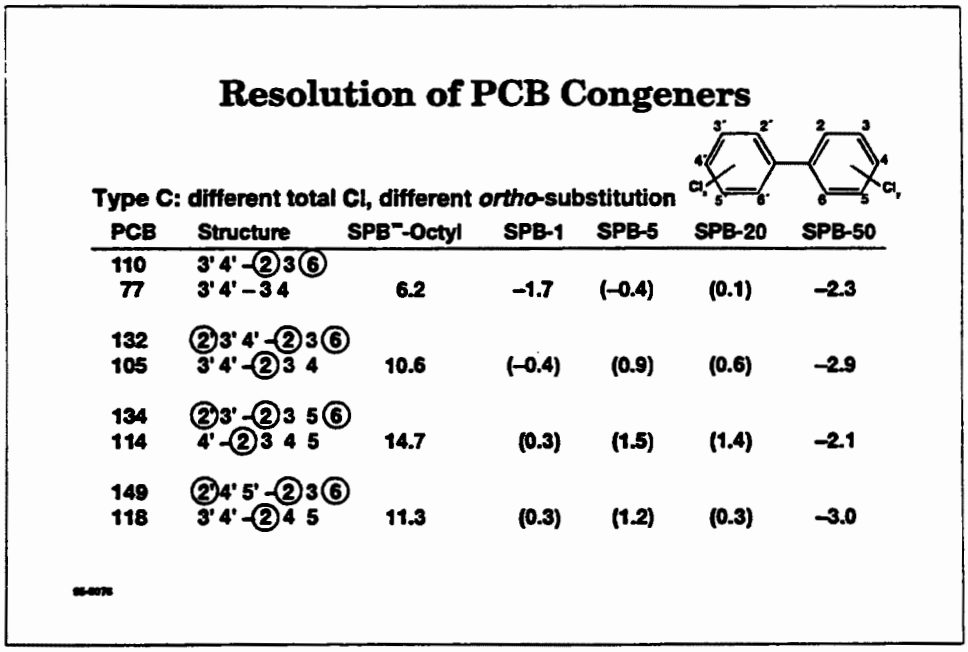


Figure M. Extraction and desorption procedures for solid phase microextraction (SPME).

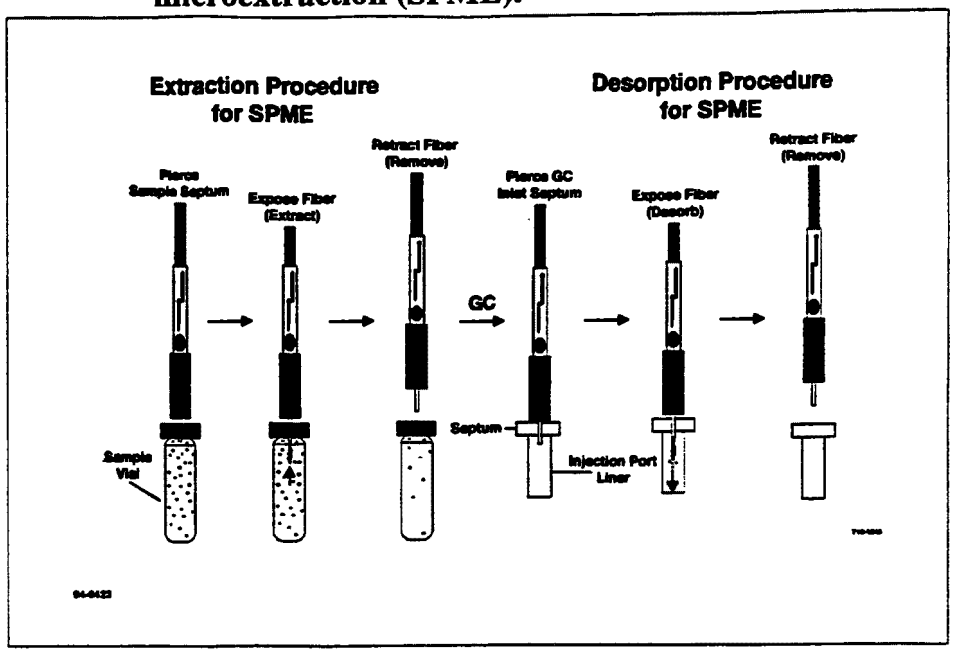
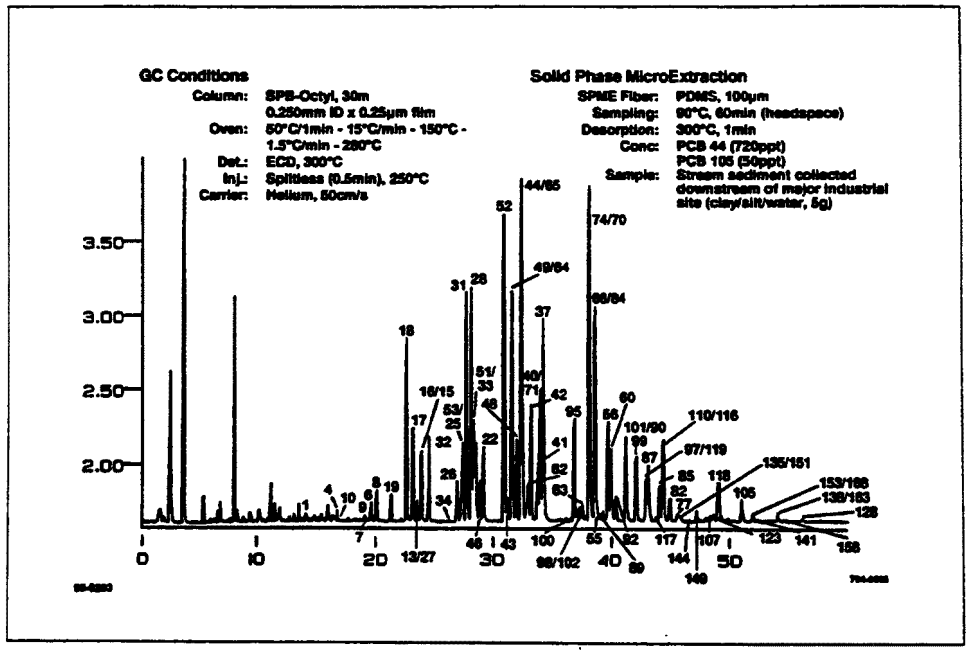


Figure N. SPME extraction of PCBs from polluted stream sedimen separated on the SPB-Octyl column.



Rapid Separation of VOCs with Short Small-Diameter Capillary GC Columns

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ABSTRACT

Rapid screening of VOCs in soil, drinking water, or waste water requires a fast extraction technique and swift separation step. This could be accomplished by extracting a sample while the previous extracted sample is being separated. Fast analysis of environmental samples increases throughput of data collection at a suspect contaminated sites. Rapid screening of collected samples can help in organizing samples for more lengthly GC/MS analyses.

Solid phase microextraction (SPME) is a fast, solventless alternative to conventional sample extraction techniques. Because no solvent is injected and the analytes are rapidly desorbed onto the column, short, narrow-bore capillary columns can be used. This greatly reduces analysis time and improves minimum detection limits, while manitaining resolution.

Three capillary columns (60m x 0.25mm ID) were initially evaluated to determine the elution order of 60 common VOCs listed in EPA Method 502.2. Two common columns for separating VOCs, an SPB-624 (1.4µm film) and a VOCOL (1.5µm film), along with a novel column, an SPB-Octyl, were run under the same chromatographic conditions. The elution order of VOCs, column efficiency, unique coelutions and separations, as well as reversal of elution order were tabulated for each column.

Finally, SPME extractions using 100µm polydimethylsiloxane fibers and 10m x 0.20mm ID capillary columns were used to obtain rapid separation of VOCs from EPA Method 624. The extraction and analysis times were optimized to provide quick sample screening by GC/FID or GC/MS in a train fashion.

INTRODUCTION

Volatile organic compounds (VOCs) are among the most common chemical pollutants tested for in soil, slugde, drinking water, and waste water. U.S. EPA methods prescribe the use of thick-film capillary GC columns for separating VOCs. Methods 502.2, 524.2, 602, 624, 5041, 8010 8015, 8020, 8260, and CLP-VOA prescribe purge-and-trap sample preparation and GC separation with

30m - 105m long 0.530mm ID thick-film capillary columns. Current emphasis of determining and controlling the VOC contaminants in outdoor and indoor air has prompted methods by OSHA, NIOSH, ASTM and US EPA (e.g., TO-14).

The great number and chemical diversity of possible VOCs in air, water and soil require capillary GC columns that are capable of separating close to 100 compounds. Of the 189 hazardous air pollutants (HAPs) designated in Title III of the Clean Air Act Amendments of 1990, 15 are classified as very volatile organic compounds (VVOC) and 82 as volatile organic compounds (VOC). These 97 VOCs in air, the 93 VOCs cited in Method 8260 (multimedia), the 84 VOCs in Method 524.2 for drinking water are commonly extracted with adsorbant tube or purge-and-trap technology. To obtain accurate qualification and quantitation of these VOCs capillary GC columns used must provide high separating power. This separating power can be accomplished with columns that have high theoretical plates, high selectivity or both. Long 0.53mm ID columns of 75m and 105m provide high number of theoretical plates. This is also accomplished with smaller diameter columns (0.25mm ID) with shorter lengths (e.g., 10m, 30m and 60m). Columns with specially designed bonded stationary phases provide the polar, polarizable and dispersive interactions needed to separate numerous VOCs. Columns with distinctly different bonded stationary phases provide a means of eluting VOCs in different elution orders or separating VOCs that cannot be separated with other columns.

The first half of this poster describes the comparison of three new 60m x 0.25mm ID capillary columns for the separation of VOCs. The elution order of 60 common VOCs on these three capillary columns was compared. The second half of this poster describes the combined use of SPME and fast GC for screening VOCs using short, 0.20mmID capillary columns.

EXPERIMENTAL

The capillary columns used for comparing VOC elution order were 60m x 0.25mm ID. The VOCOL column (1.5µm film), the SPB-624 column (1.4µm film) and the SPB-Octyl (1.0µm film) were examined with an HP 5890/5721 GC/MS (scan m/z = 45-300) under identical pressures (25psig) and temperature programs (40°C/4min - 4°C/min - 200°C/10min). VOC standards in water and soil were extracted with a manual solid phase microextraction holder using a 100µm polydimethylsiloxane fiber. SPME extractions were obtained with the fiber immersed in water or held in the soil headspace. The length of the SPB-1 and VOCOL 0.20mm ID capillary columns for rapid sample/site screening was shortened to 10m - long enough for adequate resolution, yet short enough for rapid separation.

RESULTS AND DISCUSSION

THE SPB-624 COLUMN. The SPB-624 capillary is a key column for separating volatile organic compounds (VOCs) extracted from drinking water, waste water, indoor air, outdoor air, and soil/sludge. The SPB-624 column is commonly used in the separation of VOCs in flavor and fragrance additives as well as residual solvents in industrial and pharmaceutical products. The SPB-624 column can be used with purge-and-trap, automated headspace and automated solid phase microextraction (SPME) systems for the multimedial extraction and separation of VOC pollutants. The SPB-624 column (**Figure A**) provided the highest column efficiencies (i.e., Trennzahls - Separation Numbers above 200 between a set of chlorinated ethenes and a set of chlorinated benzenes) and a unique selectivity for certain VOCs that typically coelute on VOCOL columns. The identification of the 60 VOCs used to compare the column elution orders are listed in **Table A**.

Trennzahl (Separation Number)

211 between vinyl chloride (3) **and** tetrachloroethene (28)
204 between chlorobenzene (32) **and** 1,2,3-trichlorobenzene (60)

Unique VOC Separations Using SPB-624

28 & 29 etrachloroethene **&** 1,3-dichloropropane
32 & 33/34 chlorobenzene **&** 1,1,1-2-tetrachloroethane **/** ethylbenzene

The instances of coeluting VOCs on the SPB-624 column could be resolved using MS (extracted ions), PID/ELCD or FTIR. However, m- and p-xylenes (35/36) could not be resolved with the SPB-624 column with these selective detectors. Although the instances of partially coeluting VOCs were numerous, all pairs could be resolved for accurate identification and quantitation by MS or PID/ELCD

Resolution of Coeluting VOCs by Selective Detection:

		MS	PID/ELCD
11/12	2,2-dichloropropane / cis-1,2-dichloroethene	yes	yes
16/17	1,1-dichloropropene / carbon tetrachloride	yes	yes
35/36	m-xylene / p-xylene	**no**	**no**
41/42	1,1,2,2-tetrachloroethane / bromobenzene	yes	yes
Partially Coeluting VOCs			
18,19	benzene / 1,2-dichloroethane	yes	yes
33,34	1,1,1,2-tetrachloroethane / ethylbenzene	yes	yes
37,38	o-xylene / styrene	yes	**no**
51,52	1,3-dichlorobenzene / p-isopropyltoluene	yes	yes

THE VOCOL COLUMN. The VOCOL capillary is an industry-standard GC column for the separation of environmental VOCs. It is widely used in purge-and-trap with GC-PID/ELCD and GC-MS systems. VOCOL columns are commonly used in U.S. EPA Methods 502.2, 524.2, 624, 8020, TO-14, 8260 and CLP-VOA. THE VOCOL column yielded the lowest Trennzahl values of the three columns, yet produced the least number of coeluting VOCs due to the designed selectivity of the stationary phase (**Figure B**).

Trennzahl (Separation Number)

197 between vinyl chloride (3) **and** tetrachloroethene (28)
130 between chlorobenzene (32) **and** 1,2,3-trichlorobenzene (60)

Unique VOC Separations Using VOCOL

11 & 12	2,2-dichloropropane **&** cis-1,2-dichloroethene
16 & 17	1,1-dichloropropene **&** carbon tetrachloride
37 & 38	o-xylene **&** styrene
41 & 42	1,1,2,2-tetrachloroethane **&** bromobenzene
52 & 51	p-isopropyltoluene **&** 1,3-dichlorobenzene (elution order reversed relative to SPB-624)

The VOCOL column provided superior separation of substituted benzenes (40-55) and with the substituted alkanes and alkenes (11-19). Coeluting VOCs on the VOCOL column could also be resolved using MS (extracted ions), PID/ELCD or FT-IR (except for 35/36, m-xylene and p-xylene).

Resolution of Coeluting VOCs by Selective Detection:

		MS	PID/ELCD
18/19	benzene / 1,2-dichloroethane	yes	yes
33/34	1,1,1,2-tetrachloroethane / ethylbenzene	yes	yes
35/36	m-xylene **/** p-xylene	**no**	**no**

Partially Coeluting VOCs

28,29	tetrachloroethene **&** 1,3-dichloropropane	yes	yes
32 & 33/34	chlorobenzene **&** 1,1,1-2-TCA **/** ethylbenzene	yes	**no**

Relative to SPB-624, the VOCOL column **reversed** the elution order of a few VOCs. The VOCOL column has a higher average polarity than the SPB-624 column, thereby creating a stronger interaction with the longer retained VOCs.

Elution Order Reversed (relative to SPB-624) Using VOCOL

14 & 13	chloroform **&** bromochloromethane
23 & 22	bromodichloromethane **&** dibromomethane
40 & 39	isopropylbenzene **&** bromoform

THE SPB-OCTYL COLUMN. The new SPB-Octyl capillary column (50% n-octyl,50% methyl polysiloxane) was desinged for detailed separations of petroleum hydrocarbons and PCB congeners. The SPB-Octyl bonded phase is less polar than polydimethylsiloxane (SPB-1), and slightly more polar than the totally hydrocarbon, nonbonded squalane phase. The SPB-Octyl column has high theoretical plates, even at subzero temperatures, and increases the retention of aromatics and alkenes (**Figure C**).

Trennzahl (Separation Number)

200 between vinyl chloride (3) **and** tetrachloroethene (28)
165 between chlorobenzene (32) **and** 1,2,3-trichlorobenzene (60)

Unique VOC Separations Using SPB-Octyl

35 & 36	m-xylene **&** p-xylene
43 & 44	1,2,3-trichloropropane **&** n-propylbenzene
33 & 32 & 34	1,1,1-2-tetrachloroethane **&** chlorobenzene **&** ethylbenzene

High Resolution and Reversed Order - relative to SPB-624 and VOCOL

12 & 11	cis-1,2-dichloroethene **&** 2,2-dichloropropane
19 &18	1,2-dichloroethane **&** benzene
29 & 28	1,3-dichloropropane **&** tetrachloroethene
38 & 37	styrene **&** o-xylene

The elution order of VOCs was quite similar for VOCOL and SPB-624 columns. However, the SPB-Octyl column greatly shifted the elution order of many VOCs compared to the elution orders on VOCOL and SPB-624 columns.

Coeluting VOCs Resolved by Selective Detection:		**MS**	**PID/ELCD**
14/11	chloroform / 2,2-dichloropropane	yes	**no**
43/41	1,2,3-trichloropropane / 1,1,2,2-tetrachloroethane	yes	**no**
45/47	2-chlorotoluene **/** 4-chlorotoluene	**no**	**no**
51/53	1,3-dichlorobenzene **/** 1,4-dichlorobenzene	**no**	**no**

Partially Coeluting VOCs

10,9	1,1-dichloroethane / trans-1,2-dichloroethene	yes	yes
21,22	1,2-dichloropropane / dibromomethane	yes	**no**
39 & 43/41	bromoform & trichloropropane / 1,1,2,2-TCA	yes	**no**

Elution Order Reversed (relative to SPB-624 and VOCOL)

8 & 7	13 & 12	33 & 32	55 & 54
10 & 9	18 & 17	38 & 37	59 & 58

Retention Time Greatly Affected:

Reduced:	19	39	43	41
Increased:	20	25	28	

SOLID PHASE MICROEXTRACTION. Solid phase microextraction (SPME), like purge-and-trap, is a solventless extraction procedure, but SPME does not require the complex instrumentation of purge-and-trap methodology. SPME involves immersing a polymer-coated fused silica fiber into drinking water or waste water samples, or the headspace above water or soil samples to adsorb the VOCs. The adsorbed VOCs are thermally desorbed in the injection port of any GC and focussed at the front of the cooled capillary column (**Figure D**). Extraction selectivity can be altered by changing the polymeric fiber coating or its thickness. For example, the small distribution constants and low polarity of chlorinated and aromatic VOCs dictate the use of a thick, nonpolar fiber coating for efficient extraction. Agitation, addition of salt, pH adjustment, and immersion of the fiber in the aqueous sample improve recovery of difficult-to-extract VOCs.

Comprehensive separation of SPME extracted VOCs from soil are depicted in **Figure E**. The SPME extraction of VOCs at 40ppb provided the highest sensitivity for the substituted aromatic VOCs above benzene. The more volatile halogenated alkanes and alkenes were not concentrated on the fiber as the aromatics were. The extraction of the volatile gases (dichlorodifluoromethane to chloroethane), resulted in sufficient extraction for positive identication and quantification.

RAPID SCREENING. For screening VOCs with nonspecific detectors, such as FIDs and TCDs, a dual column analysis on columns of different polarity provides better identification and quantification of VOCs. A dual-column system composed of a 10m x 0.20mm ID x 1.2µm SPB-1 column and a VOCOL column of the same dimensions provided good resolution of US EPA Method 624 VOCs in about 6 minutes. **Figures F and G** show the dual column analysis of the Method 624 VOCs at 50ppb, following a 5 minute extraction by SPME. The combined analysis time and cool-down time was 10 minutes. The 10-minute cycle time for the analysis is compatible with the sample preparation time by SPME - 5 minutes for extractions and 3 minutes for desorption.

Because wastewater samples can contain VOCs at concentrations ranging from trace ppb to ppm levels, a sample screeening technique must be suitable for quantifying VOCs over a wide range of concentrations. Ina purge-and-trap instrument, VOCs at concentrations greater than 200ppb can saturate the trap and contaminate the valves and lines, requiring downtime to clean the system. SPME was effective over a wide range of VOC concentrations, and proved its suitability for screening samples on-site or prior to purge-and-trap/GC/MS analysis. Waste water samples found to be highly concentrated can be diluted prior to the formal analysis.

The average response factors for 31 VOCs in US EPA Method 624 at a concentration range of 25ppb - 1ppm were determined using SPME. Data for SPME extractions at 7 concentrations are summarized in **Table B**. The low percent relative standard deviations (%RSD) for most VOC indicate good

linearity for the response factors for this range of concentrations. The % RSD for vinyl chloride is unusually high because vinyl chloride coelutes with methanol, the solvent used with the standard. Responses for vinyl chloride are more linear with specific detectors, such as ELCD or MS.

CONCLUSIONS

Based on this study, it was concluded that the SPB-624 column provided the highest column efficiency (Trennzahl values), resulted in numerous peak coelutions that could be separated using selective detectors (MS or PID/ELCD). The VOCOL column provided the lowest column efficiency, the longest retention times, but the fewest coelutions. The coelutions on the VOCOL column could also be separated with selective detectors. The SPB-Octyl column provided high column efficiency and a unique elution order. Although the SPB-Octyl column separated m-xylene and p-xylene, 2-chlorotoluene/4-chlorotoluene (isomers) as well as 1,4-dichlorobenzene/1,3-dichlorobenzene (isomers) were not resolved.

These results show that SPME is fast, easy and compatible with short, naroow-bore columns that provide fast analysis times. Volatile organic compounds can be extracted with good accuracy over a wide concentration range. Because the apparatus is portable and easy to use, SPME can be employed in the field for quick turn-around methods, or for screening a sample prior to GC/MS analysis. Precision and accuracy also make SPME effective in quantitative analyses.

Table A. Sixty Common VOCs in EPA Method 502.2 For Comparing Capillary Column Performance

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl Chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1-Dichloroethene
8. Methylene Chloride
9. trans-1,2-Dichloroethene
10. 1,1-Dichloroethane
11. 2,2-Dichloropropane
12. cis-1,2-Dichloroethene
13. Bromochloromethane
14. Chloroform
15. 1,1,1-Trichloroethane
16. 1,1-Dichloropropene
17. Carbon Tetrachloride
18. Benzene
19. 1,2-Dichloroethane
20. Trichloroethene
21. 1,2-Dichloropropane
22. Dibromomethane
23. Bromodichloromethane
24. cis-1,3-Dichloropropene
25. Toluene
26. trans-1,3-Dichloropropene
27. 1,1,2-Trichloroethane
28. Tetrachloroethene
29. 1,3-Dichloropropane
30. Dibromochloromethane
31. 1,2-Dibromoethane
32. Chlorobenzene
33. 1,1,1,2-Tetrachloroethane
34. Ethylbenzene
35. m-Xylene
36. p-Xylene
37. o-Xylene
38. Styrene
39. Bromoform
40. Isopropylbenzene
41. 1,1,2,2-Tetrachloroethane
42. Bromobenzene
43. 1,2,3-Trichloropropane
44. n-Propylbenzene
45. 2-Chlorotoluene
46. 1,2,3-Trimethylbenzene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. 1,3-Dichlorobenzene
52. p-Isopropyltoluene
53. 1,4-Dichlorobenzene
54. n-Butylbenzene
55. 1,2-Dichlorobenzene
56. 1,2-Dibromo-3-chloropropane
57. 1,2,4-Trichlorobenzene
58. Hexachlorobutadiene
59. Naphthalene
60. 1,2,3-Trichlorobenzene

Table B. Linearity of Response Factors for EPA Method 624 VOCs

No.	VOC	Column▲	Response Factors Mean	% RSD
1.	Chloromethane	SPB-1	0.022	17.0
2.	Vinyl chloride	SPB-1	0.663	23.0
3.	Bromomethane	SPB-1	0.025	11.4
4.	Chloroethane	SPB-1	0.229	14.7
5.	Trichlorofluoromethane	SPB-1	0.022	8.3
6.	1,1-Dichloroethene	VOCOL	0.341	13.3
7.	Methylene chloride	VOCOL	0.040	14.7
8.	trans-1,2-Dichloroethene	VOCOL	0.354	15.3
9.	1,1-Dichloroethane	VOCOL	0.272	9.1
10.	Chloroform	VOCOL	0.106	12.1
11.	1,1,1-Trichloroethane	SPB-1	0.374	5.1
12.	Carbon tetrachloride	VOCOL	0.080	11.9
13.	1,2-Dichloroethane	SPB-1	0.183	7.8
14.	Benzene	SPB-1	1.951	5.1
15.	Trichloroethene	VOCOL	0.336	3.9
16.	1,2-Dichloropropane	VOCOL	0.529	3.4
17.	Bromodichloromethane	VOCOL	0.072	9.9
18.	2-Chloroethylvinyl ether	VOCOL	0.324	6.0
19.	cis-1,3-Dichloropropene	VOCOL	0.551	3.6
20.	Toluene	VOCOL	2.091	5.2
21.	trans-1,3-Dichloropropene	VOCOL	0.501	4.3
22.	1,1,2-Trichloroethane	VOCOL	0.247	3.4
23.	Tetrachloroethene	VOCOL	0.251	13.0
24.	Dibromochloromethane	VOCOL	0.060	6.1
25.	Chlorobenzene	SPB-1	1.543	6.5
26.	Ethylbenzene	SPB-1	1.892	14.0
27.	Bromoform	SPB-1	0.086	6.4
IS	1,4-Dichlorobutane (int. std.)			
28.	1,1,2,2-Tetrachloroethane	VOCOL	0.274	4.9
29.	1,3-Dichlorobenzene	VOCOL	1.021	16.9
30.	1,4-Dichlorobenzene	VOCOL	1.078	16.3
31.	1,2-Dichlorobenzene	VOCOL	1.032	17.4

▲Column used to quantify the analyte

Sample: US EPA 624 VOCs in 1.8mL saturated salt water (2mL vial) 25ppb-1ppm, 7 concentration points
Fiber Type: 100µm polydimethylsiloxane (PDMS)
Extraction: direct immersion of fiber in sample (5 min, rapid stirring)

Figure A. Separation of 60 US EPA Method 502.2 VOCs with the SPB-624 column.

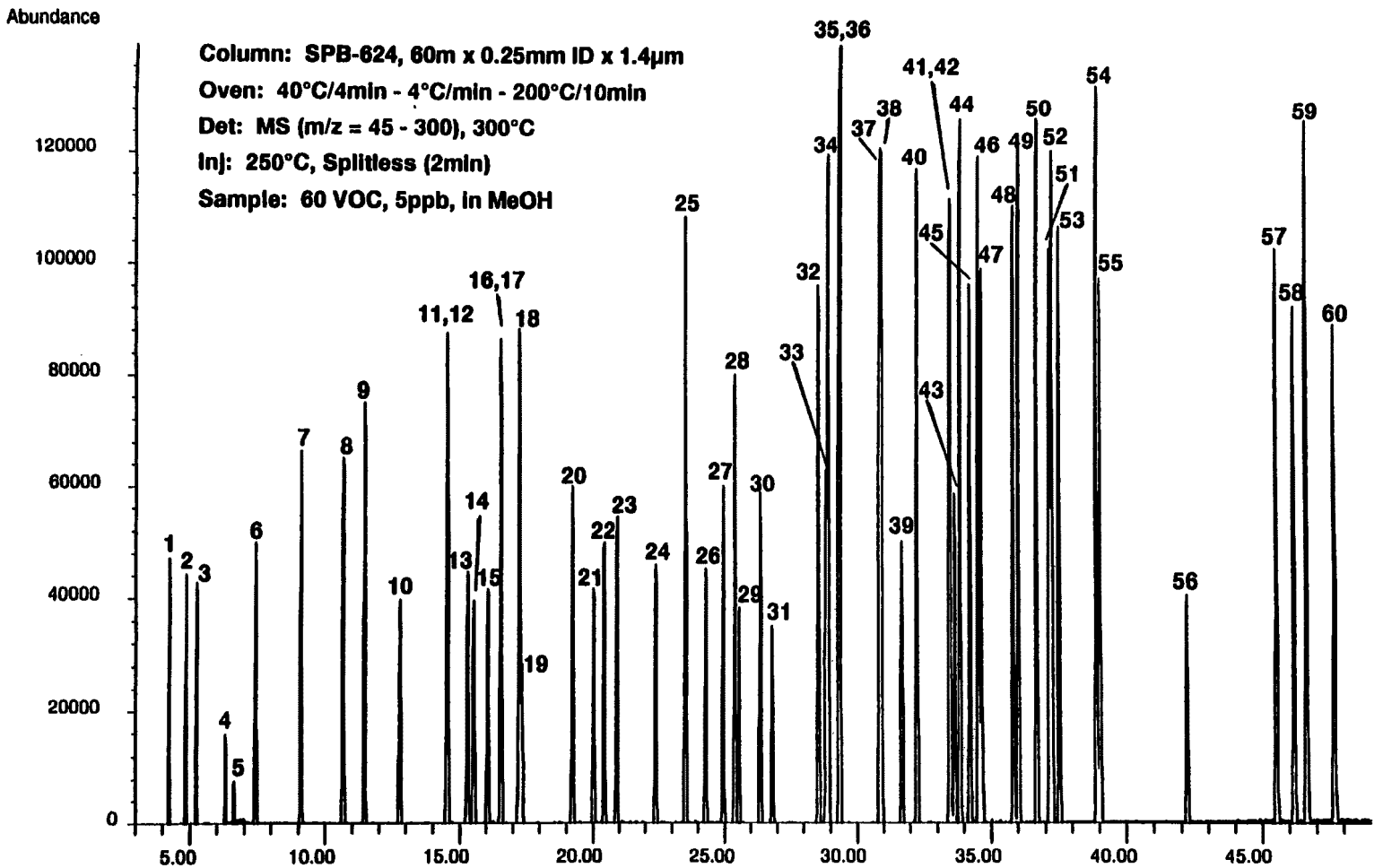


Figure B. Separation of 60 US EPA Method 502.2 VOCs with the VOCOL column.

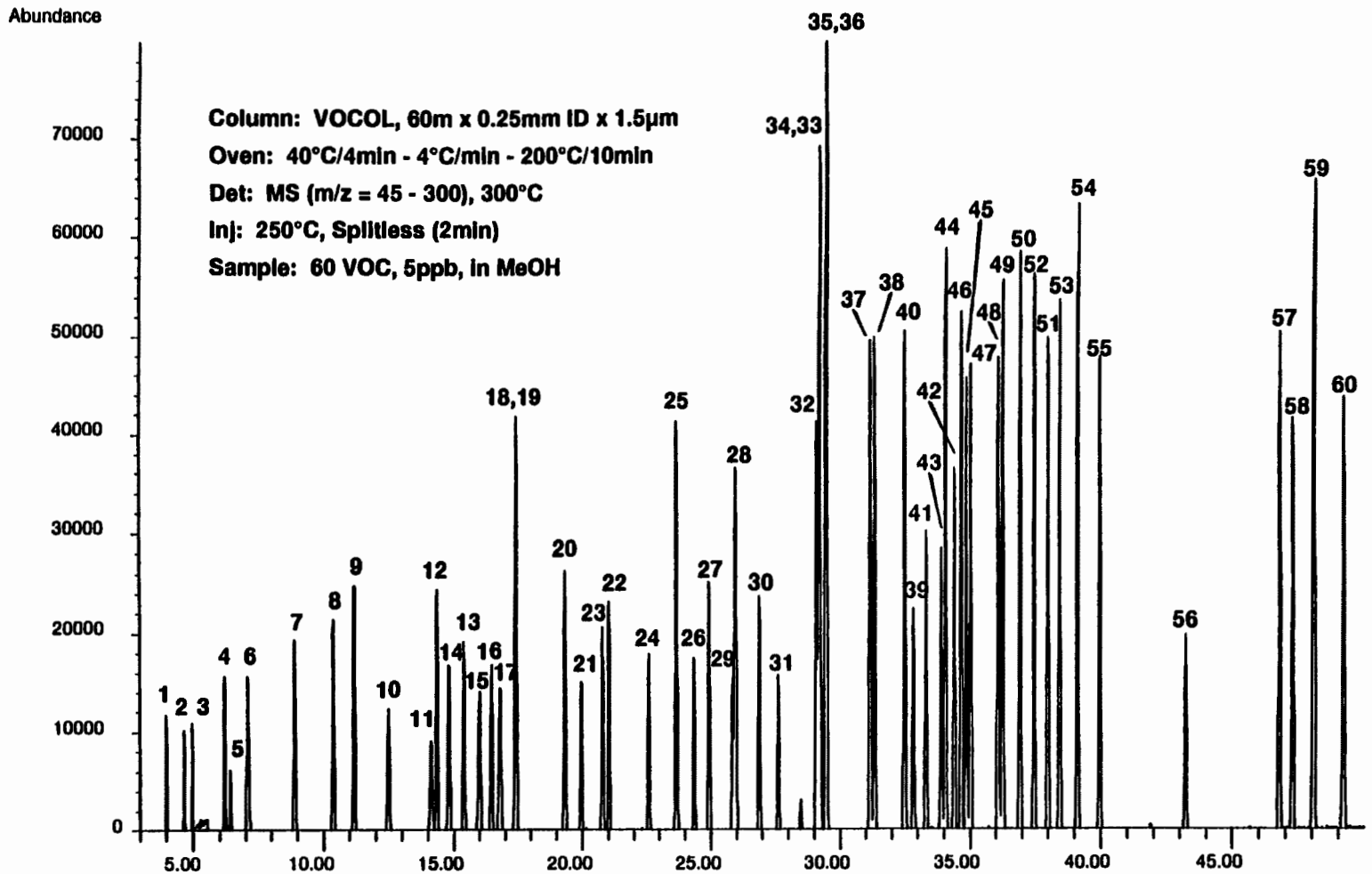


Figure C. Separation of 60 US EPA Method 502.2 VOCs with the SPB-Octyl column.

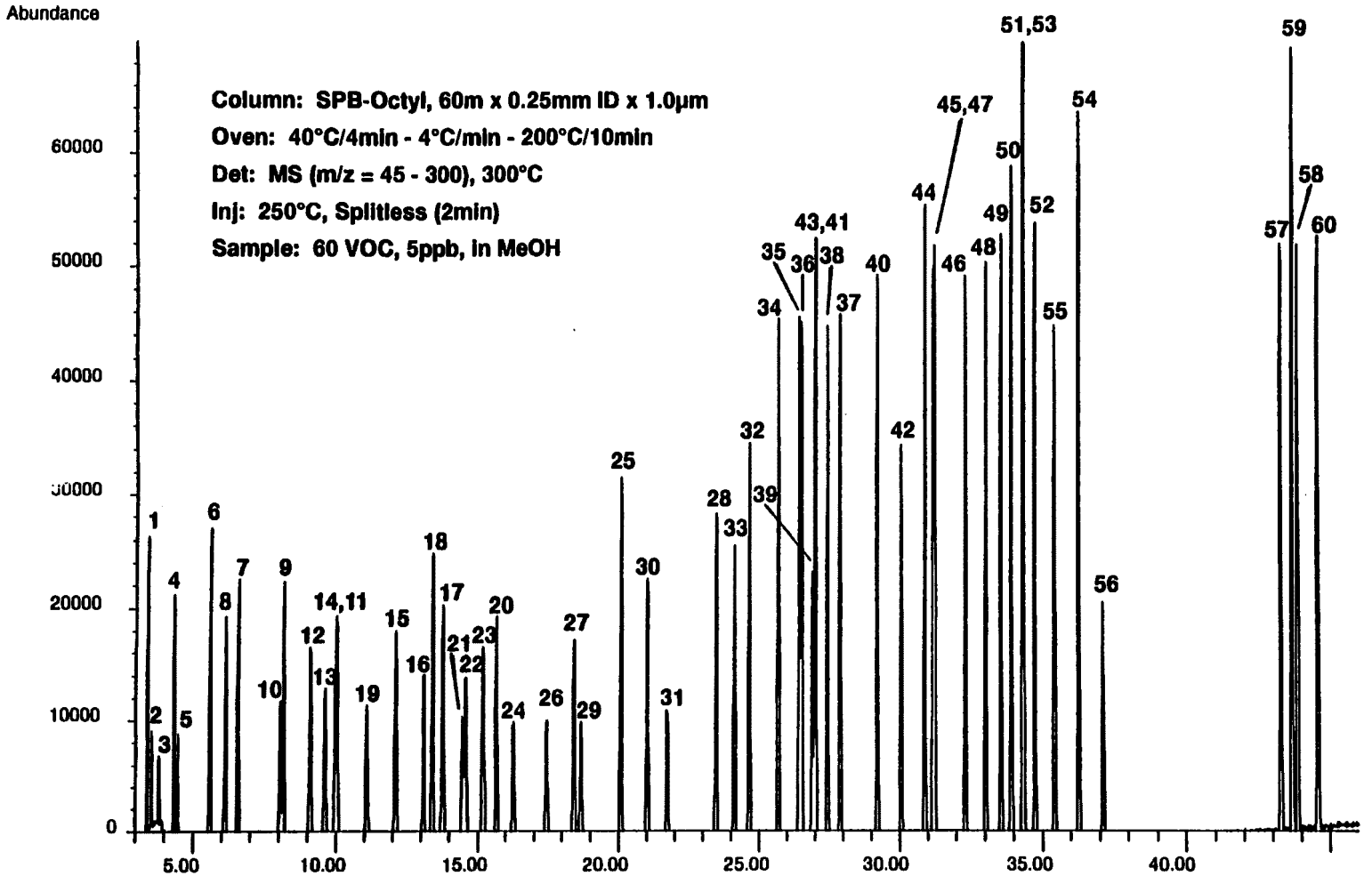


Figure D. SPME extraction and separation of 60 US EPA Method 502.2 VOCs.

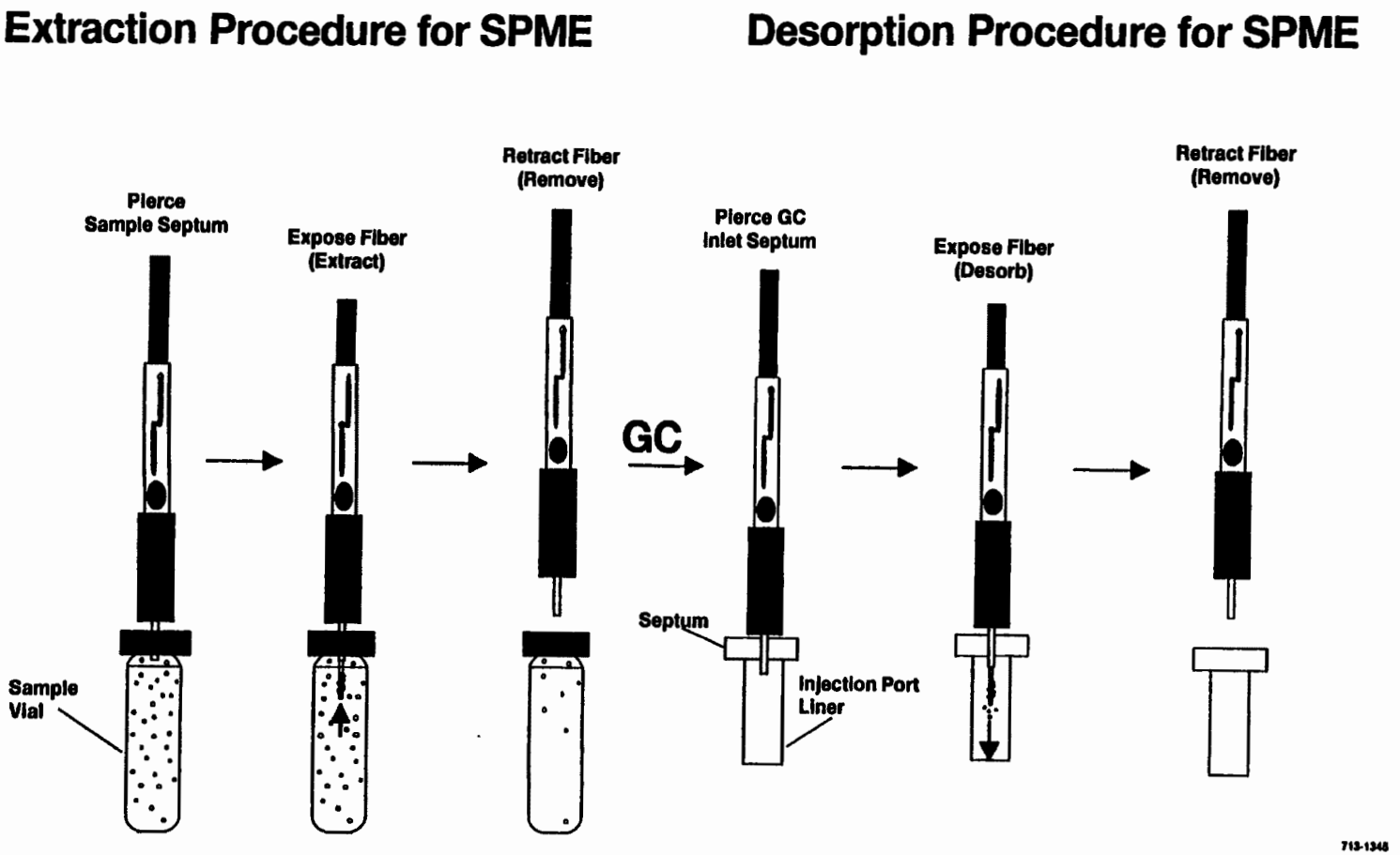


Figure E. Extraction and desorption processes for SPME.

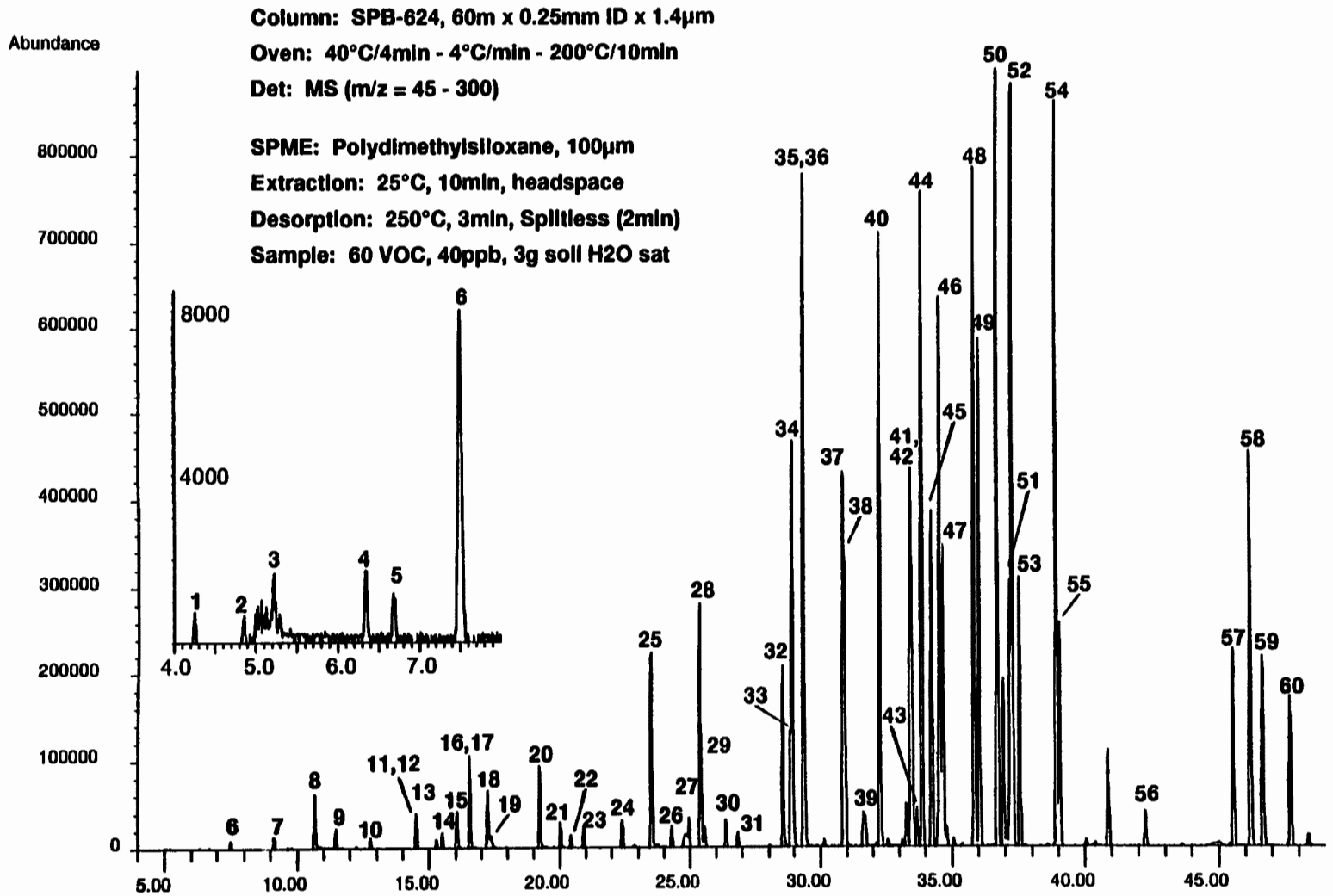


Figure F. Rapid Screening of VOCs on 10m VOCOL Column

SPME: 100µm PDMS phase fiber
immersed in 1.8mL saturated salt water (5 min)
Columns: VOCOL 10m x 0.20mm ID, 1.2µm film
Oven Temp.: 40°C (0.75 min) to 160°C at 20°C/min
Carrier: helium, 40cm/sec (set at 40°C)
Det.: FID, 260°C
Inj.: 230°C, splitless (closed 3 min)
50ppb each analyte

1. Chloromethane
2. Vinyl chloride
3. Bromomethane
4. Chloroethane
5. Trichlorofluoromethane
6. 1,1-Dichloroethene
7. Methylene chloride
8. trans-1,2-Dichloroethene
9. 1,1-Dichloroethane
10. Chloroform
11. 1,1,1-Trichloroethane
12. Carbon tetrachloride
13. 1,2-Dichloroethane
14. Benzene
15. Trichloroethene
16. 1,2-Dichloropropane
17. Bromodichloromethane
18. 2-Chloroethylvinyl ether
19. cis-1,3-Dichloropropene
20. Toluene
21. trans-1,3-Dichloropropene
22. 1,1,2-Trichloroethane
23. Tetrachloroethene
24. Dibromochloromethane
25. Chlorobenzene
26. Ethylbenzene
27. Bromoform
IS 1,4-Dichlorobutane (int. std.)
28. 1,1,2,2-Tetrachloroethane
29. 1,3-Dichlorobenzene
30. 1,4-Dichlorobenzene
31 1,2-Dichlorobenzene

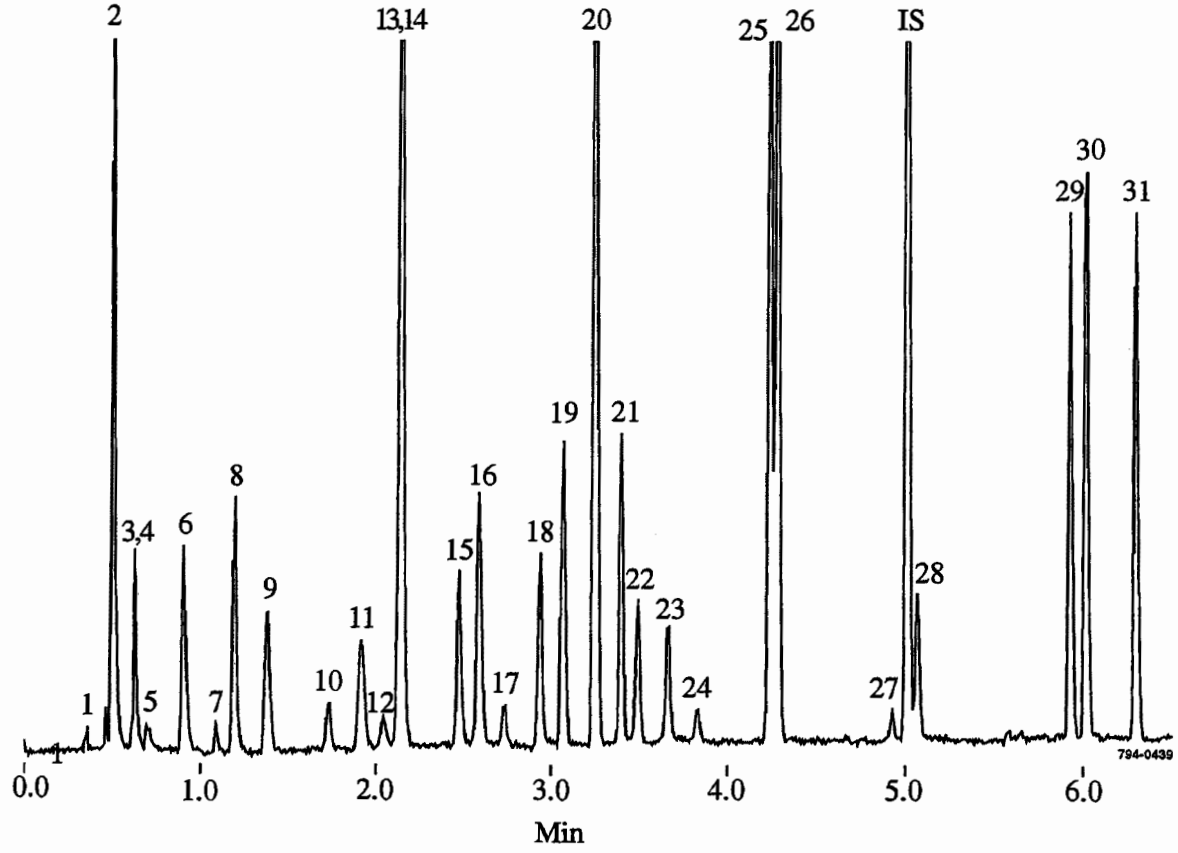
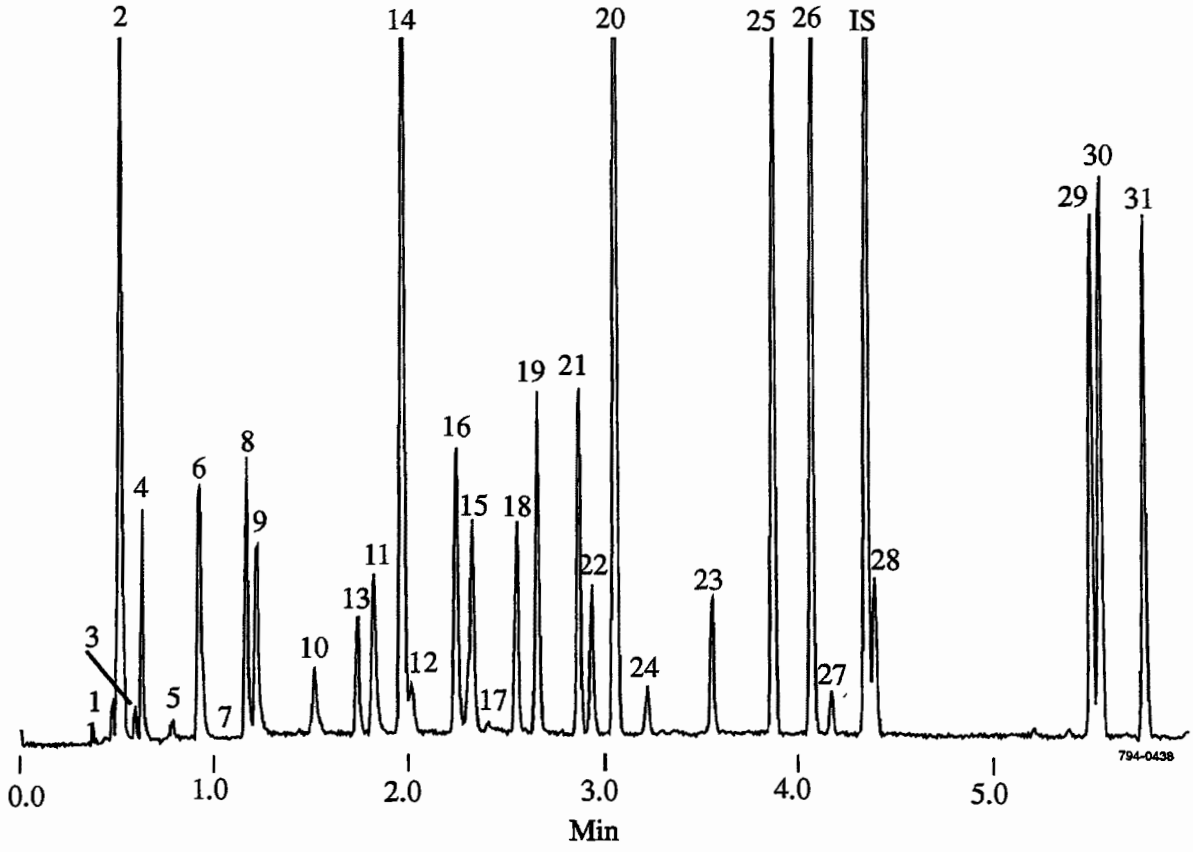


Figure G. Rapid Screening of VOCs on 10m SPB-1 Column

SPME: 100µm PDMS phase fiber
immersed in 1.8mL saturated salt water (5 min)
Columns: SPB-1 10m x 0.20mm ID, 1.2µm film
Oven Temp.: 40°C (0.75 min) to 160°C at 20°C/min
Carrier: helium, 40cm/sec (set at 40°C)
Det.: FID, 260°C
Inj.: 230°C, splitless (closed 3 min)
50ppb each analyte

1. Chloromethane
2. Vinyl chloride
3. Bromomethane
4. Chloroethane
5. Trichlorofluoromethane
6. 1,1-Dichloroethene
7. Methylene chloride
8. trans-1,2-Dichloroethene
9. 1,1-Dichloroethane
10. Chloroform
11. 1,1,1-Trichloroethane
12. Carbon tetrachloride
13. 1,2-Dichloroethane
14. Benzene
15. Trichloroethene
16. 1,2-Dichloropropane
17. Bromodichloromethane
18. 2-Chloroethylvinyl ether
19. cis-1,3-Dichloropropene
20. Toluene
21. trans-1,3-Dichloropropene
22. 1,1,2-Trichloroethane
23. Tetrachloroethene
24. Dibromochloromethane
25. Chlorobenzene
26. Ethylbenzene
27. Bromoform
IS 1,4-Dichlorobutane (int. std.)
28. 1,1,2,2-Tetrachloroethane
29. 1,3-Dichlorobenzene
30. 1,4-Dichlorobenzene
31. 1,2-Dichlorobenzene



Inorganics

AN IMPROVED TEMPERATURE FEEDBACK CONTROL SENSOR FOR MICROWAVE SAMPLE PREPARATION

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ABSTRACT

A patent-pending microbulb thermometry sensor for microwave-assisted sample preparation systems has been developed. It performs as well as the currently employed sensors in accuracy and precision. The theory behind the microwave-transparent temperature sensor is based on gas law principles. In practice, the sensor has a linear response from -50°C to 250°C, for an extended period of time. The microbulb sensor's accuracy is enhanced by an applied linearization factor. The sensor is designed with microwave-transparent materials and is not prone to breakage as are sensors in other current technologies. Calibration is made in under a minute and replacement of the "expendable-priced" probe can be accomplished in seconds. These factors allow the sensor to be employed on a routine basis for method development or EPA method compliance. A demonstration of the new technology has been performed on sludge and sediment samples, as outlined in EPA SW-846, Method 3051, "Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils" [1]. After the timesaving microwave digestion period, the samples were analyzed for several of the approved Resource Conservation and Recovery Act (RCRA) metals by inductively coupled plasma (ICP) spectroscopy. Excellent accuracy and precision were obtained, in addition to a significant time reduction in sample preparation. The new Microbulb Thermometry System™ allows microwave sample preparation scientists to use temperature feedback control on a routine basis.

INTRODUCTION

The improvements of microwave-assisted acid digestion over the traditional hot plate techniques, in terms of time reduction and precision, have been well documented [2]. The development and acceptance of the two EPA methods for microwave-assisted acid digestion has ignited a growth in use. EPA Methods 3015 and 3051 were written with performance-based criteria so that the transfer of the method could be made, independent of instrument manufacturer, from one laboratory to another. Future methodology will also employ performance-based criteria. Temperature is the primary factor in the microwave-assisted chemical reactions, and therefore, the most crucial variable in the performance-based methods. The need for accurate, precise, and durable temperature monitoring and control is evident. The current technologies include phosphor fiber-optic, passive IR, and thermocouple detection. These methods are accurate but have various disadvantages, ranging from cost to cumbersome use. The new microbulb sensor was developed to remove these obstacles and retain the superb accuracy that is required.

EXPERIMENTAL

An illustration of the Microbulb Thermometry System (MTS™) is displayed in Figure 1.

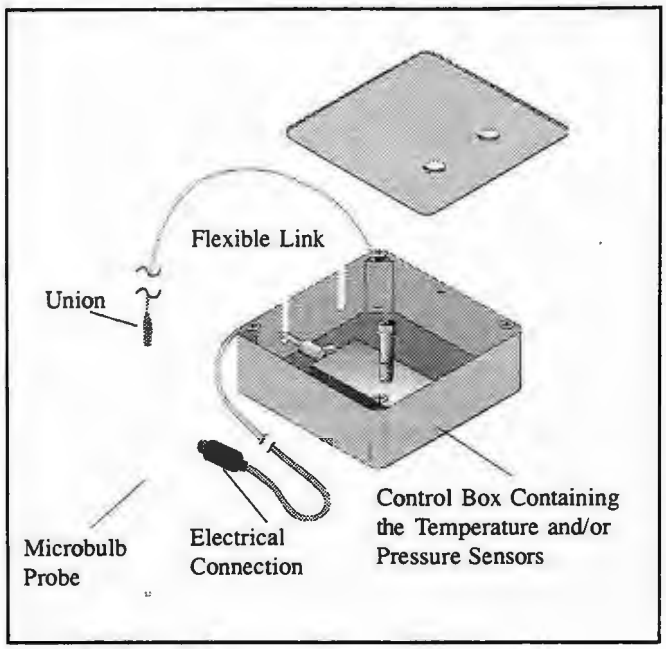

Figure 1. Microbulb Thermometry System

The patent-pending MTS is made from microwave-transparent materials and is extremely robust, unlike similar products in much of the current technology, and can therefore be used in routine applications. The MTS has an excellent thermal response, comparable to currently used sensors. The stability of the MTS is superb, having negligible drift over a period of twelve hours. The MTS was used with an Analytical Microwave System™ (AMS) Model 7195 from OI Analytical. Temperature feedback control programming was performed according to EPA Method 3051, "Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils." The method requires 10.0 mL of nitric acid with 0.5 g of sludge or sediment sample. When using temperature feedback control, the programming can be simply stated; heat the acid-sample mixture to 175°C in 5.5 minutes and maintain that temperature for an additional 4.5 minutes. This eliminates the need for the timely calibration procedure that is necessary when performing the method without temperature feedback control. The temperature program profile for an example of Method 3051 using the new thermometry technology is shown in Figure 2 and an actual temperature profile for a sediment sample is shown in Figure 3.

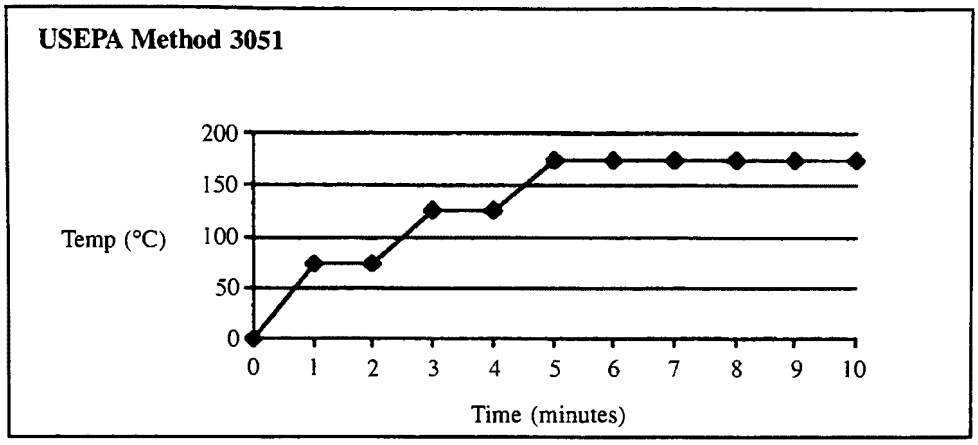

Figure 2. Microwave Heating Profile for USEPA Method 3051

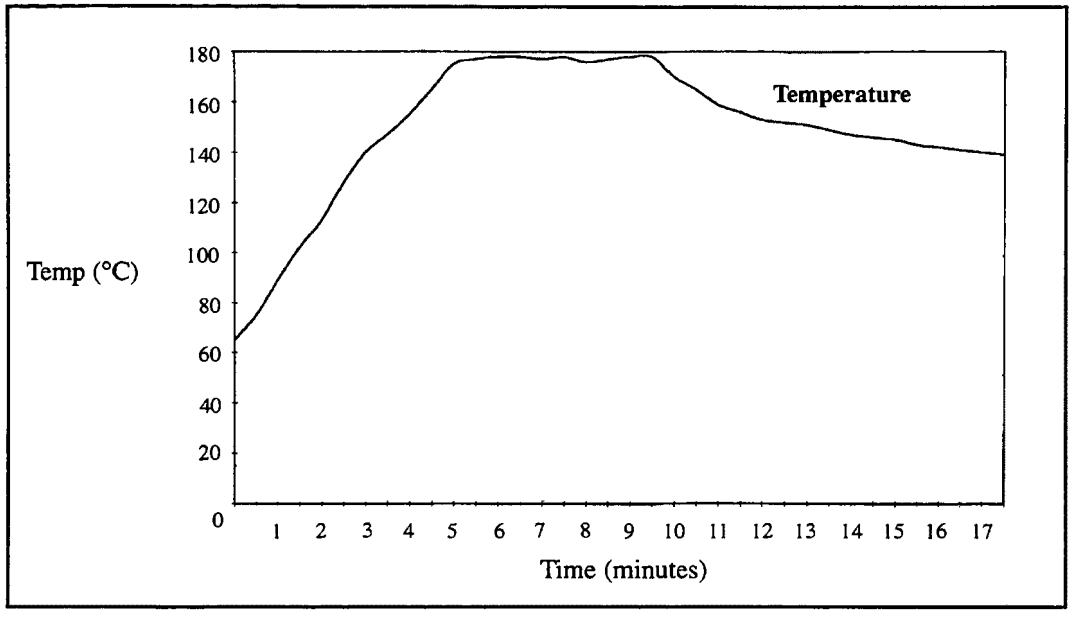

Figure 3. USEPA Method 3051 Temperature Profile for Sediment Sample

RESULTS

The ICP results for several of the RCRA metals for the sludge sample are in excellent agreement with the expected concentration, and are shown in Table 1. The bias, defined as the difference between the amount expected and the amount found, was less than 2% for each of the metals analyzed.

Good precision is displayed in the ICP analysis of several of the RCRA metals for the sediment sample. The concentrations along with the precision, based on n=4, are shown in Table 2.

Element	Concentration (ppm)
Ag	1.40
As	9.80
Ba	373
Cd	12.6
Cr	49.6
Hg	0.14
Pb	825
Se	0.86
Zn	1120

Table 1. Analysis of RCRA Metals in Tank Sludge by ICP Spectroscopy

Element	Concentration (ppm) Experimental Range	Precision (SD, n=4)
As	31–38	3.6
Ba	266–271	2.2
Cd	2–3	0.9
Cr	50.6–55.3	2.0
Hg	<0.1	–
Se	24–38	6.3
Ag	<0.5	–
Zn	129–157	12

Table 2. Analysis of RCRA Metals in Sediment by ICP Spectroscopy

SUMMARY

The demonstration of a newly developed temperature sensor for microwave-assisted sample preparation is shown. The Microbulb Thermometry System performs as accurately as current temperature-measuring technologies, and is robust and user-friendly. These differences will permit microwave users in the laboratory to perform routine temperature feedback methods, eliminating the need for power calibration steps. In addition, as more performance-based methods employing temperature criteria are created, the use for temperature sensors will escalate.

REFERENCES

[1] United States Environmental Protection Agency, "Test Methods for Evaluating Solid Waste. Physical/Chemical Methods," SW-846, 3051-1, November 1990.

[2] H.M. Kingston, L.B. Jassie, Eds., "Introduction to Microwave Sample Preparation: Theory and Practice," ACS Professional Reference Book, American Chemical Society, 1988.

IMPROVEMENTS IN SPECTRAL INTEREFERENCE AND BACKGROUND CORRECTION FOR INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETERY.

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Treatment of spectral data from an inductively coupled plasma (ICP) spectrometer is of central importance to the quality of results of CLP and RCRA analyses. A routine method is to use off-line background correction coupled with Interfering Element Correction (IEC). There are inherent limitations with this approach and known difficulties with its implementation [1]. Conventional IEC requires the operator to select background correction points. Also, there must be a linear relationship between the interfering element reference line and the interfering emission occuring at the analyte wavelength in order for the algorithm to work. In this paper, we discuss an improved version of this method called Total Interfering Element Correction (TIEC), which addresses both the mathematical limitations and the practical implementation problems of conventional IEC. Similar mathematics are used for TIEC as for IEC but the information from the spectrometer is used much more efficiently. For example, selection of background correction points is superfluous. Thus, the variability resulting from this parameter is removed in the method development step. The argon continuum background is simply treated as another interfering contribution. Furthermore, with TIEC, proper spectral interference correction is not dependent on intensity ratios to spectral lines at distant wavelengths from the analyte. The TIEC output provides the same interference correction factor information as IEC, necessary for regulatory compliance. In addition, TIEC provides diagnostic feedback useful to the operator for instrument performance verification. It will be shown that TIEC is equivalent in function to IEC but offers simpler setup for the operator and more reliable results owing to the relaxation of contraints in the older method.

[1] G.A. Laing et al. in Proceedings: *Tenth Annual Waste Testing and Quality Assurance Symposium*, July 11-15, 1994, VA.

ANALYTICAL METHODS FOR WHITE PHOSPHORUS (P_4) IN SEDIMENT AND WATER

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ABSTRACT

White phosphorus (P_4) can produce severe adverse ecological impacts if released into the environment. First produced in the United States over 100 years ago for use in matches, and subsequently for rat poisons and fireworks, today it is primarily used in the production of phosphoric acid and as a smoke-producing munition. To date, there is no standard analytical method for white phosphorus in environmental matrices. We have been using an analytical method based on solvent extraction and gas chromatography to determine white phosphorus in sediments and water from an Army training area. For sediments, a method detection limit of less than 1 µg/kg was achieved for white phosphorus extracted with isooctane and determined with a portable capillary gas chromatograph equipped with a nitrogen-phosphorus detector. For water, extraction with isooctane may be used to determine concentrations greater than 0.1 µg/L. However, to meet water quality criteria for aquatic organisms, preconcentration of the solvent extract is required. Due to the relatively high vapor pressure of white phosphorus, a nonevaporative preconcentration step is used. P_4 is extracted from water using diethyl ether (10:1 water:solvent ratio). The ether phase is collected, then reduced in volume by shaking with reagent-grade water. By using the appropriate volume of water, excess ether is dissolved away, resulting in a preconcentration factor of 500 while heat is avoided and loss of P_4 by volatilization minimized. Using this preconcentration procedure, a method detection limit of less than 0.01 µg/L was achieved.

To minimize use of solvent in the laboratory, solid phase microextraction (SPME) may be used to screen samples for contamination. Exposure of a 100-µm polydimethylsiloxane phase to the headspace above a sediment or water sample for 5 min followed by thermal desorption in the injection port of the gas chromatograph provides sensitivity similar to that obtained by solvent extraction. Since this method is based on equilibrium partitioning be-

tween the sample, headspace, and solid phase, response is matrix-specific. Work is in progress on calibrating this procedure for quantitative analyses.

This analytical method will be proposed for inclusion in SW-846 Update III as Method 7580: White Phosphorus by Solvent Extraction and Gas Chromatography.

INTRODUCTION

White phosphorus (P_4) is a synthetic chemical that has been used in poisons, smoke-screens, matches, and fireworks and as a raw material to produce phosphoric acid (1). In 1990, a waterfowl die-off at Eagle River Flats, Alaska, a U.S. Army training site, was traced to the presence of P_4 in the salt marsh sediments (2). At that time, no standard analytical method was available for the determination of P_4 in soil/sediment or water. To analyze the thousands of samples required by the site investigation, we used a published method, which was based on solvent extraction followed by gas chromatography with a phosphorus selective detector (3). The method needed modification to improve extraction efficiency and detection capability (4-6). This paper describes further work performed to validate the method in a variety of matrices and to test the use of solid phase microextraction (SPME) as a means to screen samples for P_4 contamination.

EXPERIMENTAL

An analytical standard for P_4 was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. The P_4 was supplied as a 5-g stick with a white coating under water. Pieces (100-300 mg) from the stick were obtained by placing the stick in degassed water in a nitrogen-purged glove bag and cutting with a razor blade. Care was taken to ensure that the surfaces of each piece of P_4 were freshly cut and lustrous in appearance, and showed no evidence of a white coating. These pieces were used to prepare solutions as described below.

A stock solution for calibration standards was prepared under nitrogen by dissolving 250 mg of P_4 in 500 mL isooctane (Aldrich Chemical Co.). Standards over the range 3.5 to 70 µg/L were prepared by dilution of the stock solution with isooctane or diethyl ether. Standards in isooctane are stable for months stored in ground glass stoppered flasks in the dark at 4°C. Standards in ether were prepared the same week of analysis and stored at -20°C.

Aqueous solutions of P_4 were prepared by placing pieces of P_4 into an amber jug containing 4 L of Type I water (MilliQ, Millipore) with no headspace and agitating the jug for over 60 days.

Blank matrices used to prepare spiked samples were: reagent grade

(Type I) water (MilliQ, Millipore); groundwater from a domestic well in Weathersfield, Vermont; surface water from a pond in Hanover, New Hampshire; Ottawa sand purchased from U.S. Silica, Ottawa, Illinois; a loamy soil from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland; a sandy silt from Lebanon, New Hampshire; and a Montana soil with high concentrations of metals purchased from NIST, Gaithersburg, Maryland. Soil samples were wetted to 100% moisture (dry weight basis) prior to spiking.

For each matrix, 10 replicate spiked samples (1 L for water and 40 g for wet soil) were prepared by adding an aqueous solution of P_4 to yield concentrations near the presumed detection limit (0.01 µg/L for water and 1 µg/kg for soil). This method worked well for all matrices except the Montana soil, where the dissolved P_4 in the aqueous spike was lost immediately, probably by fast reaction with metals in the soil samples. An alternative spiking method was used instead, where the Montana soil samples were spiked with small pieces of solid P_4. Spiked water samples were extracted within a day; spiked soil samples were equilibrated 24 hr prior to extraction.

Field-contaminated samples were obtained from Eagle River Flats, Fort Richardson, Alaska. Water samples were collected in 1-L amber glass bottles and soil samples were collected in 500-mL wide-mouth jars filled so that there was no headspace. Samples were maintained at 4°C until extracted. Samples were extracted and analyzed within 7 days of collection.

For extraction, a 500-mL aliquot of water was mixed with 50 mL of diethyl ether by shaking in a 500-mL separatory funnel for 5 min. After phase separation, all of the ether layer was collected. The volume of the ether layer recovered varied, depending on the temperature and the ionic strength of the samples; it generally ranged from 3 to 10 mL. The volume of the ether layer was further reduced to approximately 0.5 mL by adding the ether extract to approximately 50 mL of reagent-grade water in a 125-mL separatory funnel and shaking for 1 min. After phase separation, the ether layer was collected in a 5-mL graduated cylinder and the exact volume measured. P_4 concentration in the extract was then determined by gas chromatography. Extracts were analyzed immediately to minimize loss due to solvent evaporation.

Wet sediment samples were extracted by placing a 40-g subsample into a 120-mL jar containing 10.0 mL of degassed reagent-grade water. Then 10.0 mL of isooctane was added. Each jar was tightly sealed with a Teflon-lined cap, vortex-mixed for one minute, and then placed horizontally on a platform shaker for 18 hr. The sample then was allowed to stand undisturbed for 15 min to permit phase separation. Extracts were analyzed within a few hours.

P_4 was determined by injecting a 1.0-µL aliquot of the isooctane or ether extract on-column into an SRI Model 8610 gas chromatograph equipped with a nitrogen-phosphorus detector. The methylsilicone fused silica column (J and W DB-1, 0.53-mm-ID, 15-m, 3.0-µm film thickness) was maintained at 80°C. The carrier gas was nitrogen set at 30 mL/min. Under these conditions, P_4 eluted at 2.7 min.

The potential use of SPME as a means to distinguish blank samples from spiked or field-contaminated samples was tested. SPME fiber assemblies were obtained from Supelco, Bellefonte, Pennsylvania. These assemblies are composed of a fused silica fiber coated with a stationary phase (we used 100-µm polydimethylsiloxane). The fiber is attached to a holder that resembles a modified microliter syringe. In general, the fiber is exposed to a sample for a short period of time, during which analytes adsorb to the stationary phase. Then the fiber is placed into the injection port of a gas chromatograph to thermally desorb the analytes. We used the SPME fibers as follows. For each water sample, a 25-mL aliquot was placed in a 40-mL VOA vial. The vial was placed in a sonic bath for 5 min, during which time the SPME phase was exposed to the headspace. The SPME phase was immediately transferred to a heated (200°C) injection port of the gas chromatograph described above. For each soil sample, a 40-g subsample was placed in a 120-mL jar containing 10.0 mL of degassed reagent-grade water. The jar was sealed with a cap equipped with a septum. Each sample was shaken, then the SPME phase exposed to the headspace for 5 min. The SPME phase was thermally desorbed as described for the water samples.

RESULTS AND DISCUSSION

Method Detection Limits, Accuracy, and Precision: Method Detection Limits were computed from the standard deviation of the mean concentration found for each matrix and the appropriate Student's t value (7) (Tables 1 and 2). For the water matrices, the MDLs were similar, ranging from 0.003 to 0.005 µg/L. For the soil matrices, the range in MDLs was broader, ranging form 0.07 to 0.4 µg/kg. By definition, the spiked concentration must be within 1 to 5 times the MDL; therefore, only the MDL for the Lebanon soil should be considered a valid estimate. Based on the analysis of thousands of field-contaminated samples, where the lowest detectable concentrations reported are around 0.2 µg/kg, the MDLs obtained for the sand and Lebanon soils are reasonable estimates of the detection capability of the method.

Recovery was estimated from the mean found concentration and the spiked concentration. The spiking method we used differed from the commonly used technique where the analyte of interest is dissolved in an organic solvent, then added to a matrix. Frequently the sol-

Table 1. Method Detection Limits for water matrices.

	Spiked water samples		
	Reagent	Well	Pond
Spiked concentration (µg/L)	0.012	0.0097	0.0101
Mean found concentration (µg/L)	0.0075	0.0086	0.0081
Standard deviation	0.0012	0.0019	0.0013
RSD (%)	16	22	16
Mean recovery (%)	62	89	80
Method Detection Limit (µg/L)	0.003	0.005	0.004

Table 2. Method Detection Limits for soil matrices.

	Spiked soil samples		
	Sand	Lebanon	USAEC
Spiked concentration (µg/kg)	1.9	0.97	0.84
Mean found concentration (µg/kg)	1.4	0.83	0.71
Standard deviation	0.061	0.12	0.025
RSD (%)	4	14	4
Mean recovery (%)	73	86	85
Method Detection Limit (µg/kg)	0.17	0.34	0.07

vent used in the spike solution is the same as the extraction solvent; therefore, interaction between the analytes and the matrix is dissimilar to what may be expected in field samples. While no spiked matrix can fully mimic the interactions that occur over extended time periods in field-contaminated samples, we chose to use an aqueous solution of P_4 as a spike solution to more realistically simulate field-contaminated soils. For the water matrices, the lowest recovery was from reagent grade water (Table 1). Dissolved P_4 is readily lost from water (8); however, previous studies have shown that the rate of loss is slowed by the presence of dissolved organic matter (8), dissolved salts (9), soil (10), or iron (11). Whether or not instability played a role in the observed recoveries is unknown. Another factor may have been the more favorable partitioning of P_4 between the organic and aqueous phases when dissolved salts were present in the aqueous phase, such as in the well and pond water samples. When water from the salt marsh was spiked, recoveries were near 100%.

With the exception of the Montana soil, mean recoveries for the soil samples were greater than 70%. Recovery from the spiked Montana soil was less than 0.1%. Poor recovery was expected due to the rapid reaction of P_4 with copper (12) that was present in the soil at over 2900 µg/g. Any soil with high concentrations of copper will produce unacceptably low recovery of P_4. Preparation and analysis of matrix spikes should identify soils where matrix interactions will significantly affect recovery.

Precision was better for the soil samples (Table 2) than for the water samples (Table 1), probably due to the lack of a preconcentration step. Even at these very low concentrations, the relative standard deviations were all less than 25%.

Field-Contaminated Samples : Replicate samples of field-contaminated water and sediment were analyzed (Table 3). The concentrations in the water samples were very low, with the mean concentration within the range of MDLs obtained for the spiked matrices.

P_4 was easily detectable in all sediment samples (Table 3). Low part-per-billion (µg/kg) concentrations are typical for samples contaminated by the use of P_4 munitions (13-15). However, concentrations up to 3,000,000 µg/kg have been observed for some Eagle River Flats samples that contain particulate P_4. For samples that contain particles of P_4, concentration estimates can vary widely from subsample to subsample.

Calibration: This method utilizes a nitrogen-phosphorus detector, which has proven to be extremely sensitive to P_4 and free from interference. Drawbacks of the detector are the limited linear range and the tendency of the response to vary from day to day. To reduce the systematic error, we recommend generating a five-point calibration curve daily prior to analysis of samples. Since the gas chromatographic run times are so short (less than 5 min), less than 30 min is required to obtain these data. To check for drift in the detector response during the course of an analytical shift, a check standard should be run every 10 samples and at the end of the shift. Unless the shift is particularly long, drift should be less than 10%.

Table 3. P_4 concentrations found in field-contaminated samples.

	P_4 Concentration	
Rep	Water (µg/L)	Sediment (µg/kg)
1	0.0026	20.3
2	0.0009	14.2
3	0.0024	5.8
4	0.0015	17.9
5	0.0031	13.7
6	0.0039	21.2
7	0.0054	14.0
8	0.0061	11.6
9	0.0048	11.5
10	0.0055	18.9
Mean	0.0036	14.9
Std deviation	0.0018	4.7
RSD (%)	50%	32%

Screening by Solid Phase Microextraction: Because the majority of samples sent to analytical labs for the analysis of volatiles or semivolatiles tend to be blank or devoid of the analytes of interest, considerable time and effort could be saved by screening samples for contamination prior to extraction and analysis. Recently, several papers have been published describing the use of solid phase microextraction (SPME) as an alternative to traditional extraction techniques (16) for volatiles and semivolatiles. Using the spiked and field-contaminated

samples described above, we tested the use of SPME as a way to screen samples for P_4 contamination. The SPME fiber was simply exposed to the headspace above a subsample for 5 min, then thermally desorbed in the injection port of the gas chromatograph. P_4 was detectable in all the spiked water and soil samples, and in the field-contaminated sediment samples. P_4 was not detected in some of the samples of Eagle River Flats water, which had P_4 concentrations below the estimated MDL. Based on these results the analysis of a large number of blanks can be avoided and use of solvent minimized in the laboratory by using SPME to screen samples for contamination.

SUMMARY

Using spiked and field-contaminated matrices, analytical methods for the extraction and analysis of P_4 in water and soil matrices were evaluated. Method Detection Limits less than 1 µg/kg for soil and less than 0.01 µg/L for water were obtained using methods based on solvent extraction followed by gas chromatography with a nitrogen-phosphorus detector. Solid phase microextraction was tested and appears to have great potential as a means to screen samples for P_4 contamination.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding for this work, which was provided by the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, Martin Stutz, Project Monitor, and the U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, Ann Strong, Project Monitor. Technical reviews were provided by Thomas F. Jenkins and Alan Hewitt. This publication reflects the personal views of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or Government of the United States.

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EFFECTS OF BAROMETRIC PRESSURE ON THE ABSORPTION OF PREPARED MERCURY STANDARDS

S. Siler
D. Martini

INTRODUCTION:

Typically mercury samples can be analyzed on any given day with little variation in Quality Control Reference Standard (QCRS) recovery. However, we have noted substantial variation when storm systems move through our geographical area. Though the same standards used to define the morning calibration curve (before the thunderstorms) were used after lunch, the peak heights varied substantially. Most interesting was that a third, late afternoon curve, after storm systems had passed, showed peak heights virtually identical to those generated in the morning. On days when the weather patterns are particularly complicated we have found it virtually impossible to maintain standardization. Mechanical variables such as tubing tension, aperture blockage, intermittent valve malfunction, etc. were considered. We suspect that the barometric pressure may actually be affecting the output of the instrument. Using official barometric pressure readings provided by the National Weather Service and comparing to our recorded peak height on prepared mercury standards, we have studied the relationship and, though not yet absolute, we have noted some definite trends.

EXPERIMENTAL:

All analyses were performed at TALEM, Inc. (Texas Analytical Laboratories for Environmental Monitoring) during the routine course of business. Standards were made from reagent grade deionized water, ACS grade nitric and sulfuric acids, and either SPEX EP-8 certified mercury standard (10 ug/ml) or PlasmaPure certified mercury standard (1000 ug/ml). Analyses were performed on a PSA 10.04 Automated Mercury Analyzer using EPA 245.2 procedures. The analyzer is microprocessor controlled and aspiration times were programmed and constant.

Standards were prepared each time analyses were to be performed and, after analysis, stored in a refrigerator held at 4°C. Previously used standards were measured only for experimental reasons. The instrument blank was 2% nitric acid in deionized water. The reducing agent was 2.5% stannous chloride in 5% hydrochloric acid. Barometric pressures were obtained from the National Weather Service as recorded hourly at Dallas-Fort Worth International Airport. Peak height vs. barometric pressure was plotted and classical linear regression analysis was used to construct trends for mercury standards prepared at 0.30, 0.50, 1.0, 2.5, and 5.0 ug/L concentrations.

DISCUSSION:

All samples analyzed were used as calibration standards for regular analysis of unknown samples and yielded correlation coefficients of not less than 0.995.
To observe the effect of barometric pressure on prepared standards, several weeks of data were recorded. Table 1 shows the raw data. Graphs are included for each mercury concentration and even though there is significant scatter in the individual data points trend analysis does show a direct relationship between barometric pressure and peak height response.

Although not included here it was interesting to note a general decrease in the slope of individual calibration curves as barometric pressure decreased. Peak height gain or loss seems to be a direct relationship to changing barometric pressure.

CONCLUSIONS:

The data seems to indicate that relatively small changes in barometric pressure can have a profound affect on peak heights produced by mercury standards. With many of these types of systems being automated, the magnitude of the affect can compromise validity of calibrations causing more frequent recalibrations to be required. Possible explanations for the change in response could have to do with residence time changes in the cold vapor cell due to flow rate changes induced by fluctuations in barometric pressure although this and other plausible explanations have not been explored to this point.

ACKNOWLEDGMENTS:

This work was supported by TALEM, Inc. Fort Worth, Texas. We are especially grateful for the generous professional help of Ted R. Skingel, Quality Assurance Administrator, and Tyler Tull, V. P. Environmental Services. We also extend special thanks to the staff at the National Weather Service in Fort Worth for opening records, accessing files and generally being helpful and cooperative on our Saturday afternoon raids of their data files.

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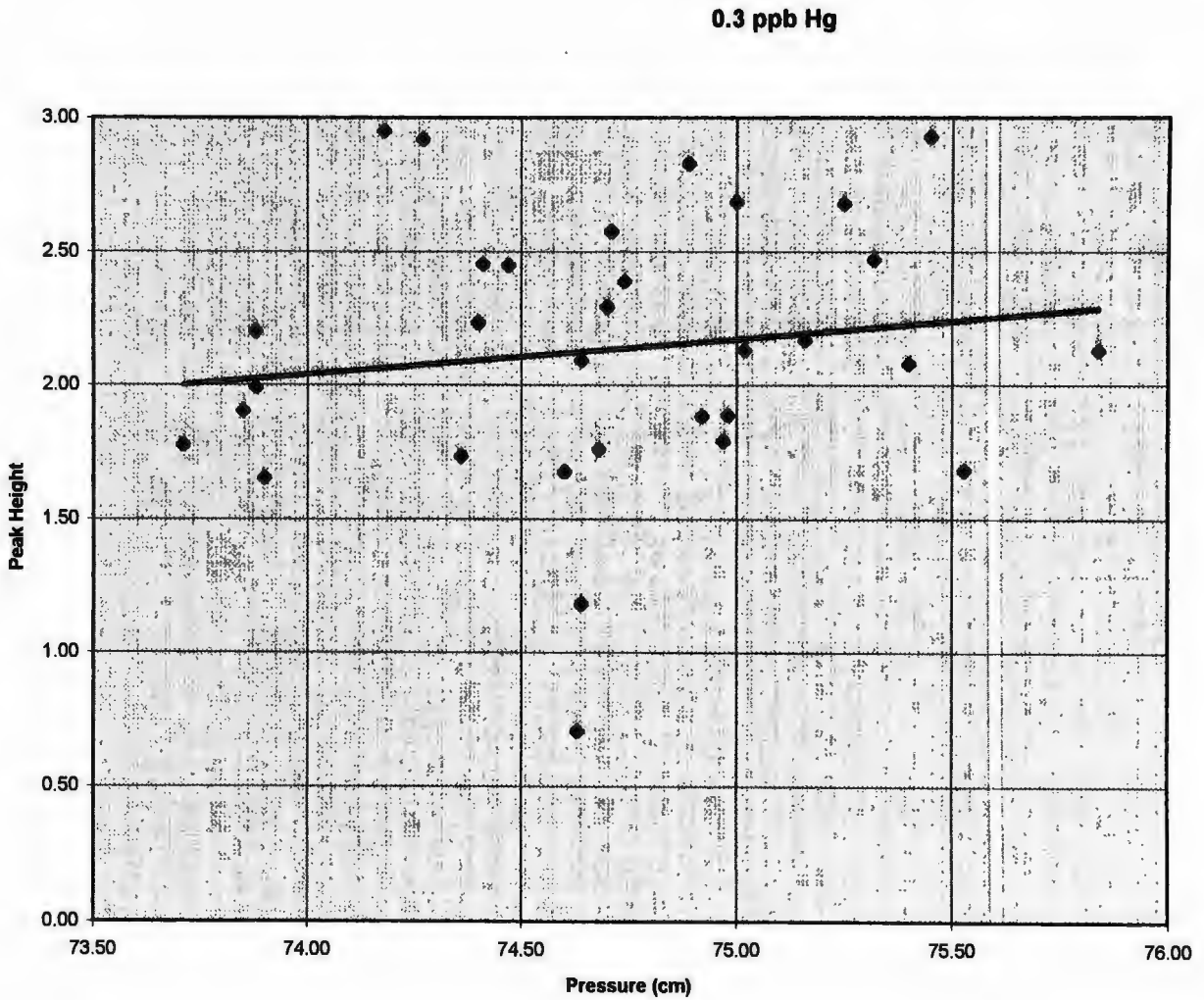
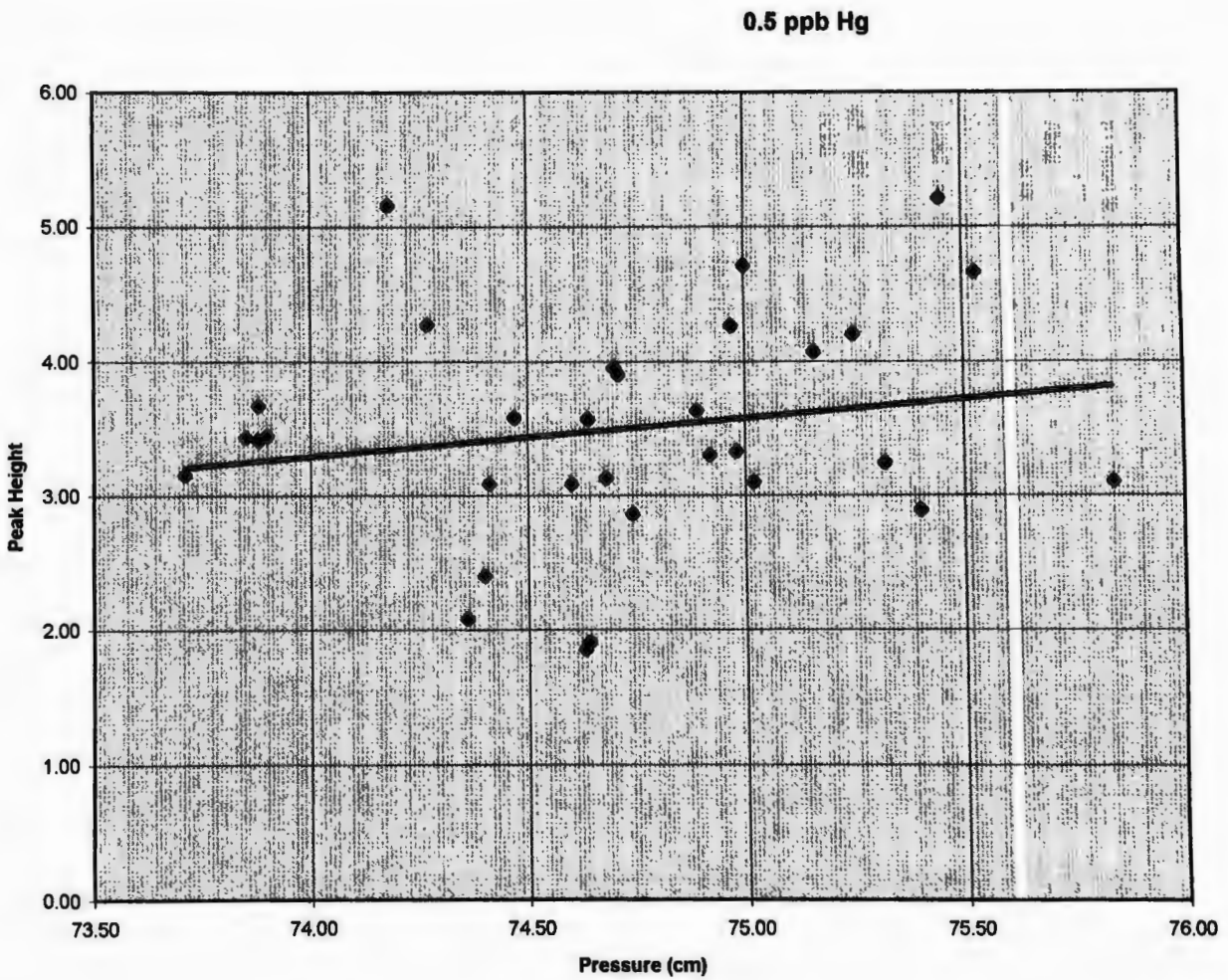
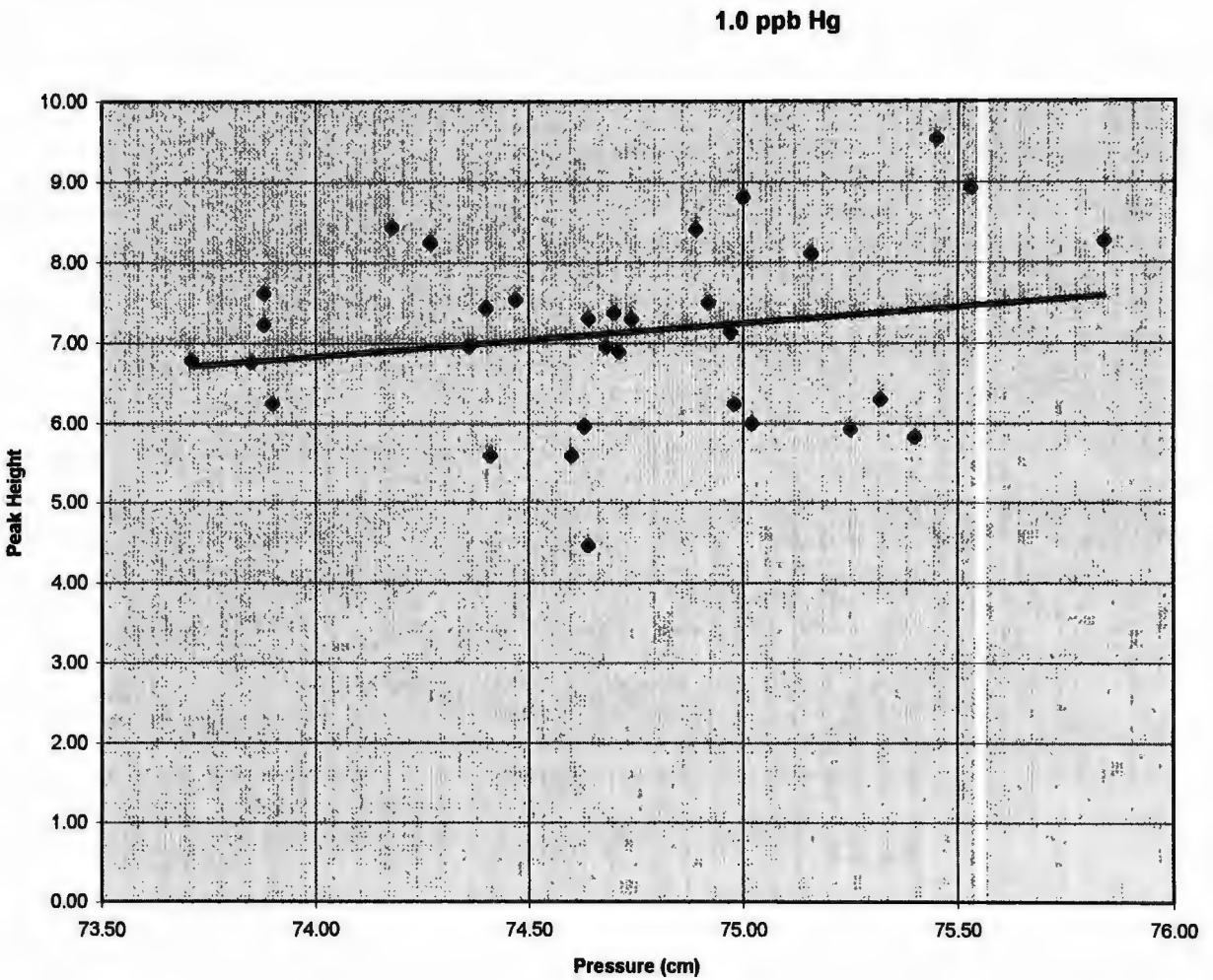
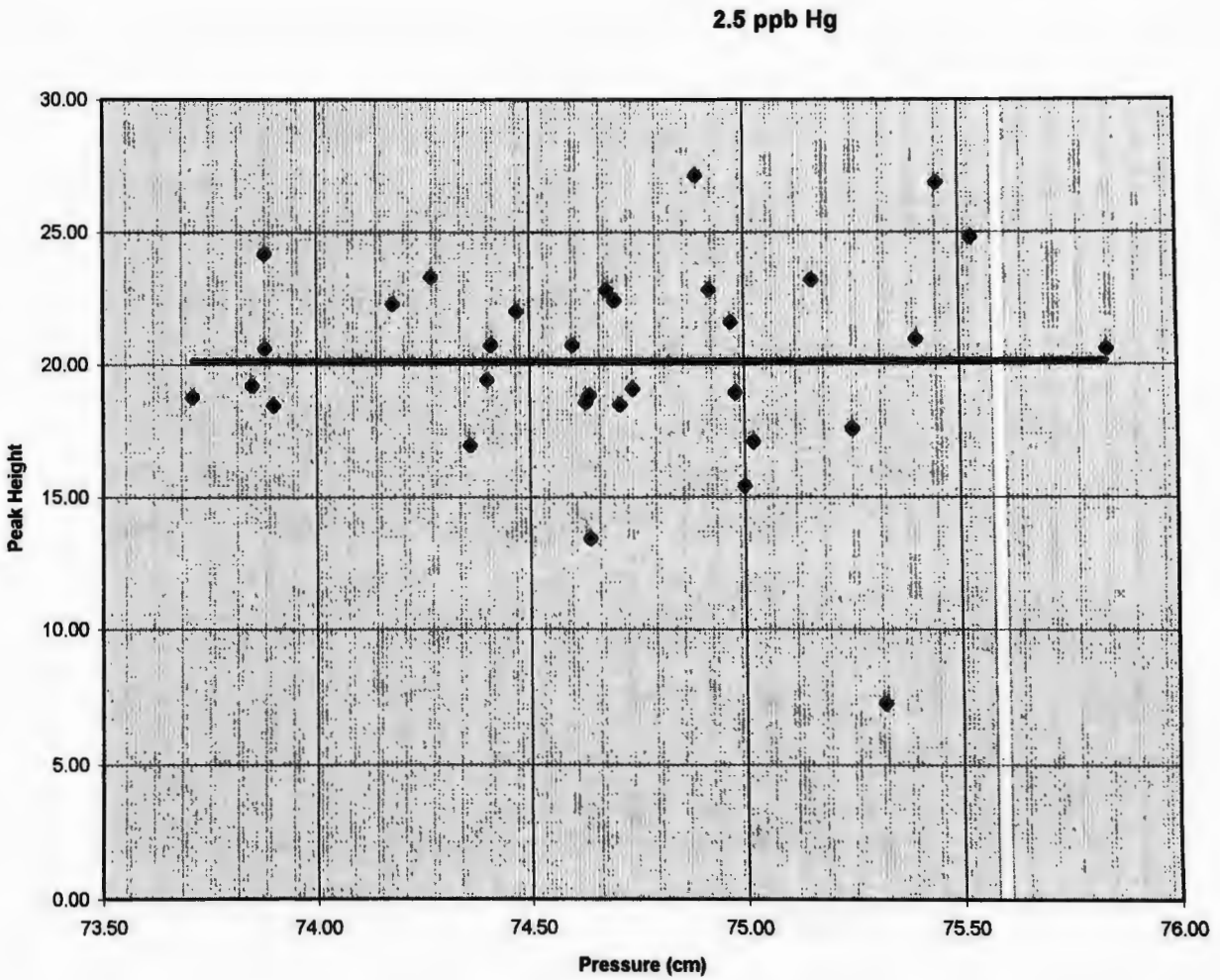
TABLE 1

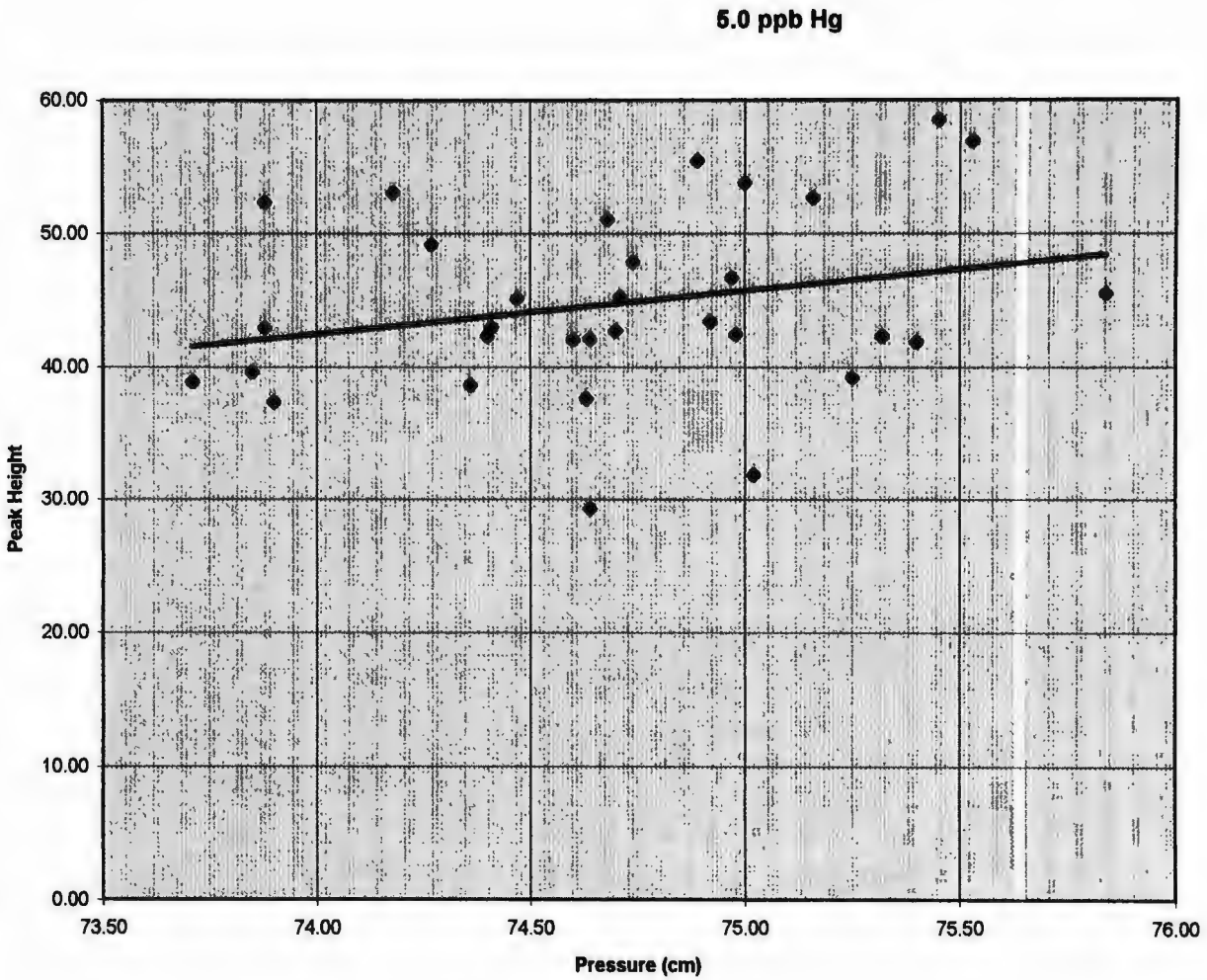
DATE	P (cm)	0.3ppb Hg	0.5ppb Hg	1.0ppb Hg	2.5ppb Hg	5.0ppb Hg
2/2/95	74.60	1.68	3.09	5.60	20.74	42.05
2/4/95	74.92	1.88	3.30	7.49	22.82	43.40
2/7/95	75.32	2.47	3.24	6.30	7.26	42.32
2/7/95	75.40	2.08	2.89	5.83	20.96	41.86
2/9/95	74.36	1.73	2.08	6.96	16.94	38.63
2/9/95	74.89	2.83	3.63	8.41	27.13	55.48
2/11/95	74.71	2.58	3.90	6.90	18.47	45.22
2/13/95	74.98	1.89	3.32	6.24	18.92	42.45
2/14/95	74.68	1.76	3.13	6.95	22.80	51.08
3/3/95	75.25	2.68	4.20	5.93	17.56	39.21
3/8/95	75.84	2.13	3.10	8.27	20.58	45.49
3/9/95	75.45	2.93	5.21	9.54	26.86	58.54
3/10/95	75.16	2.17	4.07	8.11	23.19	52.70
3/10/95	75.53	1.68	4.66	8.93	24.82	56.99
3/13/95	74.27	2.92	4.27	8.25	23.30	49.20
3/14/95	74.41	2.45	3.09	5.60	20.74	42.96
3/17/95	74.97	1.79	4.26	7.13	21.60	46.70
3/22/95	73.88	2.20	3.41	7.61	24.19	52.33
3/30/95	74.70	2.29	3.95	7.37	22.40	42.70
3/30/95	75.00	2.69	4.71	8.81	15.42	53.83
4/4/95	74.64	1.18	1.91	4.47	13.44	29.30
4/11/95	74.47	2.45	3.58	7.54	22.00	45.09
4/12/95	75.02	2.13	3.10	6.00	17.08	31.84
4/20/95	73.71	1.77	3.15	6.79	18.74	38.86
4/20/95	73.85	1.90	3.44	6.77	19.19	39.57
4/20/95	73.88	1.99	3.67	7.23	20.60	42.94
4/26/95	74.18	2.95	5.16	8.44	22.30	53.09
5/1/95	74.40	2.23	2.40	7.43	19.40	42.32
5/2/95	74.64	2.09	3.56	7.30	18.81	42.10
5/4/95	74.74	2.39	2.86	7.29	19.05	47.88
5/5/95	74.63	0.71	1.85	5.97	18.55	37.61
5/8/95	73.90	1.65	3.45	6.25	18.43	37.37


0.3 ppb Hg
Peak Height
3.00
2.50
2.00
1.50
1.00
0.50
0.00
73.50
74.00
74.50
75.00
75.50
76.00
Pressure (cm)


0.5 ppb Hg
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Peak Height
73.50
74.00
74.50
75.00
75.50
76.00
Pressure (cm)


1.0 ppb Hg
Peak Height
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
73.50
74.00
74.50
75.00
75.50
76.00
Pressure (cm)


2.5 ppb Hg
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Peak Height
73.50
74.00
74.50
75.00
75.50
76.00
Pressure (cm)


5.0 ppb Hg
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Peak Height
73.50
74.00
74.50
75.00
75.50
76.00
Pressure (cm)

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A Simple Silver Analysis

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Abstract

A simple, inexpensive colorimetric silver analysis has been developed that is capable of measuring silver concentrations in varying solutions over a range of 0.2 to 20,000 mg/l. The technique rivals AA and ICP for accuracy and precision, but is easily performed by inexperienced personnel in a few minutes using inexpensive equipment.

With increasingly stringent governmental regulation of heavy metal discharges, it has become more important for manufacturers and processors to be able to monitor their silver usage, recovery operations and discharge levels. To date, this has been difficult at best for all except the largest facilities. The current options available are:

Copper test strips. Under the right conditions, silver will plate out from solution onto copper metal. This very inexpensive "test" (it only costs a penny, and you get to keep the penny) merely indicates the presence of silver without measuring concentration. At least one purveyor of copper test strips claims to be able to distinguish 5 mg/L with an extended dip time. In general, this technology is of very limited use.

Silver Estimation Papers. These are (usually) cadmium sulfide impregnated porous papers designed to be dipped into the solution to be tested. Any silver present will form a brown silver sulfide stain that is compared to a color chart to estimate the silver concentration. The drawbacks are: 1) a lack of sensitivity. Intensity differences become quite difficult to distinguish below 0.5 gm/L of silver, and 2) the lack of specificity. Other metal ions can react, creating a similar brown stain, producing confounding results. The chealated iron compounds in a photographic bleach or bleach-fixer may leave a brownish stain that could be confused with a silver response. In short, these indicator papers can be misleading.

Potentiometric titration. Potentiometry measures the intensity of silver ions in solution by ion specific electrode (I.S.E.). As the silver is removed from solution by titration with a standard titrant, the solution potential is monitored. This technique requires equipment that can range from mildly to highly expensive. It also requires the talents of an experienced operator familiar with laboratory

techniques and interpretation of data. The titrants can be dangerous (generally sulfides) and the range of delectability in many working solutions is limited. The I.S.E. readings are effected by any species that reacts with silver, possibly interfering with the accuracy. This technology is most effective when applied as a control of a process such as electrolytic silver recovery, where the actual readings are not as important as the relative changes in potential.

Atomic absorption (includes ICP). This technique is generally considered the most accurate and precise analytical procedure. It is the methodology recommended by most regulatory agencies requiring compliance monitoring. However, it involves extremely expensive instrumentation operated by an highly skilled analyst. It also utilizes compressed gasses for fuel. Only the very largest facilities are able to avail themselves of this technology. Most often when analyses are required, the generator turns to:

The independent (reference) laboratory. Although this is the route mandated by some agencies for the monitoring of compliance, results from these operations are necessarily delayed by shipping and, are never timely. Any problems may not be caught for several days. This is also an expensive alternative, the costs ranging from $25-75 for a single analysis.

Considering the above options, there was a clear need for an analytical technique to fill the gap between the expensive, difficult analytical technologies and the simple, undependable estimations. Such a technique would have to be:

1) simple. Most businesses can ill afford the expense of a full time laboratory analyst.
2) inexpensive. There is seldom much in the budget to purchase equipment that doesn't directly produce profit.
3) accurate. If decisions effecting process controls, recovery operations, and discharge parameters are to be based on the results of a silver analysis, the analysis had better be accurate.
4) compact. Most businesses have set aside little or no space for non revenue producing activities.
5) sensitive. The technique must be usable to analyze solutions containing several gm/L of silver, yet at the same time be able to accurately measure to less than 1 mg/L in wash waters and effluents.

The above criteria seemed to be best met using colorimetry, which is the measurement of the intensity of an uniquely colored compound in solution, which would be formed by the reaction of the silver with a reagent compound.

There are many chemical compounds which will react with silver to form new compounds, but most either demonstrate no visible change, or result in a precipitate that precludes their use as colorimetric reagents. The proprietary compound used as the silver sensing reagent in the silver test is a thiol-type metal ion complexing agent that is soluble and active at pH's of 12 or higher. In high pH aqueous solution, this thiol combines on a one-to-one basis with silver ions to form a reddish-purple compound that demonstrates a λ_{max} at 545 nm. Under the conditions of the test, the thiol will not only react with free silver ions, but also

with those tied up in complexes such as with thiosulfate and thiocyanate. This product is indeed insoluble, but initially it is so finely dispersed as to appear and measure as a solution.

In actuality, this thiol forms unique colored complexes with many metals, each complex having its own distinctive λ_{max}. Although the technology described herein was developed for the measurement of silver in photoprocessing solutions, it could apply to any one of several metal ion concentrations in other venues. In fact, several could be determined simultaneously with readings at various points, or by scanning the visible wavelengths.

The orange color of the reagent has a λ_{max} at 460 nm, but the curve is sufficiently wide to overlap with readings in the mid 500 nm range. For this reason, the absorbance of the reagent alone is measured and subtracted from the reading of the silver complex formed (To affect this, the colorimeter is actually zeroed on the reagent prior to its use). The molar absorptivity of the silver complex calculated from measurements made at 560 nm was 6×10^3. This indicated sufficient sensitivity to measure silver in the concentration range of interest (0.2 to 20,000 mg/L).

A reagent mixture was devised containing the thiol complexing agent, a compound to maintain the pH, a compound to complex iron in order to prevent the formation of ferric hydroxide at the working pH, an antioxidant to protect the thiol, and a dispersant to keep the silver complex in fine suspension for measurement.

Calibration curves were generated from standard silver concentrations combined in varying matrices of photoprocessing solutions demonstrated that, under the conditions recommended for testing, no matrix effects were evident. It made essentially no difference whether fixer, bleach-fix, or silver nitrate solution was being measured. Like silver concentrations yielded like absorbances.

Over the past two years, several thousands of samples have been analyzed both by this technique and by ICP or AA. These samples have been of varying composition, containing significant concentrations of thiosulfate, thiocyanate, metal ion chealators such as EDTA, ferrocyanide, halides and many other compounds typically found in photoprocessing effluents. The silver levels in these samples ranged from less than 1 mg/L to nearly 20 Gm/l. The correlation constants (r^2) calculated from these data as compared to the reference methods mandated by regulatory agencies were consistently greater than 0.98. A typical correlation study is shown in Figure 1. The samples used were taken from a photoprocessing operation and include samples of fixers, EDTA bleach-fixers. ferrocyanide containing fixers, and wash waters. Silver levels ranged from 2 mg/L to over 10 gm/L.

The chemistry of this analysis has also been applied to a continuously sampling analyzer monitoring the output from an ion exchange silver recovery system. The hardware utilized segmented flow technology, measuring in a flow-through cell mounted in a colorimeter. The colorimeter converted the colorimetric intensities

to a millivolt output which was monitored by a process controller. The controller used the signal to alert of silver breakthrough and initiate the resin regeneration cycle. A characterization of this system is shown in Figure 2. This type of monitor could also be used to control the addition of a silver precipitating agent prior to the treatment of a fixer for reuse. It would assure that there would be no excess precipitant in the recycled solution.

The greatest need, in the industry, however, is for a low cost, discrete analysis. To this end, Kodak has produced a silver test kit which contains all the hardware necessary to perform the silver analyses. Included are the colorimeter and three sampling pipettors that cover the entire range of the sensitivity, along with a dispenser for the liquid portion of the reagents. Reagents are supplied separately in multiples of 100 tests. The reagents are in a single test format, which includes a sealed packet, the contents of which are dissolved into an aliquot of a provided liquid reagent in preparation for measurement. To this reagent mixture, the proper measured sample is added and mixed, and the absorbance of the resultant solution is measured in a colorimeter. The entire process takes less than two minutes.

Full strength fixes and bleach-fixes may be measured as low as 20 mg/L of silver. The measurement of lower levels in these media would necessitate a larger sample size than that recommended. At this point, the thiosulfate competes more far favorably for the silver, so the sensitivity falls off drastically. Because the thiosulfate in wash waters is diluted 50-100X, the measurement of silver in these solutions is possible to less than 0.5 mg/L.

Given the versatility, accuracy, and sensitivity of this technique, it is possible to monitor the silver throughout the process, allowing the operator to optimize replenishment of process chemicals and washes, to control and verify the recovery process, and monitor the discharge for compliance.

I would like to acknowledge the contributions of Andrew Hoffmann and Dr. Richard Horn of the Eastman Kodak Company for their contributions to the optimization of this technique, the generation of thousands of results, and the coordination of the correlation studies. Their efforts have been invaluable.

Figure 1.

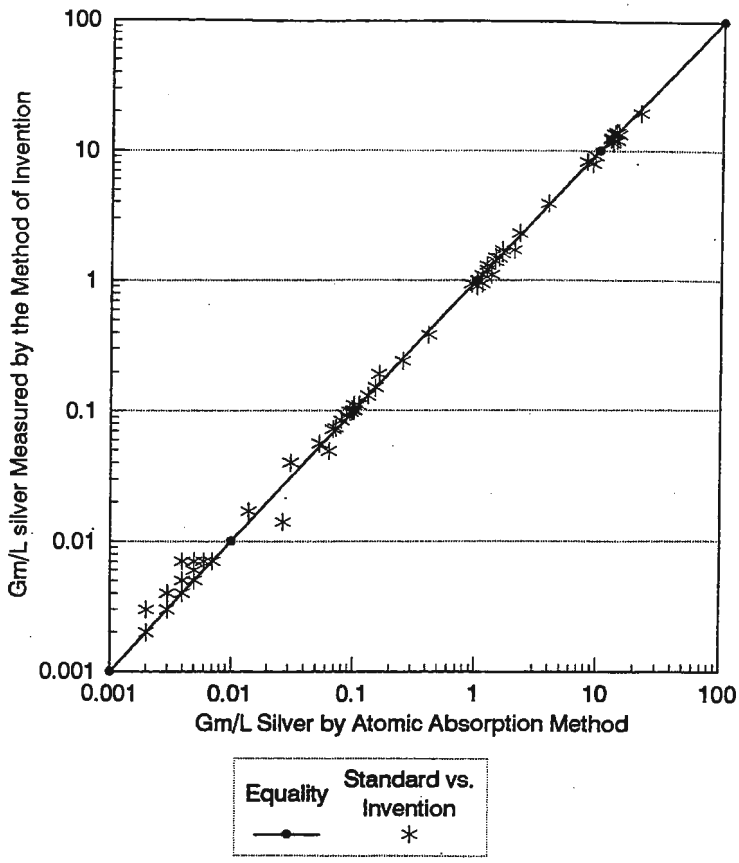
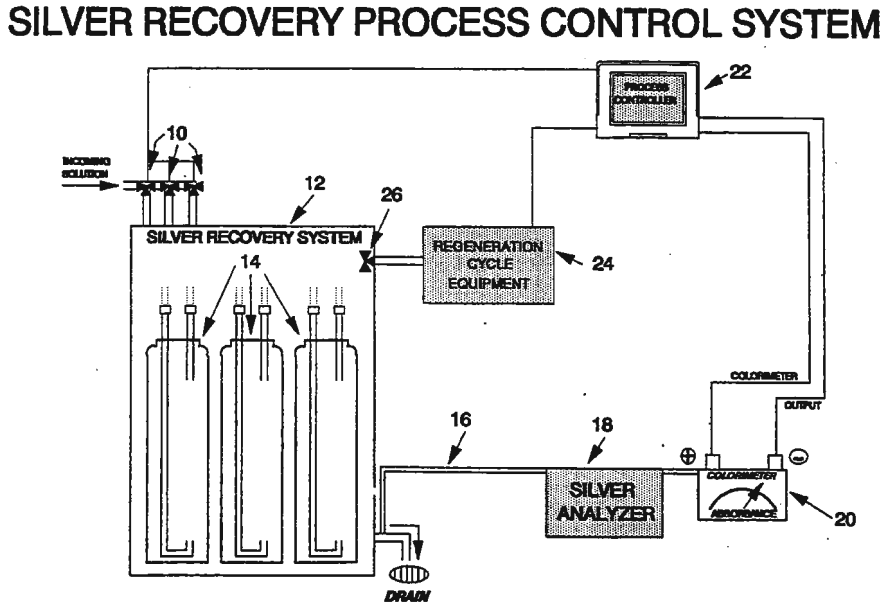


Figure 2.



Capillary Ion Electrophoresis, An Effective Technique for Analyzing Inorganic and Small Organic Ions in Environmental Matrices

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Waters Corporation
34 Maple Street
Milford, MA 01757

Capillary Ion Electrophoresis is a mode of capillary electrophoresis which is optimized for the rapid analysis of inorganic anions, cations, low molecular weight organic acids and amines. This use is also termed Capillary Ion Analysis (CIA). It is characterized by high speed, high resolution separations which are achieved by applying an electric field to a sample contained in a capillary filled with an electrolyte. Since no chromatography column is involved, complex samples can often be analyzed without the extensive sample preparation commonly needed prior to ion chromatography or other modes of HPLC.

The mechanism of separation is different from ion chromatography making it possible to easily analyze anions and organic acids simultaneously. Similarly cations and organic amines can be monitored in a single run, Figure 1. As shown in Figure 2, the instrumentation for performing CIA is very simple. Instead of a chromatography pump, the separation is driven by a power supply. A portion of the capillary in which the separation takes place forms the detector cell. Direct UV/vis detection is used as well as indirect detection for ions which do not absorb UV.

Figure 3 illustrates the rapid, high resolution separations which are provided by CIA. It also demonstrates significant chloride speciation. Total analysis times are typically 4 to 6 minutes. As indicated by the response shown for the low ppm concentrations, detection limits are typically in the low to mid ppb levels for the common anions using a simple hydrostatic injection mode. There is also a method for combined concentration and injection of ultra pure samples which extends the detection limit into the low ppb/high ppt range, but this is generally not used for environmental samples.

Capillary Ion Analysis is an effective compliment to ion chromatography and has been shown to produce comparable results to both single column and chemically suppressed modes of IC, Figures 5, 6 and 7. Typical sample preparation, such as the waste water analysis shown in Figure 8, is often confined to filtration and dilution. Since the waste water was diluted 1:10, the very small fluoride peak is actually 7 ppb concentration. With CIA there are no early eluting water dip, carbonate or cation peaks to complicate the analysis or quantitation.

A recent study compared the values obtained by a commercial testing laboratory using official wet chemical methods to those produced by CIA and ion chromatography. Samples included drinking water, process and waste water as well as landfill leachate. The results of one such comparison are shown in Figure 9. Overall agreement among the techniques was considered to be excellent. The wet chemical Nitrate-Nitrite results were composite values provided by the cadmium reduction method. Individual values for each ion were obtained by CIA and IC and then summed for comparison purposes.

Other studies have demonstrated the utility of this technique for analyzing cations[1] and nerve agent degradation products[2] in environmental samples. The characteristics of CIA listed in Figure 10 have already resulted in investigation of its use for additional environmental problems ranging from characterizing nuclear waste sites to monitoring acid rain. The technique is rugged and especially well suited for used by the environmental analyst.

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Figure 1
Capillary Ion Analysis
Definition

Capillary Ion Analysis is a form of
Free Zone Capillary Electrophoresis (CE)
Introduced in 1990 by Waters
for the Analysis of
Inorganic Anions & Organic Acids and
Inorganic Cations and Organic Amines

CE Has Different Separation and Detection
Chemistry and Physics
Compared to Liquid / Ion Chromatography

Figure 2
Capillary Ion Analysis System Configuration

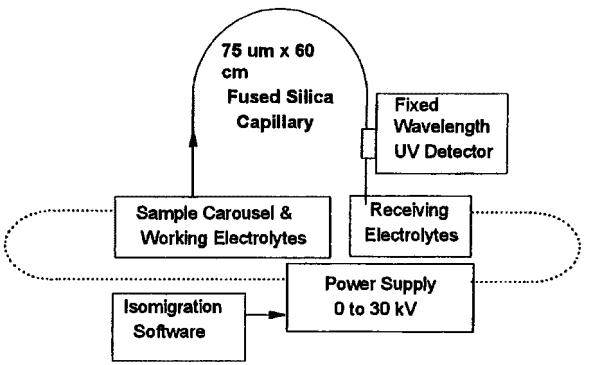
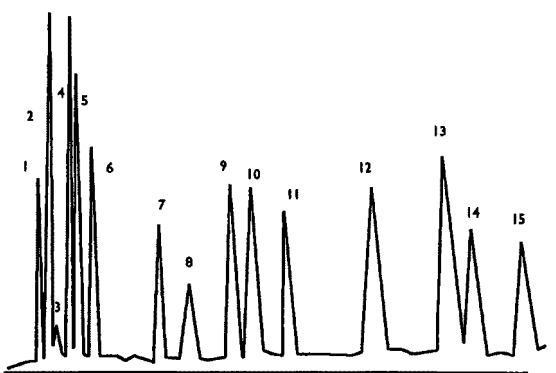


Figure 3
Powerful Anion Separations



1 Bromide	4
2 Chloride	2
3 Iodide	4
4 Sulfate	4
5 Nitrite	4
6 Nitrate	4
7 Chlorate	4
8 Perchlorate	4
9 Fluoride	1
10 Phosphate	4
11 Chlorite	4
12 Carbonate	4
13 Acetate	5
14 Monochloro-acetate	5
15 Dichloro-acetate	5

Figure 4
Capillary Ion Analysis
Advantages vs IC/LC

- Small Scale of Operation
  - Minimal sample & electrolyte used
  - Minimal waste generated (<100 mL/day)
  - Fast analyses (typically 6 minutes)
- No Column Involved
  - Minimal sample prep needed
  - Fast methods turnaround
  - Fast run-to-run times
  - Increased cost effectiveness

Figure 5
Elution Order of Major Analytes

IC (Borate/Gluc)	CIA	
1. Water Dip	Bromide	7
2. Cations	Chloride	5
3. Fluoride	Sulfate	10
4. Carbonate	Nitrite	6
5. Chloride	Nitrate	8
6. Nitrite	Fluoride	3
7. Bromide	Phosphate	9
8. Nitrate	Carbonate	4
9. Phosphate	Water Peak	1
10. Sulfate	No Cations	2

15 min

5-7min

Figure 6
Why Use Capillary Ion Analysis?

- Rapidly analyze:
  - inorganic anions,
  - organic acids,
  - alkali & alkaline earth cations,
  - alkanolamines
- Results equivalent to ion chromatography
- Different separation selectivity than ion chromatography (confirm peak identity)

Figure 7
CIA Anion Analysis
Comparison to Ion Chromatography

	Anion	IC (ppm)	CIA (ppm)	CIA/IC
Tapwater	Chloride	20.22	20.04	0.991
	Sulfate	14.77	14.04	0.951
	Nitrate	3.55	3.53	0.994
	Fluoride	Not Detected	0.06	
Wellwater	Chloride	37.65	36.48	0.969
	Sulfate	11.95	11.42	0.956
	Nitrate	3.17	3.18	1.004
Industrial	Chloride	83.15	83.03	0.998
Wastewater	Sulfate	23.83	23.07	0.967
	Fluoride	Not Detected	0.13	
Power Plant	Chloride	191.83	199.77	1.041
Wastewater	Sulfate	79.86	76.76	0.961
	Nitrate	2.38	2.23	0.937

- CIA Anion Analysis results using proposed ASTM Method are equivalent to Ion Chromatography results

Figure 8
CIA Anion Analysis
Chromate Electrolyte - N601b

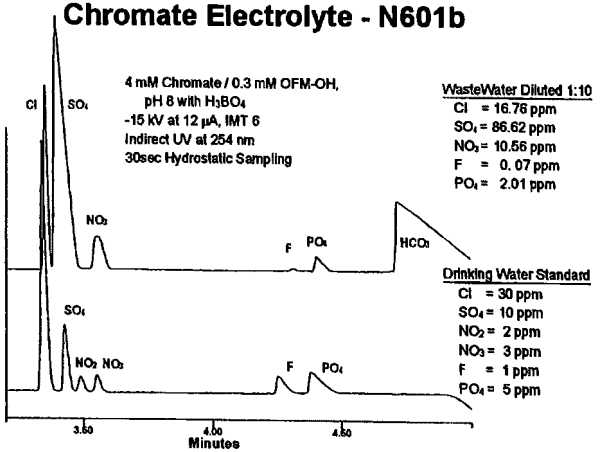
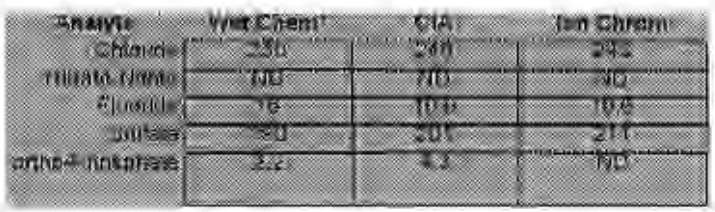


Figure 9
Anions in Landfill Leachate
Method Comparison

Sample # 60730-2 Concentrations in mg/L



Analyte	Wet Chem*	CIA	Ion Chrom
Chloride	250	240	242
Nitrate-Nitrite	ND	7.0	ND
Fluoride	1.6	10.1	10.6
Sulfate	20	20.1	21.1
ortho-Phosphate	2.2	4.2	ND

*By EPA methods: Chloride 325.3, Nitrate-Nitrite 353.2, Sulfate 375.4, Fluoride 340.2, ortho-Phosphate 365.2

Figure 10
Why Use Capillary Ion Analysis?

- Easy to change among applications
- Simple hardware and operation
  - Low operating costs
  - Minimal waste, less than 100 mL per day
  - No column to foul or void
  - Fast sample turnaround
  - Streamlined sample preparation
  - Amenable to multi-user operation
- Technology for the 90's and beyond

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The Determination of Adamsite, a Non-Phosphorus Chemical Warfare Agent, in Soil Using Reversed-Phase High Performance Liquid Chromatography

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ABSTRACT

An analytical method was developed to determine low-level concentrations of Adamsite in soil and sediment matrices. Air-dried soil samples are extracted with methanol in an ultrasonic bath. A portion of the extract is diluted with aqueous $CaCl_2$, filtered, and analyzed by high-performance liquid chromatography. The procedure provides linearity over the range of 0.2 to 15 µg/g. The method detection limit study yielded a detection limit of 0.1 µg/g. Matrix spike recoveries were greater than 90% for all tests conducted.

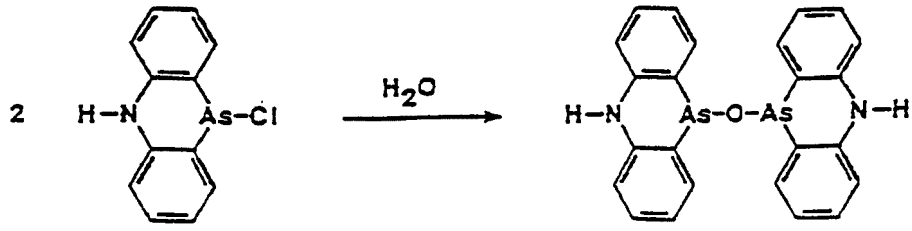
INTRODUCTION

Chemical warfare agents have been in existence since World War I and before. These agents have been stored at chemical arsenals on military installations, in both small and stockpiled quantities, depending on their use. Because chemical warfare agents are extremely hazardous materials, their clean-up and disposal of these chemicals presents significant problems.

Chemical warfare agents are generally classified as organophosphorus (nerve agents) and non-phosphorus containing compounds. These compounds can be further divided by their physiological effects (nerve agents, sensory irritants, psychotoxics, vesicants, etc.) This paper will deal specifically with a non-phosphorus containing compound called adamsite, 10-chloro-5,10-dihydrophenarsazine and its hydrolysis product, 10,10'-oxybis-(5,10-dihydrophenarsazine). Figure 1 presents the chemical structures for both compounds and Table 1 describes the physical properties of each.

Adamsite was developed in 1919 by the British army. It belongs to the riot control family of agents. Its physiological effects include vomiting, difficulty in breathing, and death in large doses. With more effective incapacitating agents available, adamsite did not see wartime use due to its low toxicity. Its use in controlling civilian riots was considered too harsh, therefore its use was limited. Adamsite was used commercially for some years as a pesticide to treat wood used for water vessels. Its toxic effects and by-products (arsine-based) led to its ban in the 1930's [1].

In recent years, with an increasing awareness in potential health and environmental concerns from long-term storage of chemical warfare agents, a need has developed to determine low-level concentrations of agents in various matrices. As a result, MRI has developed a solvent extraction method followed by HPLC analysis with UV detection.



DM
Adamsite

Hydolysis
Product of
Adamsite

Figure 1. Structure of Adamsite and the Formation of the Adamsite Hydrolysis Product

Abbreviation	Name	Formula	CAS #	M.W.	M.P.°C	B.P.°C
DM Adamsite	10-chloro-5,10-dihydrophen-arsazine	$C_{12}H_9AsClN$	578-94-9	277.6	195	410
Hydolysis Product of Adamsite	10'10'-oxybis-(5,10-dihydro-phenarsazine)	$C_{24}H_{18}As_2N_2O$	4095-45-8	500.3	350	-----

Table 1. Physical Properties of Adamsite and its Hydrolysis Product

EXPERIMENTAL

An analytical standard for adamsite was obtained from the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD. Individual stock standard solutions were prepared in both acetonitrile and methanol. Methanol was used in the preparation of eluant.

Standard soil used for method development was obtained from USATHAMA SARM Repository Soil. Field-contaminated soils were obtained from a military site.

Analytical separations were obtained on a modular system composed of a Dionex Gradient pump, Dionex Variable Wavelength detector, Spectra-Physics SP8880 autosampler equipped with a Rheodyne Model 9010 injector, and a Turbochrom acquisition system. Sample concentrations were determined by UV response(peak height) and calculated by internal standard technique relative to the standard data.

RESULTS AND DISCUSSION

Samples were initially extracted with both acetonitrile and methanol. Methanol was preferred to acetonitrile, in part due to better solubility of adamsite in methanol and also because of better recoveries for spiked samples. Samples were also extracted using a sonic cell disrupter and an ultrasonic bath. No significant differences in recoveries were observed, therefore the ultrasonic bath is preferred to allow for larger sample throughput simultaneously. Additional studies were performed to examine various extraction times. The times examined included 1 to 24 hours. An extraction time of 1 hour yielded recoveries in excess of 90% and allows for processing of an extraction batch in one day. It should be noted that no significant differences were seen in the longer extraction times. A summary of the final extraction procedure follows.

An air-dried sample is extracted with methanol in an ultrasonic bath. A portion of the extract is diluted with aqueous calcium chloride [2], filtered, and analyzed by Reverse-Phase HPLC.

Analysis parameters evaluated included wavelength and eluant concentrations. The two wavelengths evaluated were 229nm and 254nm based on absorption maxima and molar absorptivities [3]. The 229 nm wavelength was chosen based on increased mv response of both the hydrolysis product and internal standard. Several eluant concentrations were evaluated under isocratic conditions. The objective was to find a wavelength/eluant combination to produce baseline resolution of the hydrolysis product of adamsite in a reasonable amount of time. This objective was accomplished with a 25 cm × 4.6 mm (5μm) C-18 column and eluted with 70/30 v/v methanol/water (Figure 2). Retention times and capacity factors for the hydrolysis product and internal standard are shown in Table 2. It should be noted that it is the hydrolysis product of adamsite that is seen in the chromatography. As described by Kuronen (1990), adamsite is rapidly and completely converted to its hydrolysis product when in contact with steel (i.e. chromatography tubing, steel frits, column, etc.).

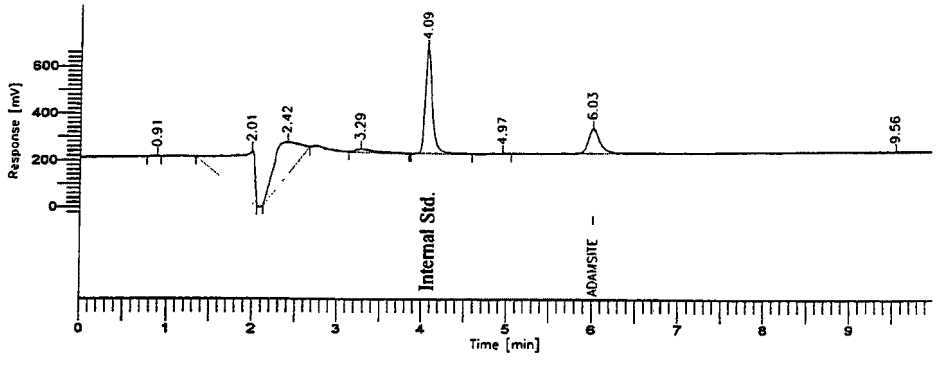


Figure 2. Chromatogram of Adamsite Hydrolysis Product on C-18 column, eluted with Methanol/Water at 1.3 mL/min.

Analyte	Retention Time (min.)	Capacity Factor (k')
DM Hydrolysis Product	6.03	1.97
Internal Standard	4.09	-----

Table 2. Retention Time and Capacity Factors for Adamsite Hydrolysis Product

Using peak height and internal standard calibration, a linear curve was produced to cover the range of 0.2 to 15 μg/g. The correlation coefficient was 0.999 or greater with a %RSD of 15% or less (Figure 3).

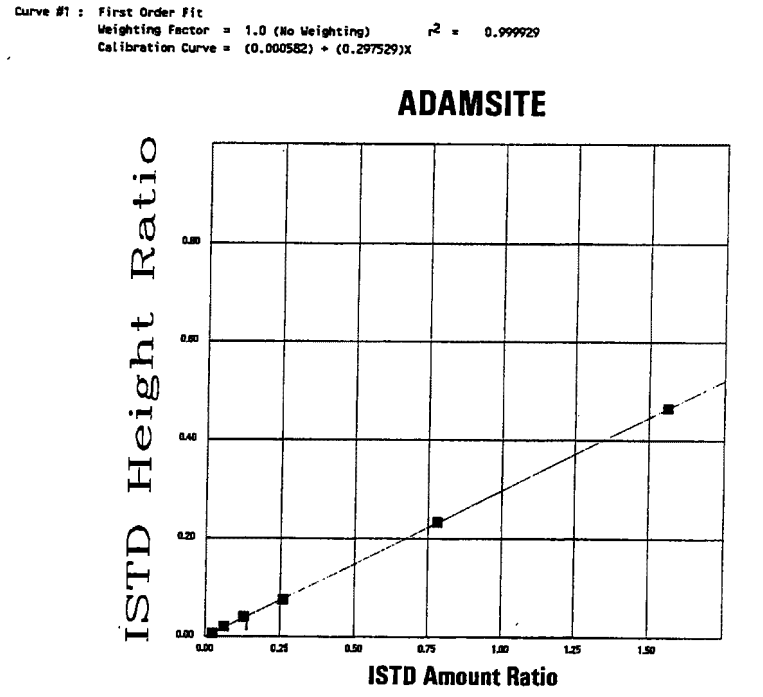


Figure 3. Internal Standard Calibration Curve for the Adamsite Hydrolysis Product

The method-detection limit study was performed according to USAEC protocol. The spiking concentration used in the MDL study was 1.5X the lowest standard of the calibration curve. Seven replicates of SARM Repository soil were spiked, extracted, and analyzed. MDL's were determined by calculating the standard deviation of the seven replicates and multiplying the result by the t-value at the 99% confidence level. The obtained MDL (0.11 μg/g) was 2X less than the DL (0.26 μg/g) based on instrument response. The actual percent recovery values ranged from 87% to 122%. These values were derived from an internal standard calibration method using a linear regression equation with zero-intercept for the spiked concentrations versus the found. The actual found concentrations ranged from 0.27 μg/g to 0.38 μg/g. The results are presented in Table 3.

Analyte	MDL (µg/g)	Reporting Limit (µg/g)	Average % Recovery
DM Hydrolysis Product	0.12	0.26	101

Table 3. MDL and RL Results

ACKNOWLEDGEMENTS

The authors would like to thank Dennis Hooton for suggestions during method development and editorials on the manuscript.

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[1] Compton, James. *Military Chemical and Biological Agents*. New Jersey. Telford Press. 1987.

[2] Jenkins, T. F., Schumacher, P. W., Walsh, M. E., Bauer, C. F. (1988) USA Cold Regions Research and Engineering Laboratory Special Report 88-8, Hanover, NH

[3] Kuronen, P. (1990) Development of a Retention Index Monitoring Method for Reversed-Phase High-Performance Liquid Chromatography of Non-Phosphorus Chemical Warfare Agents, Helsinki, Finland.

MICROWAVE CLOSED VESSEL SAMPLE PREPARATION

of

PAINT CHIPS, SOIL, DUST WIPES, BABY WIPES, & BABY WIPES

for

ANALYSIS of LEAD by ICAP

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Slide No.	Description
1	Title Slide - Microwave Closed Vessel Sample Preparation of Paint Chips, Soil, Dust Wipes, and Air Sampling Filters for Analysis of Lead by ICAP.
2	Introduction - Exposure to lead in the environment has an adverse affect on our health even at low levels. It can cause Central nervous system impairment Mental retardation Behavioral disorders. Domestic sources of lead exposure are primarily paint, dust, and secondarily food, water, and airborne dust. Industrial sources of lead exposure are abrasive blasting, acid and alkali cleaning of metals, forging, molding, welding, and painting. For this work we will investigate the contribution from the primary domestic sources to lead exposure. The samples selected are reference samples from the American Industrial Hygiene Association. We will review the 1. Microwave Sample Preparation Instrumentation 2. Heating (Digestion) Programs 3. Conditions used for Lead Analysis by ICAP 4. Lead Recoveries vs the Certified Value.
3	Thermo Jarrell Ash ICAP 61E Trace Analyzer - All elemental analyses were performed with the TJA - ICAP 61E Trace Analyzer.
4	MDS-2000 Microwave Sample Preparation System - All samples were prepared (digested) using a CEM Corporation Model MDS-2000 with temperature and closed vessels to allow elevated temperatures and pressures to accelerate the digestion step.
5	Advanced Composite Vessel - All samples, except the baby wipes, were prepared using this vessel design. The vessels have an operating pressure and temperature of 200 psig and 200°C. This slide provides an exploded view of the vessel.
6	PFA Digestion Vessel - The baby wipe samples were prepared using this vessel design. The vessels have an operating pressure and temperature of 200 psig and 200° C. It was used for the 3.0 gram baby wipe samples due to the automatic venting / resealing capabilities.

Slide No.	Description
7	Microwave Closed Vessel Heating Conditions for the Digestion of Lead in Paint Chips - AIHA (American Industrial Hygiene Association) Reference Material ELPAT (Environmental Lead Proficiency Analytical Testing) Round 009 Paint Chips. As a precaution with the first digestion of unknown samples, all paint and soil samples were allowed to predigest for 10 minutes prior to sealing the vessels. The digestion was performed as shown. For this sample type, the vessel pressure increased to 45 psig. Twelve samples were simultaneously digested. At the end of the digestion, the samples were filtered through Whatman #40 filter paper.
8	Lead Recovery from Paint Chips - ELPAT 009 samples. Four different lead levels. All recovery data within acceptance limits. Low RSD.
9	Lead Recovery from "Real World" Paint Chips - Samples A and B were paint chips removed from walls and woodwork in homes and spiked with ELPAT paint chips. Calculated lead was based on the average lead values determined for samples A and B plus the ELPAT paint chip spike. At the end of the digestion, vessel pressure was 74 psig. Vessel pressure at the end of a digestion is dependent on the temperature, the paint chip sample composition, and any other material such as wood or plaster adhering to the paint chips that can be oxidized to produce carbon dioxide.
10	Microwave Closed Vessel Heating Conditions for the Digestion of Lead in Soil - Twelve simultaneous digestions of ELPAT Round 009 soils. Samples were predigested for 10 minutes prior to sealing the vessels. Performed digestion as shown. Vessel pressure increased to 46 psig. The pressure in the vessels after digestion will be dependent on the temperature of the acid and the amount of carbonate or organic material present in the soil sample.
11	Lead Recovery From Soil - AIHA samples ELPAT Round 009. All recoveries are within the certificate acceptance limits and RSD's.
12	Microwave Closed Vessel Heating Conditions for the Digestion of Dust Wipes - A dust wipe, ELPAT Sample, is a 9cm round filter paper folded and spiked with dust containing lead. Since the sample weight is approximately 0.8 gram of organic material, a ramped temperature and pressure digestion program was used to avoid pressure overruns. Maximum operating pressure is 200 psig for ACV vessels. A total of 12 samples were simultaneously prepared.

Slide No.	Description
13	Temperature and Pressure Curves for Digestion of Dust Wipes (These are for the T & P curves). In **Stage 1** the temperature increased to 122°C before dropping off as the pressure was held constant. In **Stage 2** the temperature increased to 133°C before dropping off as the pressure was held constant. In **Stage 3** the temperature increased to 135°C before dropping off as the pressure was held constant. In **Stage 4** the temperature increased to 140°C before dropping off as the pressure was held constant. In **Stage 5** the temperature increased to 154°C. At the end of the fifth stage, the temperature had dropped to 136°C. Temperature in the last 4 stages of the program was always greater than 120°C which is the atmospheric boiling temperature of nitric acid. A small amount of filter paper residue remained. Samples were filtered through Whatman filter paper #40.
14	Lead Recovery From Dust Wipes - This was the first lead recovery data in this study using a ramped temperature and pressure heating program. The recoveries were all within the certified acceptance limits.
15	Microwave Closed Vessel Heating Conditions for the Digestion of Lead Spiked Air Filters - The cellulose ester filters were spiked with a known concentration of lead. This is the heating program for the simultaneous digestion of 12 filters. Temperature was controlled at 160°C for 5 minutes. The vessel pressure at the end of this digestion was 35 psig. This relatively low pressure results from the inorganic matrix of the spike material and from the low organic filter weight of <0.1 g.
16	Lead Recovery From Spiked Mixed Esters of Cellulose Filters - Average recoveries were 88 to 93%. Interesting to note that as the lead concentration increases the recovery decreases.
17	Microwave Open Vessel Heating Conditions for the Partial Digestion of Lead Spiked Baby Wipes - Since there has been no regulation specifying the type of wipe used to sample surfaces for lead contamination, we used

Slide No.	Description
	a 3g wipe (Wash-a-Bye Baby brand) to minimize wipe weight. The majority of the baby wipe weight is organic material. Since the sample size is greater than the recommended sample size for closed vessel digestion of organic materials, we were required to do some open vessel digestion to oxidize some of the organic material prior to closed vessel digestion. The safety relief disks were placed on the 120 mL PFA vessels during the open vessel heating. The disks produced some acid refluxing and also reduce the possibility of contamination during the open vessel digestion. A five stage program using power control was used to control the rate of heating and eliminate spattering. Approximately 10 - 12 mL of the acid and wipe mixture remained in the vessel after completion of the open vessel heating program. The vessels were cooled and sealed. A total of 12 samples were simultaneously digested.
18	Microwave Closed Vessel Heating Conditions for the Digestion of Lead Spiked Baby Wipes - Samples were then digested use the pressure ramping program shown. Some residue remained in the vessel after completion of the digestion. All samples were filtered.
19	Temperature and Pressure Curves for Digestion of Lead Spiked Baby Wipes - These are the temperature and pressure curves for the pressure ramped digestion.
20	Lead Recovery From Spiked Baby Wipes - ELPAT Round 009 soil and paint chips were used for the spike material. All recoveries were above 90%. The highest spike concentration did produce the lowest recovery. All samples were prepared and analyzed in triplicate. Lead recovered for all spiked sample types.
21	Conclusion - *Rapid sample preparation for lead analysis. Paint Chips 15 minutes Soil 15 minutes Dust Wipes 20 minutes Filters 11 minutes *Unattended sample digestion. *No special vessel cleaning required. *Excellent lead recoveries. ELPAT Round 009 Reference Material Real world samples

Microwave Closed Vessel Sample Preparation of Paint Chips, Soil, Dust Wipes, Baby Wipes, and Air Sampling Filters for Analysis of Lead by ICAP

Introduction

- Interest in environmental lead analysis:
  - Domestic concerns
  - Industrial concerns
- Sample preparation equipment
- Sample types
  - Paint chips
  - Soil
  - Dust wipes
    1. Filter paper (9 cm)
    2. Baby wipes
  - Cellulose acetate filters (37 mm)
- Heating programs
- Lead analysis by ICAP
- Lead recoveries

Analytical Instrumentation

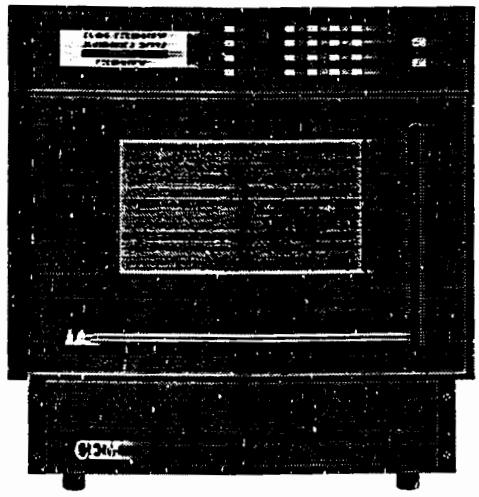
Thermo Jarrell Ash; ICAP, 61E Trace Analyzer*

Instrument configuration:

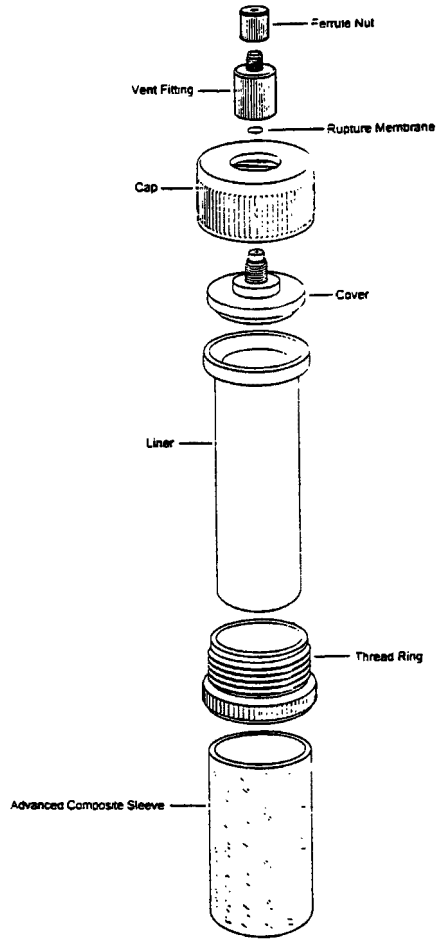
Cyclone Spray Chamber
Meinhard nebulizer
Wavelength - 220.353

* Lead detection limit - 1.02 ng/mL

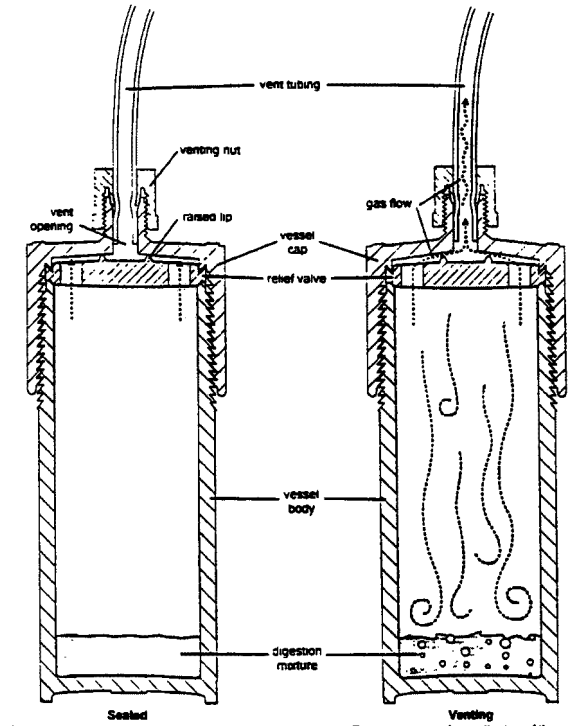
Microwave Sample Preparation System



Model MDS-2000



Cutaway View of Vessel Cap and Pressure Relief Valve Assembly, Sealed and Venting



Sealed
At pressures below 630 kPa (120 psig), the raised lip remains sealed against the cap.

Venting
Excess pressure forces the top of the cap to flex upward, breaking the seal around the raised lip, and exhausting the pressurized gas. Cap reseals when pressure drops below 690 kPa (100 psig).

Microwave* Closed Vessel Heating Conditions for the Digestion of Lead in Paint Chips[1]

Stage	(1)	(2)[2]
Power (%)	100	000
Pressure (psig)	100	000
Run Time (min)	20:00	5:00
TAP (min)	10:00	0:00
Temperature (°C)[3]	160	000

Vessel type	ACV
Acid and volume	10 mL of nitric acid (70%)
Sample wt.	0.1 g
Total time	15 min

* MDS-2000 Digestion System
1. ELPAT ROUND 009 Reference Material
2. Cool down stage
3. Control parameter

Lead Recovery From Paint Chips*

Sample	Average Lead Recovery[1] (weight %)	RSD (%)	Certificate Acceptance Limits (weight %)	Certificate RSD (%)
1	0.5124	0.74	0.4025 - 0.6973	8.9
2	0.0442	0.54	0.0354 - 0.0608	8.8
3	4.441	3.49	3.8909 - 5.6496	6.1
4	0.4098	0.46	0.3189 - 0.5301	8.3

* ELPAT ROUND 009 Reference Material
1. All samples were prepared and analyzed in triplicate. Analyzed by ICAP

Lead Recovery From Real World Paint Chip Samples*

Sample	Average Lead Recovery[1] (weight %)	Calculated Lead Present (weight %)	RSD (%)
A	5.23	5.58	2.00
B	1.72	1.69	5.68

* Spiked with ELPAT ROUND 009 Reference Material (paint chips).
1. All samples were prepared and analyzed in triplicate. Analysis by ICAP

Microwave* Closed Vessel Heating Conditions for the Digestion of Lead in Soil[1]

Stage	(1)	(2)[2]
Power (%)	100	000
Pressure (psig)	100	000
Run Time (min)	20:00	5:00
TAP (min)	10:00	0:00
Temperature (°C)[3]	160	000

Vessel type	ACV
Acid and volume	10 mL of nitric acid (70%)
Sample wt.	0.1 g
Total time	15 min

* MDS-2000 Digestion System
1. ELPAT ROUND 009 Reference Material
2. Cool down stage
3. Control parameter

Lead Recovery From Soil*

Sample	Average Lead Recovery[1] (mg/kg)	RSD (%)	Certificate Acceptance Limits (mg/kg)	Certificate RSD (%)
1	465	1.2	433.3 - 568.5	4.5
2	921	2.3	794.6 - 1119.7	5.7
3	479	0.7	431.9 - 573	4.7
4	83.7	1.9	69.5 - 109.5	7.4

* ELPAT ROUND 009 Reference Material
1. All samples were prepared and analyzed in triplicate. Analyzed by ICAP.

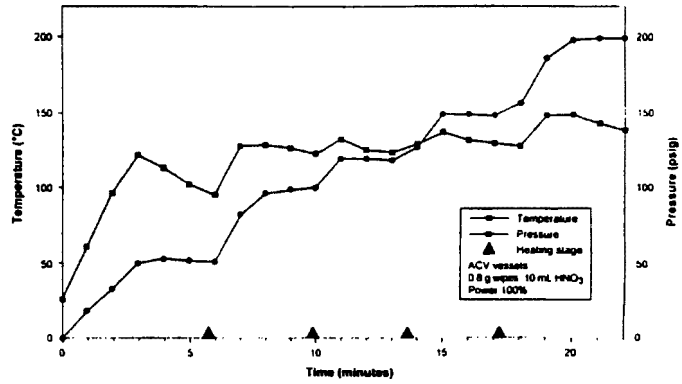
Microwave* Closed Vessel Heating Conditions for the Digestion of Lead on Dust Wipes[1]

Stage	(1)	(2)	(3)	(4)	(5)
Power (%)	100	100	100	100	100
Pressure (psig)	50	100	120	150	200
Run Time (min)	10:00	10:00	10:00	10:00	10:00
TAP (min)	3:00	3:00	3:00	3:00	3:00
Temperature (°C)	120	130	140	150	160

Vessel type	ACV
Acid and volume	10 mL of nitric acid (70%)
Sample wt.	0.8 g
Total time	22 min

* MDS-2000 Digestion System
1. ELPAT ROUND 009 Reference Material (9 cm filter paper)

Temperature and Pressure Curves for Digestion of Dust Wipes (MDS-2000)



Lead Recovery From Dust Wipes*

Sample	Average Lead Recovery[1] (µg/wipe)	Certificate Acceptance Limits (µg/wipe)
1	900	729.4 - 1040.2
2	325	224.9 - 437
3	102	84 - 132.8
4	476	376.6 - 580.6
Blank Wipe	0.13	—

* ELPAT ROUND 009 Reference Material
1. All samples were prepared and analyzed in triplicate. Analyzed by ICAP

Microwave* Closed Vessel Heating Conditions for the Digestion of Lead Spiked Air Filters[1]

Stage	(1)	(2)[2]
Power (%)	100	000
Pressure (psig)	100	000
Run Time (min)	15:00	5:00
TAP (min)	5:00	5:00
Temperature (°C)[3]	160	000

Vessel type	ACV
Acid and volume	10 mL of nitric acid (70%)
Sample wt.	< 0.1 g
Total time	11 min

* MDS-2000 Digestion System
1. Mixed esters of cellulose (37 mm)
2. Cool down stage
3. Control parameter

Lead Recovery From Spiked MEC* Filters

Sample	Spike Value (mg)	Average Lead Recovery[1] (mg)	Average Recovery (%)	RSD (%)
1	100	93.4	93	0.51
2	250	231	92	2.42
3	500	441	88	0.03

* Mixed esters of cellulose
1. All samples were prepared and analyzed in quadruplicate. Analysis by ICAP.

Microwave* Open Vessel Heating Conditions for the Partial Digestion of Lead Spiked[1] Baby Wipes[2]

Stage	(1)	(2)	(3)	(4)	(5)
Power (%)[3]	85	65	70	90	100
Pressure (psig)	000	000	000	000	000
Run Time (min)	3:00	15:00	5:00	5:00	10:00
TAP (min)	0:00	0:00	0:00	0:00	0:00
Temperature (°C)	000	000	000	000	000

Vessel type	120 mL PFA[3]
Acid and volume	30 mL of nitric acid (70%)
Sample wt.	3 g
Total time	38 min

* MDS-2000 Digestion System
1. Spiked with ELPAT ROUND 009 Reference Material (paint chips and soil)
2. Wash-a-Bye Baby brand
3. Vessels not sealed, covered with the Relief Disk only.

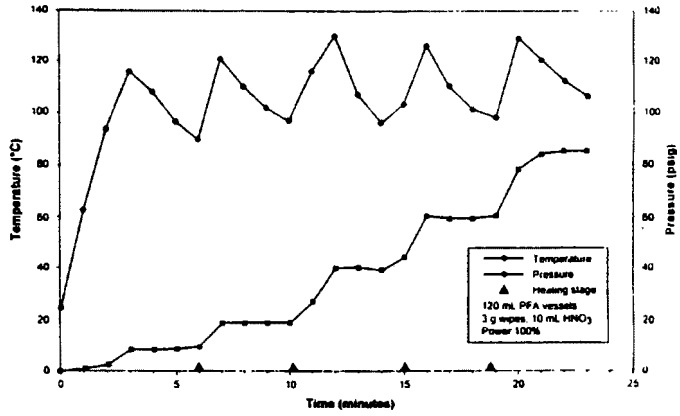
MICROWAVE* CLOSED VESSEL HEATING CONDITIONS FOR the DIGESTION of LEAD SPIKED[1] on BABY WIPES[2]

Stage	1	2	3	4	5
Power (%)	100	100	100	100	100
Pressure (psig)[3]	10	20	40	65	90
Run Time (min)	10:00	10:00	10:00	10:00	10:00
TAP (min)	3:00	3:00	3:00	3:00	3:00
temperature (°C)	monitored only				

Vessel Type	120 ml PFA [4]
Acid and Volume	Approximately 10 mL of nitric acid
Sample Wt.	3 gram (Weight of wipe)
Total Time	24 min.

* MDS-2000 Digestion System
[1] Spiked with ELPAT Round 009 Reference Material (paint chips and soil)
[2] Wash - a - Bye Baby Brand
[3] Control Parameter
[4] Sealed Vessels

Temperature and Pressure Curves for Digestion of Lead Spiked Baby Wipes (MDS-2000)



Lead Recovery From Spiked* Baby Wipes[1]

Sample	Spike Value (mg/kg)	Average Lead Recovery[2] (mg/kg)	Average Recovery (%)	RSD (%)
Wipe + Soil #1	500.9	489	98	3.55
Wipe + Soil #4	89.5	87.8	98	7.67
Wipe + Paint Chips #3	47,702	43,202	91	2.62
Blank Wipe	—	—		

* Spiked with ELPAT ROUND 009 Reference Material (paint chips and soil)
1. Wash-a-Bye Baby brand
2. All samples were prepared and analyzed in triplicate. Analyzed by ICAP.
Open and closed vessel digestion sample preparation

Conclusions

- Rapid sample preparation for lead analysis
  - Paint chips 15 minutes
  - Soil 15 minutes
  - Dust wipes 20 minutes
  - Filters 11 minutes
- Unattended sample digestion
- No special vessel cleaning required
- Excellent lead recoveries
  - ELPAT ROUND 009 Reference Materials
  - Real world samples

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Removal of Zinc Contamination from Teflon® PFA Microwave Digestion Vessels

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ABSTRACT

Laboratory contamination is one of the largest single producers of error in analysis of environmental samples. ASI, as many laboratories have, converted to use of Teflon® digestion beakers for hot acid digestion of samples for metals analysis. The digestion liners in the microwave digestion system were made of Teflon® and favorable experiences with them prompted the change. The Teflon® beakers and liners have some very desirable properties such as ease of cleaning and unbreakability which more than offsets the high initial purchase cost of the containers. However, over time while using the Teflon® containers, the blank values for zinc were noted to be slowly increasing. This became of increasing concern when the background zinc values in the blanks passed our minimum reporting level and still continued to rise. We had an idea that use of a strong chelating agent would serve to reduce the contamination levels in the Teflon® beakers and liners and performed a series of experiments to test the hypothesis. The development and description of a highly successful, simple and inexpensive cleaning procedure which eliminates the use of hot concentrated acid leaches, yet completely removes the background metal contamination problem from Teflon® digestion beakers and liners, is the subject of this presentation.

INTRODUCTION

Recent advances in the sensitivity of analytical instruments have led to the ability to reliabily quantitate target analytes at substantially lower levels than those previously possible. These sensitivity increases have proceeded hand-in-hand with the lowering of regulatory thresholds, for instance the Ambient Water Quality Criteria Levels. These analytical advances and stricter monitoring requirements have simultaneously increased concerns about laboratory contamination introduced during the collection and preparation of samples[1]. This paper discusses the identification and elimination of one significant source of laboratory contamination encountered in the preparation of samples for analysis of trace metals.

EPA methods 3015 and 3051[2] are for microwave digestion of water and solid samples. They recommend (Section 7.2) use of hot acid leaches with first 1:1 hydrochloric acid for at least 2 hours followed by 1:1 nitric acid for a minimum of 2 hours to remove contamination from the Teflon® PFA digestion vessels. Some of the samples we run exhibit rather high levels of zinc and copper and we have found that repeated cycles of microwave digestion in the Teflon® liners cleaned daily by the EPA procedure or alternatively with hot aqua regia (concentrated 3:1 hydrochloric-nitric acid), leads to permanent establishment of background zinc levels above detection limits in the blanks and samples. This form of laboratory contamination can be remedied by purchase of new Teflon® digestion vessels. However at $50 to $100 each,

even doubling the useful life of a liner results in a considerable savings to the overhead operating costs of the facility.

EDTA (ethylenediaminetetraacetic acid disodium salt, CAS number 6381-92-6) is well known as a sequestering agent for divalent and higher charged cations. Approximately 40 different cations are known to be complexed by EDTA. There is a pH dependance for optimum complexation. For instance pH 1 is optimum for Fe^{+3}, pH 4 for Zn^{+2}, pH 8 for Ca^{+2}, and pH 10 for Mg^{+2}. Environmental analytical applications of EDTA include the complexometric titration of calcium and magnesium in hardness determinations in a pH 10.0 ammonia-ammonium chloride buffer. We felt that soaking the Teflon® liners with EDTA might serve to chelate and solubilize the zinc out of the walls of the Teflon® liner and reduce the overall level of carry-over contamination. We performed a series of experiments to test this hypothesis.

A saturated solution (approximately 5%) of EDTA in reagent grade water was prepared, which exhibited a pH of 4.6. The original samples were 6 contaminated Teflon® liners which were cleaned with the EPA procedure and with aqua regia. A blank digestion of acid and 45 mL reagent grade water were performed in each liner by EPA method 3015 and the digestate assayed by EPA method 6010 (ICP-AES). A series of cleaning procedures were devised and performed sequentially on the liners. The mildest procedure was performed first, followed by more rigorous schemes. Test 1 was an EDTA soak for 1 hour at ambient temperature followed by rinsing with DI water. Test 2 was an EDTA soak overnight at ambient temperature, followed by rinsing with DI water. Test 3 was an EDTA soak for 1.5 hrs at 60°C, followed by rinsing with DI water. After each test treatment, the blank digestion was repeated and the digestate analyzed. The results of these tests are presented in the Table.

Table. Analytical results (mg/L) for tests of Teflon® cleaning experiments with EDTA. ND = Not Detected.

Calcium

Vessel	1	2	3	4	5	6
Original	.500	1.02	1.03	.733	.947	.969
Test 1	.844	1.16	1.42	.924	.910	.605
Test 2	.891	.873	.854	.651	.776	-
Test 3	.538	.417	.368	.474	.314	.514

Iron

Vessel	1	2	3	4	5	6
Original	.038	.024	.031	.017	.020	.018
Test 1	.020	.056	.020	.011	.014	.009
Test 2	.041	.025	.044	.017	.022	-
Test 3	ND	ND	ND	ND	ND	ND

Potassium

Vessel	1	2	3	4	5	6
Original	.054	.074	.029	.023	.013	.064
Test 1	ND	.018	ND	.003	ND	ND
Test 2	.106	.145	.073	.078	.090	-
Test 3	.003	.064	.028	.059	.054	.069

Magnesium

Vessel	1	2	3	4	5	6
Original	.042	.049	.048	.025	.057	.044
Test 1	.033	.047	.037	.030	.032	.018
Test 2	.067	.073	.055	.051	.038	-
Test 3	.007	.009	ND	.011	.002	.035

Sodium

Vessel	1	2	3	4	5	6
Original	.607	1.10	1.29	.976	1.18	1.34
Test 1	1.06	1.35	1.25	1.08	1.08	.700
Test 2	1.29	1.37	1.28	1.05	1.18	-
Test 3	.845	.643	.547	.688	.514	.790

Zinc

Vessel	1	2	3	4	5	6
Original	.052	.038	.040	.023	.034	.021
Test 1	.037	.052	.064	.024	.024	.021
Test 2	.033	.034	.023	.019	.020	-
Test 3	.014	.006	.017	.019	.006	.009

Although we had undertaken these experiments with the specific objective of reducing a zinc contamination problem, examination of the other metals determined in the ICP-AES printout, indicated we had also significantly reduced calcium, iron and magnesium levels in the blanks. The background contamination levels of these metals had yet to reach the PQL and were not as yet viewed as a problem.

To understand these results the following formation constants for EDTA complexes[3] are helpful: Mg^{+2} 4.9×10^{8}, Ca^{+2} 5.0×10^{10}, Zn^{+2} 3.2×10^{16}, Al^{+3} 1.3×10^{16}, and Fe^{+3} 1.3×10^{25}. The larger the formation constant, the greater the ability of EDTA to dissolve the ion. The observations recorded in the Table are in line with the magnitude of the formation constants. For example the iron contamination is completely removed, the zinc is substantially reduced, there is a significant reduction in magnesium and calcium, and finally, potassium and sodium levels are unchanged. The last results are not surprising as EDTA is not noted for any complexation of alkali metal cations. Examination of the formation constants further suggest that aluminum contamination, should it be encountered, will be completely removed.
Even further reductions in background contamination for specific contaminants should be possible through judicious pH adjustment. For example use of ammonia-ammonium chloride buffer with EDTA should improve the removal of calcium and magnesium from the plastic, however we have not explored this.

How the metal ions are attached to the Teflon® PFA surface is unknown. It may be that the pores in the polymer are allowing the metal ions inside, where they are stabilized by the high electronegativity of the fluorine atoms or by Lewis base coordination to the oxygen atoms present in the PFA resin. The oxygen atom complexation may the culprit which led to the zinc problem, however other mechanisms can not be ruled out as we have seen similar although lower level contamination in Teflon® PTFE beakers which we use for hotplate digestions. At any rate it appears that the EDTA presents a more suitable resting place for the metals and they are efficiently removed from the polymer.

Encouraged by the initial experimental results, we developed an SOP for cleaning Teflon® digestion vessels which added a weekly treatment with EDTA to the existing EPA procedure and the regular aqua regia soaking. The treatment is to take a room temperature saturated solution of EDTA in reagent grade water, heat it to at least 60°C, then submerge the Teflon® container in the bath. The bath is heated for 2 hours, then the container rinsed with reagent grade water and allowed to dry. Although we have reused the EDTA solution up to 4 times during a month, the current practice is to prepare a new solution every week. We treat the Teflon® PTFE beakers weekly with EDTA by filling them with the hot solution, then heating the beakers on a hotplate for 2 hours.

SUMMARY

This improved cleaning procedure using EDTA has been in place in our laboratory for over a year and we have extended the usable life of Teflon® PFA microwave digestion liners by a factor of at least 5 and Teflon® PTFE beakers by a factor of 3.

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A COMPARATIVE INVESTIGATION OF THREE ANALYTICAL METHODS FOR THE CHEMICAL QUANTIFICATION OF INORGANIC CYANIDE IN INDUSTRIAL WASTEWATERS

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ABSTRACT

A frightening volume of toxic cyanide-containing liquid waste is generated annually in industries involved in the mining and extraction of metals, metal plating and finishing, hardening of steel, manufacture of synthetic fibers and the processing of such cyanogenic crops as cassava, bitter almonds, white clover, apricots, etc. The U.S. Environmental Protection Agency requires that the cyanide in this liquid waste be destroyed and its level brought down to less than 1ppm before the waste can be discharged into aquatic environments. This requirement can only be met if a sensitive, reliable and rapid analytical method suitable for quantifying cyanide in industrial liquid wastes exists. As part of an ongoing cyanide degradation project using immobilized enzymes and immobilized microbial cells, we have investigated and compared three chemically-related spectrophotometric methods for determining cyanide namely, the 4-picoline-barbituric acid, the isonicotinate-barbiturate and the pyridine-pyrazolone methods for their suitability in the routine determination of cyanide in industrial wastewaters. Data from recovery experiments carried out with standard cyanide solutions and those from analyses of actual cyanide-containing liquid wastes obtained from metal and cassava processing, indicate that the three methods are about equally sensitive and capable of reliably detecting free cyanide ions down to less than 0.1 ppm. In these methods, the soluble colored dyestuff is formed within reasonable time (5-30 min) and is stable for upwards of 1-2 hr. at room temperature (22-28 C). The chromogenic reagent for the 4-picoline -barbituric acid method is stable for 2-4 hr while those for the other two methods can be stored in dark brown bottles for up to 20 days without affecting cyanide measurement. The three methods are affected to varying extents by interferences from various cationic, anionic and organic substances that are usually encountered in industrial cyanide-containing wastewaters. The error in cyanide measurement associated with these interferences is sufficiently serious as to warrant a distillation step as part of the analytical protocol.

INTRODUCTION

Large amounts of concentrated cyanide solution are generated annually from such human activities as the mining and extraction of metals (e.g. gold and silver), cleaning and electroplating of metals, hardening of steel and production of synthetic fibers (1-2). The processing of cyanogenic crops like cassava, bitter almonds, apricots, butter beans etc. which contain significant amounts of cyanide in the form of cyanogenic glycosides also produces large volumes of cyanide-rich waste liquor in the food industries (3). Hydrolysis of cyanogenic glycosides by the endogenous enzyme systems of these plant raw materials during processing results in the conversion of large amounts of organic cyanides (e.g. nitriles) into inorganic cyanide. Since cyanide is a potent respiratory poison (3) undetoxified cyanide-containing liquid wastes could easily contaminate fishes and ultimately extinguish aquatic life if discharged into aquatic environments.

Chemical methods for the detoxification of cyanide-containing industrial wastes are expensive, energy intensive and leave other environmentally undesirable byproducts (4). This fact coupled with EPA's stringent requirements regarding cyanide levels in detoxified cyanide-containing liquid wastes, has encouraged us to embark on an investigation of the use of immobilized enzymes and microbial cells in the degradation of cyanide in industrial wastewaters in collaboration with Norris Industries. An important part of this collaborative effort calls for the identification and adapting of existing methods of cyanide determination to the analysis of concentrated industrial cyanide-containing liquid wastes. The modifications introduced in the three methods reported in this work have enabled us to integrate these analytical methods into our ongoing project on waste cyanide degradation by biotechnological methods.

EXPERIMENTAL

Materials: 4-Picoline, barbituric acid, isonicotinic acid, chloramine-T, 3-methyl-1-phenyl-5-pyrazolone, bis-pyrazolone, spectroscopic-grade pyridine and potassium cyanide were purchased from Sigma Chemical Company, St. Louis, Missouri. Other chemicals and reagents used were of analytical grade. Doubly-distilled and deionized water was used throughout the work. Two different samples of cyanide-containing wastewater (referred to as SP and Nu) were gratefully obtained from Norris Industries, Los Angeles, CA.

Cassava Waste Liquor: This was prepared with cassava tubers from two different varieties of cassava (var. A and B). Cassava tubers were peeled to remove the back and expose the cortex. These tubers were cut into small cubes measuring about 3x3x3 cm. Approximately 500g of these were blended in batches of 100 g with 300 ml of cold distilled water each time. The pooled homogenate was filtered. The residue was reextracted with 500 ml of water and filtered again. The filtrate was left to stand over might at room temperature. The precipitated starch was subsequent removed by filtration and the resulting cyanide-rich filtrate referred to as cassava waste liquor (A and B) was used for all cyanide analysis described below.

Preparation of Chromogenic Reagents: Sodium isonicotinate, sodium barbiturate, 4-picolone-barbituric acid, and sodium isonicotinate-sodium barbiturate reagents were prepared as described by Nagashima (5-6). The pyridine-pyrazolone reagent was a pyridine solution of 0.1% bispyrazolone and 0.5% 3-methyl-1-phenyl-5-pyrazolone prepared in situ as recommended by Cooke (7) and Ikediobi et al. (8-9)

Cyanide by the 4-Picoline-barbituric acid method: Six milliters of a sample containing less than 10ug of cyanide was pipetted into a dry reaction test tube. To this were added 3.0 ml of phosphate buffer (pH 5.2) and 0.2 ml of 1% (w/v) solution of chloramine-T. The test tube was stoppered and the resulting solution gently mixed and left at rooom temperature for 1-3 min. Then 1.8 ml of 4-picoline-barbituric acid reagent was added, the tube stoppered again, the contents mixed and the solution kept at 25 C for 5 min. in a fume hood for color development. The absorbance of the blue-violet color was read at 605 nm against a suitable reagent blank in a Shimadzu-160 double beam spectrophotometer.

Cyanide by the Isonicotinate-barbiturate method: Into a dry test tube was pipetted 6 ml of sample containing less than 10ug CN^-. To this solution was added 1.8 ml of phosphate buffer followed by 0.2 ml of 1% solution of chloramine-T. The tube was stoppered and contents mixed gently. After standing for 1-3 min, 3 ml of sodium isonicotinate-sodium barbiturate reagent was added. The tube was again stoppered, contents mixed and the tube kept at 22-25 C for 30 min in a fume hood for color development. The absorbance of the blue-violet-colored dyestuff was measured at 600 nm against a reagent blank in a Shimadzu-160 double beam spectrophotometer.

Cyanide by the Pyridine-pyrazolone method: Approximately 1 ml of sample containing less than 10ug CN^- and 0.4 ml of chloramine-T were added to a dry reaction test tube. The tube was stoppered and allowed to stand for 5 min at 0 C (ice-H_2O bath) after which 6 ml of pyridine-pyrazolone reagent was added, mixed and the tube allowed to stand for 20 min at room

temperature in a fume hood. The absorbance of the resulting soluble blue dye was determined at 630 nm against a reagent blank in a Shimadzu-160 double beam spectrophotometer.

Distillation of cyanide-containing solutions: Distillation was routinely used in recovery experiments and in the preparation of complex and concentrated cyanide-containing liquid waste for cyanide analysis. The cyanide distillation train consisted of a 1-liter boiling flask connected to a glass condenser which in turn was connected to two consecutive glass traps equipped with medium-porosity sparger and each containing 1 M NaOH. Provision was made in the distillation setup for a boiling flask air inlet, a suction flask trap and a vacuum connection. Approximately 500 ml of diluted sample containing less than 10 ppm of CN^- was distilled at a time. For distillation of complex concentrated cyanide solutions, e.g. industrial wastewater, cassava waste liquor etc., 2g of sulfamic acid, 50 ml of diluted (1:1 v/v) H_2SO_4 and 20 ml of 51% solution of $MgCl_2.6H_2O$ were also added to the boiling flask through the air inlet tube before distillation. The entire setup was connected to a vacuum source and suitable air flow maintained at a rate of 1-3 air bubbles/second. Refluxing was allowed to proceed for 1-2 hr. at the rate of 40-50 drops/min from the condenser lip. At the end of distillation, heating was discontinued but air flow maintained for additional 15-30 min. while the train cooled down to room temperature. The cyanide traps were disassembled and the 1 M NaOH solutions containing the trapped CN^- were pooled, the traps were rinsed and the pooled solution was suitably diluted for CN^- determinations.

Statistical Analysis: Statistical analysis of data in Table 1 was performed using the paired t-test.

RESULTS AND DISCUSSION:

Cyanide Content of Industrial Wastewater: Our design of an enzyme-based detoxification of cyanide involves a continuous packed-bed reactor through which cyanide-containing liquid waste is recycled and the kinetics of CN^- degradation followed by accurate monitoring of the CN^- content of the inffluent and effluent wastewater. Tables 1 and 2 present data on the CN^- content of four samples of CN^- containing liquid waste two of which (NU and SP) arise from actual industrial activity while the other two (A and B) represent cyanide-containing waste liquor arising from laboratory-scale processing of two different varieties of cassava tubers for starch (3). Table 1 shows that liquid wastes SP and NU are too concentrated in cyanide to be discharged without prior detoxification. Although exceeding by an order of magnitude the EPA ceiling for CN^- in industrial wastewater, the cyanide levels in A and B are relatively low because the latter were prepared from

edible (genetically low cyanide-containing) varieties of cassava. Reports in the literature indicate that similar preparations from cassava varieties bred for industrial use, upon processing, leave behind waste liquors with cyanide levels as high as 1200-2000 ppm (3). We conclude from the statistical analysis of data in Table 1 and the standard curves shown in Figs. 1-3, that the three analytical methods are about equally sensitive and capable of detecting CN^- down to less than 0.10 ppm, a sensitivity that more than meets the EPA requirements. Data in Table 2 also show that there is a significant difference between the cyanide levels in SP and NU before and after distillation, with errors in CN^- estimation of at least 21%. This suggests the presence in the wastewater samples of substances capable of interfering in the determination of cyanide by any of these methods, although data shown in Table 2 have been presented for only one of these methods. The fact that each method is capable of detecting 100% of the CN^- in standard cyanide solutions as shown in Table 1 is additional proof that the three methods are about equally responsive to the presence of cyanide in aqueous solutions.

Comparative Chemistry of the three spectrophotometric methods: Figs. 4 and 5 summarize the color-forming reactions of the three spectrophotometric methods studied. As can be seen from these Figs., the three-step color-forming reaction is similar in the three methods. Essentially it consists of the reaction between the free cyanide (CN^-) ion and chloramine-T (N-chloro-p-toluene sulfo-namide) to yield cyanogen chloride as one of the products. The cyanogen chloride (CNCl) in turn attacks 4-picoline (in the 4-picoline-barbituric acid method), isonicotinate (in the isoni- cotinate-barbiturate method) or pyridine (pyridine-pyrazolone method) to form glutaconic dialdehyde or its derivative. The last reaction involves a condensation between the glutaconic dialdehyde and barbiturate or pyrazolone to yield a soluble blue to violet colored dye that absorbs strongly in the range of 600-630 nm as specified in the text.

In all these methods, the formation of the soluble colored dye occurred within reasonable time period (5-30 min) while the dye-stuff formed in each case was stable for upwards of 1 hr. at room temperature. The chromogenic reagent for the 4-picoline-barbituric acid method was stable for about 1-2 hr. while those for the isonicotinate-barbiturate and the pyridine-pyrazolone methods stored well for up to 20 days without significantly affecting cyanide measurements. The pyridine-pyrazolone method, however, is limited by the expensiveness, offensive odor and toxicity of the chemicals used. The three methods are affected to varying extents by interferences from cations, anions and organics that are likely to be found in industrial cyanide-containing liquid

waste. The cummulative effect of the interfering substances in industrial wastewater is sufficiently serious to require distillation of wastewater samples before cyanide determination is carried out by any of the three method investigated.

Interferences In the Determination of Cyanide: While Table 2 demonstrates vividly the additive effect of the various interfering substances on cyanide determination, Table 3 presents data on the effect, on cyanide determination, of specific substances added to standard cyanide solutions. The presence of the two cations - Ca^{2+} and Mg^{2+} - generally found in hard water typical of most municipal water supplies results in slight to moderate overestimates or underestimates in cyanide content especially with the pyridine-pyrazolone method. Of the anions tested, the thiocyanate (SCN^-) caused the most error in the analysis particularly with the pyridine-pyrazolone and isonicotinate-barbiturate methods. The two organics, benzaldehyde and 1-butanol, at most of the concentrations tested, caused moderate underestimation in the level of cyanide. Aldehydes may react with CN^- ions to form nitriles which cannot be detected by any of these methods. The data in Table 3 also reveal that for the ions and organic compounds tested, the magnitude of the error caused, is roughly related to the concentration of the interfering substance. Although in most cases, the mechanism of interference is unclear, there is little doubt about the wisdom of distilling complex cyanide-containing liquid wastes prior to CN^- determination (Table 2).

CONCLUSIONS

Three related spectrophotometric methods have been compared for their suitability in the determination of cyanide in industrial wastewaters. Data presented demonstrate that they are about equally and reliably capable of detecting CN^- ions down to less than 0.1 ppm and comparably affected by some interfering inorganics and organics many of which can be encountered in CN^- - containing liquid wastes. The three analytical methods are successfully and interchangeably in use to monitor the kinetics of cyanide degradation in cyanide-containing wastewaters by immobilized enzymes and immobilized microbial cells.

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Table 1. Determination of the Cyanide Content of a Standard Cyanide Solution and Samples of Industrial Wastewater[a].

Analytical Method	Standard CN^- solution (10 ppm)	Industrial Wastewater		Cassava Processing Waste Liquor	
		SP (ppm)	NU (ppm)	A (ppm)	B (ppm)
4-Picoline-barbituric acid	10.10	13812 ± 467^b	16660 ± 1318^b	7.40 ± 0.04^b	6.22 ± 0.14^b
Isonicotinate-barbiturate	10.44	12665 ± 51^c	15337 ± 281^b	8.21 ± 0.06^c	6.98 ± 0.08^c
Pyridine-pyrazolone	9.98	12390 ± 144^d	15890 ± 782^b	7.38 ± 0.10^b	5.99 ± 0.17^b

[a]Mean $\pm$ SD. The differences in the CN^- values for SP, A and B as determined by the three methods are statistically significant ($P < 0.01$) as indicated above by different superscripts.

Table 2. Effect of Distillation on Cyanide Content of Industrial Wastewater

	CN^- before distillation (ppm)	CN^- after distillation (ppm)	% Error in CN^- Content
Standard Cyanide Solution	10.08	10.08	0
Wastewater, SP	14800	12270	21
Wastewater, NU	17530	10540	66

Table 3. Effect of Diverse Substances on the Determination of 2.4 gCN^-/11ml

Ion/Compound	Added as	Amount added (g)	Percent of Cyanide recovered Method I[a]	Method II[b]	Method III[c]
Mg^{2+}	$MgCl_2$	1600	97.4	98.6	101.7
		8000	96.6	98	97.3
		400	98.3	99.4	103.2
		80	98.9	100.6	104.2
Ca^{2+}	$CaCl_2$	16000	107.6	117.1	124.3
		3200	102.0	104.2	120.0
		80	100.6	102.3	113.5
		16	99.7	101.3	111.0
NO_2	$NaNO_2$	6400	100.9	101.7	107.1
		1280	100.4	101.3	102.2
		320	98.7	100.4	99.2
		64	98.9	100.8	100.2
SO^{2-}	Na_2SO_3	9000	0	0	0
		90	83.8	83.6	82.5
		9	98.8	95.5	90.4
		0.9	99.5	100.8	99.7
SCN^-	KSCN	2	136.4	133.4	148.4
		0.2	103.7	106.1	136.0
		0.1	101.1	103.4	118.4
		0.02	99.7	102	108.1
I^-	NaI	7000	0	ND	ND
		700	53.1	ND	ND
		350	-	94.1	93.3
		7	96.4	96	96.3
Benzaldehyde		104000	82.6	82.4	86.5
		10,400	98.5	97.6	97.3
1-Butanol		405,000	92.6	ND	ND
		81000	97.4	92.5	98.3
		40,500	ND	100.4	101.2

[a]4-Picoline-barbituric acid; [b]Isonicotinate-barbiturate; [c]Pyridine-pyrazolone
ND = not determined due to solubility or color problems.

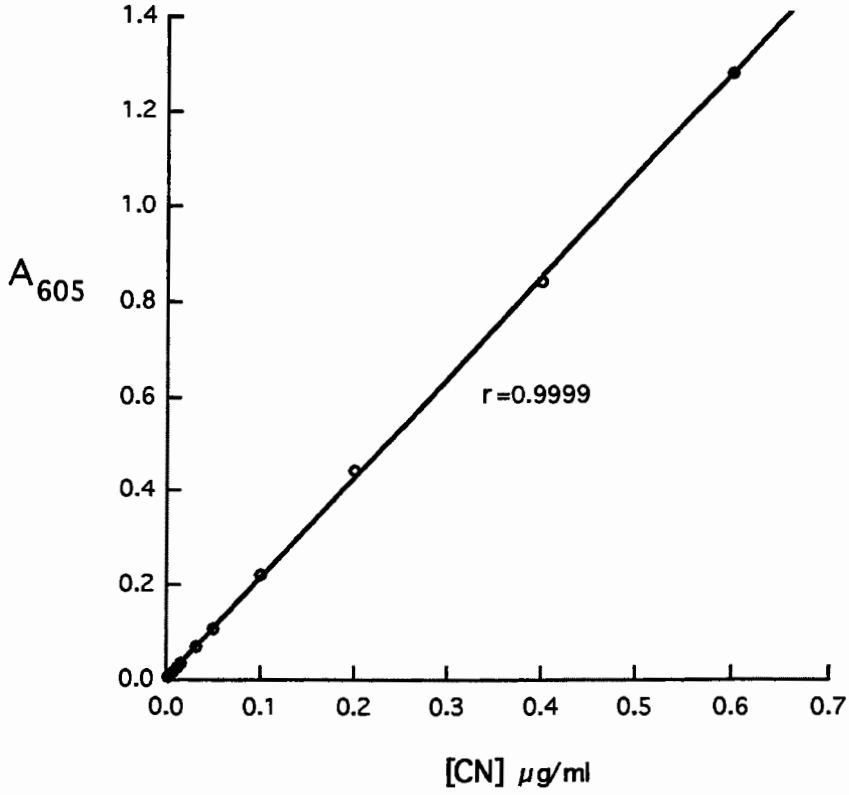

Fig 1 : Standard Curve for Cyanide Determination by the 4-Picoline - Barbituric acid Method

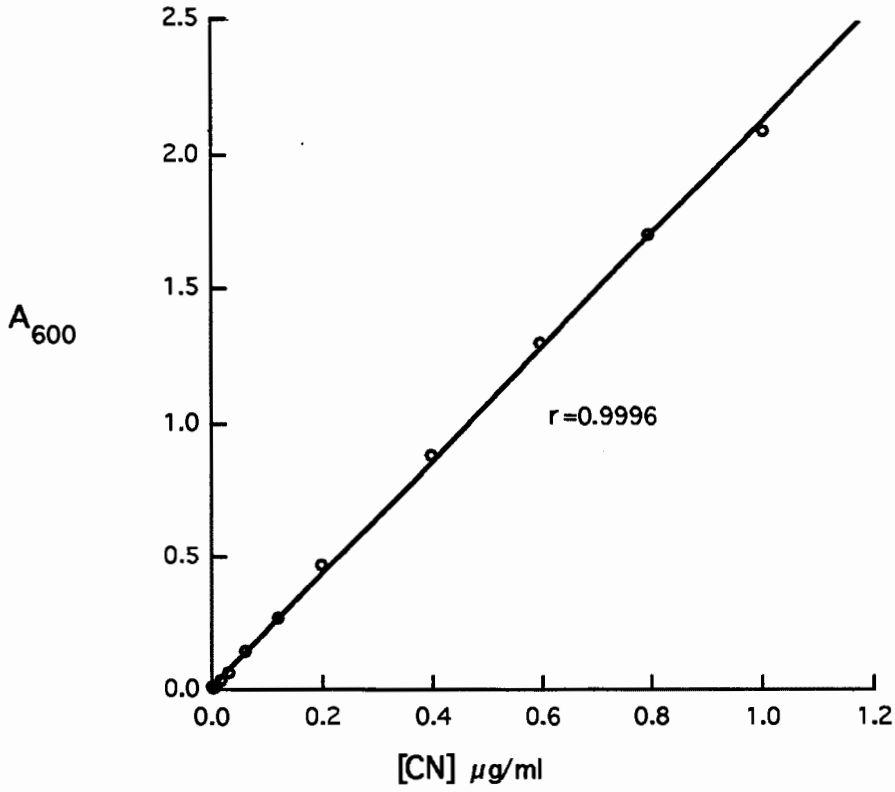

Fig 2 : Standard Curve for cyanide determination by the Isonicotinate - barbiturate Method

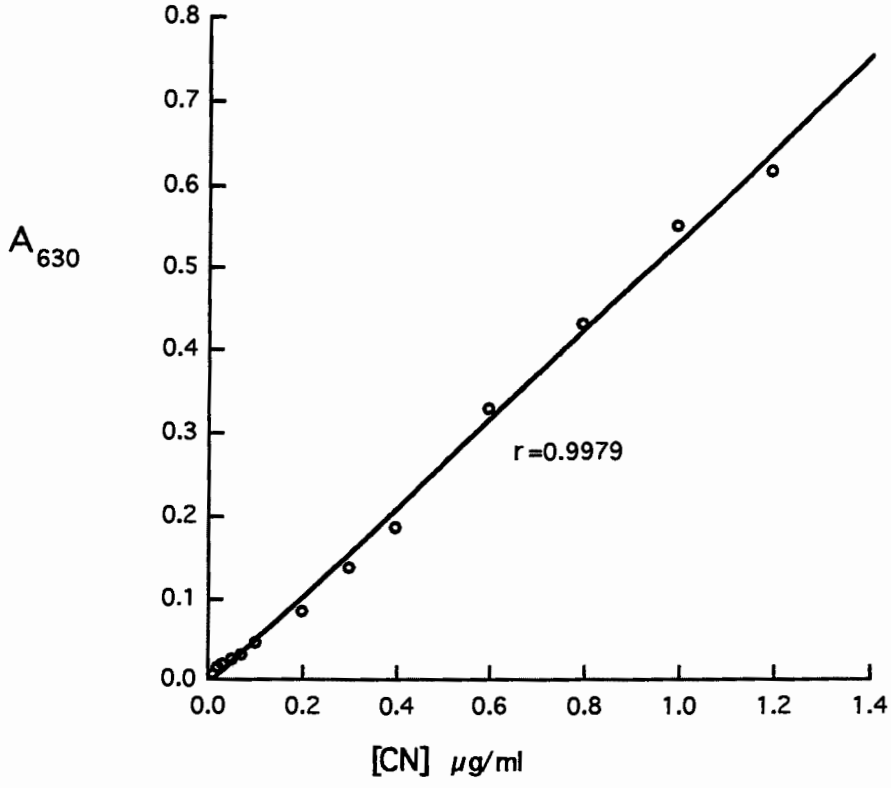

Fig 3 : Standard Curve for Cyanide Determination by the Pyridine - Pyrazolone Method

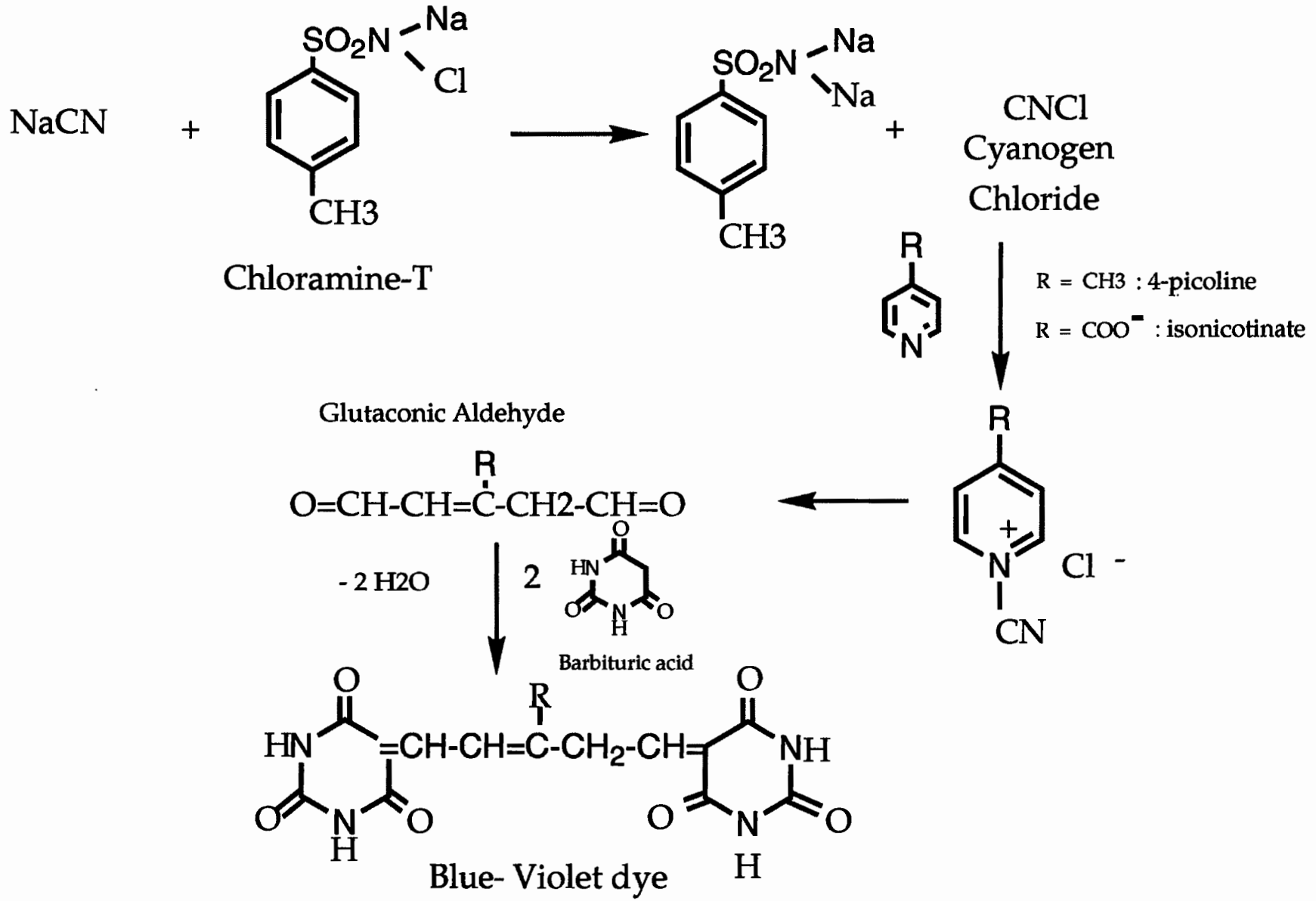

Fig 4 : Chemical reactions for cyanide determination by the 4-picoline - barbituric acid and isonicotinate - barbiturate methods

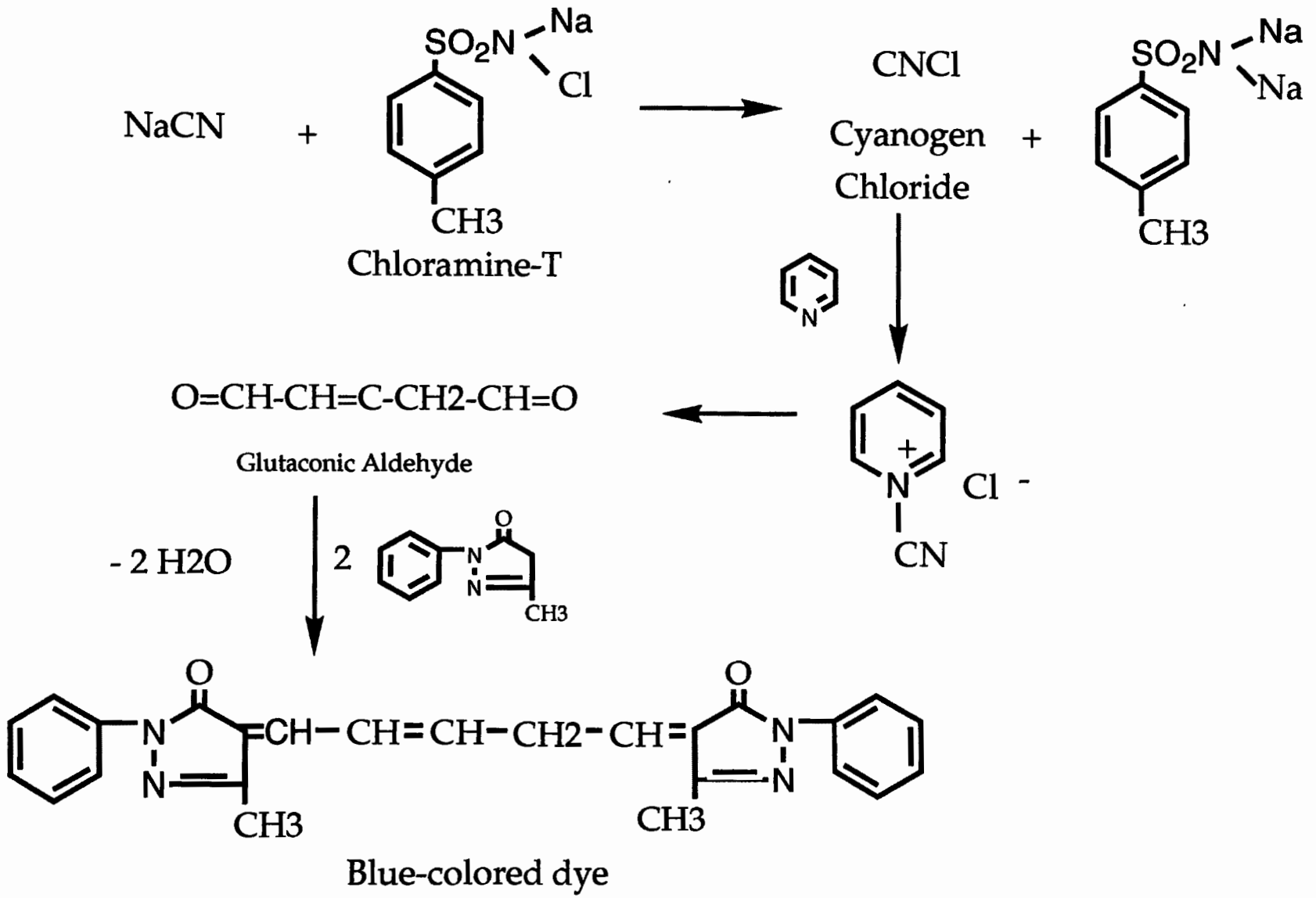

Fig 5 : Chemical reactions for cyanide determination by the pyridine - pyrazolone method

Air and Groundwater

MANAGING RCRA STATISTICAL REQUIREMENTS TO MINIMIZE GROUND WATER MONITORING COSTS

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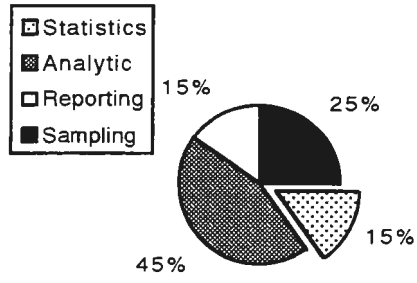
ABSTRACT

This paper will provide an overview of how ground water monitoring statistical choices can significantly impact a facility's ground water monitoring costs. For example, a recent study analyzed the long term ground-water monitoring cost impacts of different statistical analysis approaches on over 20 landfills. The study found that the choice of statistical approach can make over a 50% difference in long term monitoring costs. Four key issues in choosing a statistical approach that minimizes monitoring costs were:

- Minimizing retesting because of inappropriate hydrogeologic assumptions;
- Minimizing site-wide false positive rates;
- Minimizing sample size requirements; and
- Maximizing statistical flexibility when data characteristics change.

INTRODUCTION

Usually, the costs of performing statistical analyses range between 10% to 15% and rarely should exceed 20% of the total ground water monitoring costs. Field sampling, analytic laboratory and regulatory reporting costs comprise most of the monitoring costs. For example, analytic laboratory costs for the Subtitle D Appendix 1 constituents required under detection monitoring usually cost between $350 and $400 per well per sample. When sampling and reporting costs are also included, the per well ground water monitoring costs often will



Typical Distribution Of Monitoring Costs

climb to $700 or more. If a facility is forced into a retesting situation because an inappropriate statistical test was used, the sampling, lab and reporting costs will often exceed $2000. And if the facility is inappropriately forced into assessment monitoring the analytic laboratory costs alone can easily exceed $1900 per well.

By contrast, with the prudent use of appropriate statistics, the statistical analysis cost for a detection monitoring program should run from $125 to $175 per monitoring well per reporting period and may prevent a facility from being inappropriately forced into retesting or assessment monitoring. Usually, when statistical costs exceed 20% of the total ground water monitoring costs, the cost advantages of specialized ground-water statistical software are being overlooked. For example, EMCON, IT Corporation and Law Environment along with a number of other national and regional solid waste consulting companies use the Groundwater Statistical Analysis System (GSAS™) software at many sites to automate the statistical analyses and ensure that the most appropriate statistical tests are being used. This decision support system developed by Intelligent Decision Technologies in Boulder, Colorado is one example of how artificial intelligence software is being used to reduce solid waste management operating costs.

Ironically, at sites which do not have large analytic programs, when statistics comprise less than 10% of the total ground water monitoring costs, this is often an indication that the inappropriate use of statistics has forced a facility into extensive retesting or assessment monitoring which drives the sampling and analytic costs through the roof. There is no single statistical approach for all sites that minimizes ground-water monitoring costs. There are, however, general considerations that apply to most sites. These considerations are summarized in four steps that you can take to gain better control over your monitoring costs.

APPROPRIATE HYDROGEOLOGIC ASSUMPTIONS

The first step in controlling your ground water monitoring costs is to ensure that the hydrogeologic assumptions of your statistics accurately reflect your site's hydrogeology. Many site managers are surprised to find that different statistical tests implicitly make different assumptions about the site hydrogeology and monitoring program. Misunderstanding these implicit assumptions is the greatest cause of sky rocketing ground water monitoring costs.

For example, we have seen sites where interwell statistics indicate a release from the facility when no waste has yet been placed [See Sidebar On Different Types Of Statistics]. These and other studies have demonstrated that an intrawell statistical approach is generally more appropriate than an interwell approach when there is evidence of spatial variation in the site's

hydrogeology. However, demonstrating to regulators the need for and effectiveness of an intrawell approach can be difficult, especially for sites where the monitoring program began after waste was placed.

Intrawell statistics compare historical data at the compliance well against recent observations from that well. This eliminates the possibility that spatial variation between upgradient and downgradient wells can cause an erroneous conclusion that a release has occurred, but assumes that the historical data at the compliance wells have not been impacted by the facility. The fundamental regulatory concern about the intrawell approach is whether the historical data have been impacted. Otherwise, the historic data do not provide an accurate baseline to detect a future impact. This is a common problem faced by older facilities where the monitoring wells were installed after waste had been placed at the facility. How do they demonstrate that their historical data are "clean"?

Generally, the facility should first use hydrogeologic information supplemented with statistical evidence to demonstrate that there is significant natural spatial variation in the site's hydrogeology. One statistical approach is to evaluate whether there is significant statistical differences among the upgradient wells. If there are, this is usually evidence of significant spatial variation at the site and therefore it can be reasonably concluded that an interwell approach will make erroneous conclusions about the facility's water quality.

The facility can then screen the historical data at the compliance wells to ensure that only clearly unimpacted data are used to develop each compliance well's background standard. Statistical approaches used to assist in the screening include VOC tests, trend tests and even interwell limit based analyses. This approach has worked for many facilities. It has received regulatory acceptance in a number of states including California and Colorado and has allowed facilities to significantly reduce their ground water monitoring costs by reducing retesting and keeping facilities out of unnecessary assessment monitoring.

MINIMIZING SITE WIDE FALSE POSITIVES

The second step in controlling your ground water monitoring costs is to minimize your site wide false positives. False positive rates in the original EPA guidance[1] and in most state and Federal regulations are considered only on a test or individual comparison basis. Facilities, however, need to focus on the site-wide false positive rate which is the possibility of finding at least one statistical false positive result in a regulatory reporting period.

Site-wide false positive rates are far higher than the individual test false positive rates and site-wide false positive rates increase with the number of

statistical tests being performed. For example, if an interwell statistical test is run on only 10 constituents at a 5% false positive rate per constituent, the site-wide false positive rate will be approximately 40%. Consequently, many facilities have at least a 50% chance of one or more false positives in each reporting period. The site-wide false positive rate is critical because it only takes one finding of a statistically significant difference to move a facility into retesting and/or assessment monitoring.

One approach to minimizing the site-wide false positive rate is to reduce the number of constituents that are statistically analyzed under detection monitoring. Federal Subtitle D regulations do not require that every Appendix I constituent be statistically analyzed. In fact, the EPA regulators who promulgated the EPA guidance recognize that in detection monitoring it may be preferable to statistically analyze a subset of the inorganic and organic Appendix I constituents.[2, 3] The choice of the subset should be based upon prior monitoring results, local hydrogeology and leachate characteristics. Some state regulatory agencies such as the regional water quality boards in California have specified shortened lists of inorganic parameters to be statistically analyzed.

A second approach to reducing site-wide false positive rates for VOC analyses is to use composite analyses. Analyses such as Poisson based limits or the California screening method reduce site-wide false positive rates and are usually far more appropriate for VOCs because of the high proportion of non-detects commonly found in VOC data. Care must be taken, however, in the application of Poisson based limits. A recent EPA review[4] criticized a commonly used formulation for the Poisson limit. This is just one example of how the application of statistics to ground water quality data is continuing to change rapidly as more is learnt about the ramifications of using the various statistical tests.

A third approach to reducing site-wide false positive rates is to reduce the false positive rate of the individual tests. Reducing the false positive rate will, however, increase the false negative rate. In such situations, increasing the background sample size can offset the potential increase in the false negative rate. An equation for computing a reduced false positive rate has been developed by California regulators and approved by EPA. Alternatively, power analyses can be performed to justify the use of a reduced false positive rate.

MAXIMIZING STATISTICAL POWER FOR A GIVEN SAMPLE SIZE

The third step in controlling your ground water monitoring costs is to maximize statistical power for a given sample size. The power of a statistical test is its ability to detect a "true" difference or change. There are a number of factors that can affect the power of a test and unfortunately, not all statistical

tests have the same power under the same circumstances. A key determinant of power is the statistical sample size (e.g. the number of analytic results). For example, parametric tests usually have more power than nonparametric tests for the same sample size. Thus, a parametric test is often the test of choice for ground water monitoring, especially when sample sizes are limited if the data are normally distributed.

The difficulty in using a parametric test is that ground water quality data often do not fit a normal or log transformed normal distribution when rigorous normality tests such as the Shapiro-Wilks or Shapiro-Francia tests are used. The general response to this situation is to proceed with a parametric analysis which will yield unpredictable results or to move to a nonparametric analysis. The disadvantage of the parametric analysis in such circumstances is that it is impossible to accurately control the power or false positive rate of the test. The disadvantage of the nonparametric analysis is that it has much lower power for a given sample size when compared to the parametric test if the data are normally or transformed normally distributed.

There is one other option that can be employed when the data do not fit a normal or log transformed normal distribution. This option is to utilize a family of transforms identified by Dennis Helsel, one of the US Geological Survey's water quality statistical analysis experts[5]. These transforms, called "The Ladder Of Powers", significantly increase the possibility that the data can be transformed into a normal distribution and that a parametric analysis can be used. This increases the power of the test for a given false positive rate and sample size. Thus additional sampling, expensive retests, and/or being unnecessarily forced into assessment monitoring can be avoided. Unfortunately, the computations required to perform and evaluate the effectiveness of these transforms are quite extensive and thus using specialized statistical software is often a necessity.

ENSURING FLEXIBILITY

The fourth step in controlling your ground water monitoring costs is to develop a site specific analysis methodology that incorporates the spectrum of possible changes in data characteristics over time. For example, data distributions, percentage of non detects, or equality of variances can and often do dramatically change as ground water monitoring programs mature. All too often facilities do not plan for these possible changes. Instead of proposing in their permit applications and monitoring plans a decision logic for choosing the most appropriate statistical approach based upon the current characteristics of the data, they propose one statistical test based solely on the limited data available at the time the application was submitted. In turn, when data characteristics do change, and the facility does not adjust its statistical approaches, retesting and assessment monitoring with all their associated increased monitoring costs are highly probable.

Unfortunately, adjusting the statistical approach once the permit has been issued can be costly and used as a mechanism by other parties to raise a host of other unrelated issues. The approach we use is to incorporate into permit applications and monitoring plans a decision logic for choosing the most appropriate statistical approach based upon the current characteristics of the data. On a regular basis, the data characteristics are reviewed and the most appropriate statistical test is selected based upon the permit decision logic. While the test may change, so long as the decision logic remains consistent, no permit modification is required. This is a concept that has been accepted by US EPA and numerous state regulatory agencies but again, to cost effectively implement this type of flexibility, specialized software is often a necessity.

SUMMARY

Statistical issues are driving both short and long term monitoring costs at municipal landfills around the nation. Utilizing specialized ground-water statistical analysis software, the costs of performing the statistical analyses should rarely exceed 20% of the total ground water monitoring costs for ongoing monitoring programs. The cost of initial statistical evaluation and permit preparation, however, may often exceed this amount. When knowledgeably applied, statistics can reduce the number of samples required, minimize retesting, and prevent a facility from being unnecessarily forced into assessment monitoring, yet provide a reliable indication of a release. Unfortunately, when statistical tests are inappropriately applied, the statistical findings can result in grossly inflated monitoring costs and yet still provide inaccurate answers.

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[1]United States Environmental Protection Agency, "Statistical Analysis Of Ground-Water Monitoring Data At RCRA Facilities - Interim Final Guidance", Office Of Solid Waste, Washington, D.C., Series No. EPA/530-SW-89-026, April, 1989.

[2]United States Environmental Protection Agency, "Statistical Analysis Of Ground-Water Monitoring Data At RCRA Facilities - Addendum To Interim Final Guidance", Office Of Solid Waste, Washington, D.C., Series No. EPA/530-R-93-003, July, 1992.

[3]United States Environmental Protection Agency, "Regulatory Impact Analysis For Amendments To The Hazardous Waste Facility Corrective Actions Regulations – Draft Report", Office Of Solid Waste, Washington, D.C., 1993

[4]Cameron, Kirk, M. D., "RCRA Leapfrog: How Statistics Shape And In Turn Are Shaped By Regulatory Mandates", presented at The International Biometric Society - Eastern North America Region Spring Meeting, Birmingham, Alabama, March, 1995.

[5]Helsel, H.R. and Hirsch, R. M., "Statistical Methods In Water Resources", Elsevier Scientific Publishing, New York, 1992.

EIS/GWM - AN INTEGRATED AUTOMATED COMPUTER PLATFORM FOR RISK BASED REMEDIATION OF HAZARDOUS WASTE CONTAMINATION - A HOLISTIC APPROACH

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ABSTRACT

The cleanup of contaminated sites is likely to remain the number one environmental concern for the foreseeable future. Successful remediation must be based on a thorough understanding of the contaminant migration and fate. Existing simplified empirical modeling and simulation tools are no longer sufficient to design, regulate and manage the contamination problem effectively. For example, the simple exponential decay law does not adequately describe the chemical and biological interactions between the contaminant and the terminal electron acceptors, the soil matrix and the available nutrients that take place in **bioremediation**. Likewise, for in situ remediation technologies such as **bioventing** (interaction of thermal and chemical processes); **pump-and-treat** (interaction of mechanical and chemical processes); **vitrification** (interaction of thermal, chemical and mechanical processes); **electrokinetics** (interaction of electrical chemical and mechanical processes); **chemical barriers** and in situ **containment technologies** (interaction of chemical and mechanical processes), there usually lacks a 3-D simulation model capable of quantifying their impact on the geomedia environment. *This results in an inaccurate evaluation of the risk assessment and in excessive cleanup costs, presenting a heavy burden to the Nation's economy.* Furthermore, the environment must be considered holistically, where remediation of one medium (e.g., soil) must not result in the contamination of another (e.g., air). *Sustainable development* requires a ***holistic macroengineering*** approach where interactions of different natural processes are an integral part of the theoretical model, which must be used to simulate actual contamination episodes, so as to determine optimum innovative and effective mitigative measures. The Environmental Impact System/ Ground Water Module (**EIS/GWM**) computer platform was developed to support this novel Contaminant Migration Risk Assessment approach in a unified computational framework based on the development of strong *Scientific Engines* or simulators embedded in the platform. The EIS/GWM integrated modeling platform is written for MS Windows and has been used to demonstrate the feasibility of embedding this holistic approach in an integrated/ automated computer platform based on the interaction of natural objects in 3-D space. Example cases from EPA Region III, including industrial and defense sites illustrate the operation, framework, and philosophy of the EIS/GWM platform.

INTRODUCTION

Context of the Environmental Risk Assessment Problem

Risk assessment of health hazard posed by contamination episodes, and site remediation to reduce and control their risk require a good understanding of how chemicals move through, and interact with the subsurface and above ground environment. To remove the source or to pump-and-treat the aquifer are simply declarations of intent not directly amenable to efficient ways of dealing with the problem. What should drive the remediation effort is *risk assessment* and *risk characterization*. In this light, the question becomes what is the level of treatment necessary to meet health risk standards at "end points," compatible with what can be physically and economically achieved.

For example, let us consider the risk of contamination from a typical hydrocarbon spill illustrated in Figure 1. The bulk of the fuel ("free product") occupies the interstitial space in the vadose zone and "floats" on top of the water table. Constituents of the fuel dissolve into the saturated part of the aquifer and tend to contaminate the aquifer by advection and dispersion. This in turn may contaminate a water supply well located downgradient from the spill and cause a health hazard. Direct use of the ground water is one of the most important "end points" to consider in a risk assessment. Others are: fumes emanating from the unsaturated zone; pollutants reaching surface waters, either through ground water discharge to them, or by runoff; and others. The credibility of a risk assessment evaluation hinges to the largest extent on the ability to accurately predict contamination pathways; and equally importantly, on the ability to predict the efficacy of treatment alternatives.

In the case of Figure 1 pumping the free product will not eliminate the entire source. The fuel adsorbed on the soil particles will continue to dissolve and contaminate the ground water. The question then is what level of *soil treatment* to seek. The way to address the problem is by determining all pathways to 'end points' and relate residual source strength to acceptable risk standards at 'end points.' For this exercise to have *any credibility* the following conditions must be met: 1/ A thorough understanding must be exhibited of the processes that link the source to 'end points' usually by means of a simulation model; and, 2/ The model must be validated to site specific data. Interestingly, in some instances nature can be shown to perform some remediation on her own with minor human intervention. But this also needs thorough proof with the use of simulation models and compliance monitoring.

The EIS/GWM platform offers the ability to go from the screen-level (rudimentary) to the most detailed level progressively, within the same platform, using all previously compiled data and calibrated models. Therefore, the distinction between levels of analysis does nor require an *apriori* selection among a hierarchy of models: all modeling needs are automatically available under the same EIS/GWM roof.

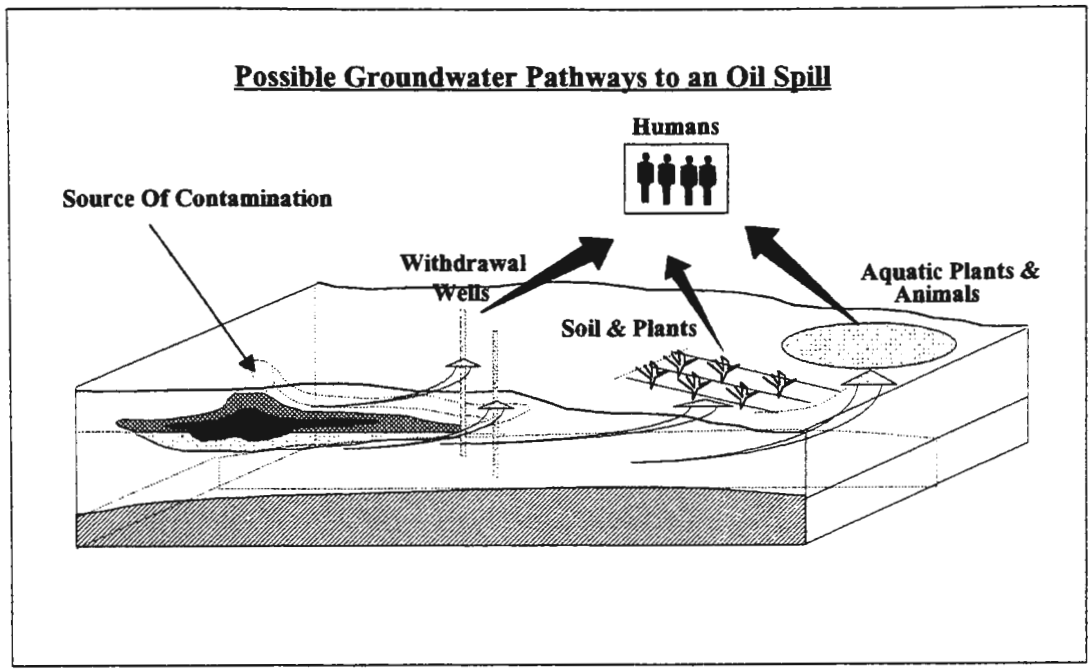

Figure 1. Typical ground water pathways to humans.

Early in the process, screening models are used to identify environmental concerns. Screening level modeling, often based on a structured-value approach, is designed to be used with regional/representative information. Models such as the EPA Hazard Ranking System (HRS) divide the site and release characteristics into predetermined categories that are assigned a point value based on answers to a set of questions. The score from such systems is useful to determine if a situation is a problem, but not to provide a risk-based relative ranking of problems.

Detailed analyses require a highly specialized assessment of potential impacts. Methodologies, such as the Chemical Migration Risk Assessment (CMRA), are composite coupled approaches that use numerically based models that are not physically linked and represent single-medium models, implemented independently in series. This approach usually is reserved for the most complex models, is data intensive, and relies on the expertise of the analyst. Although such tools are appropriate for their intended application, extension beyond site-specific applications often is either difficult or cost-prohibitive.

An alternative to these Analytical/Semi-Analytical/Empirical-Based multimedia models (designated as analytical models) is offered by the EIS/GWM platform which includes a large pool of numerical models (scientific engines) that can be used for prioritization, preliminary assessments and exhaustive risk assessments studies.

These models are all integrated in the EIS/GWM platform. They are fully coupled approaches that use numerically based algorithms, combined into a single code to describe each environmental medium.

Figure 2 illustrates the value of simulation models in the risk assessment process. They can be used in a detailed (i.e., numerical) or an initial-screening (i.e., ranking/prioritization) assessment, where data and circumstances warrant. Figure 2 also illustrates the relative relationships between input-data quality, output uncertainty, and types of problems at each level of assessment. The computational requirements tend to be less intensive at the earlier stages of an assessment when there are fewer available data, and, correspondingly, the uncertainty with the output results tends to be greater. As the assessment progresses, improved site characterization data and conceptualization of the problem increase, thereby reducing the overall uncertainty in risk estimates. As indicated in Figure 2 the EIS/GWM platform offers the most accurate site specific evaluation of risk.

EIS/GWM integrates standard approaches into a consistent and powerful tool. This multimedia (multiphase) platform incorporates medium-specific, transport-pathway, and exposure-route codes based on standard, well accepted algorithms; hence, their acceptance by regulators is favored. For example, numerical solutions to the advective-dispersive equation describe contaminant migration in the ground water environment. The platform allows to link migration models with risk exposure models, so that the analyst can immediately assess the entire process of contaminant release, migration (transport), exposure, and risk at once.

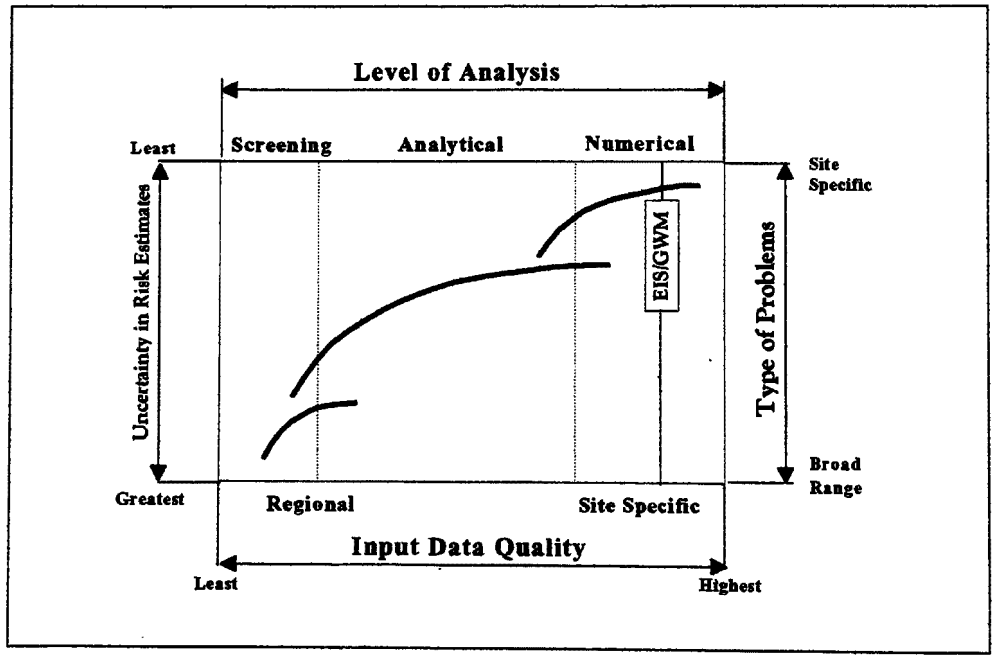

Figure 2. Relationship between input-data quality and output uncertainty (after Whelan, et al., 1994.)

The value of the platform is exemplified by an order-of-magnitude reduction in assessment time, as compared to the traditional risk assessment models. It can concurrently assess multiple waste sites with multiple constituents to include baseline (at $t = 0$), no action (at $t > 0$), during-remediation, and residual (post-remediation) assessments, including changing land-use patterns (e.g., agricultural, residential, recreational, and industrial). Its scientific engines can describe the environmental concentrations within each medium at locations surrounding the waste sites to a radius of 80-km (50 mi). Specially distributed, three-dimensional, concentration isopleths can be constructed detailing the level of contamination within each environment. By coupling land-use patterns with the environmental concentrations, three-dimensional risk isopleths can be developed (as a function of land-use pattern and location).

RISK ASSESSMENT IMPLEMENTATION UNDER EIS/GWM

The EPA risk assessment methodology for exposure assessment suggests a series of standard default exposure routes and exposure assumptions/parameters for use in conjunction with discrete current and future land use scenarios. While the exposure routes themselves may be more or less applicable to a specific site, the majority of the standard exposure assumptions advocated for use in estimating chemical intakes are not site-specific, nor are they necessarily the most current, relevant numerical values. Historically, the use of alternate *standard* assumptions of the development of site-specific assumptions has been met with varying degrees of acceptance by regulatory agencies, although the existing guidelines for these assumptions (EPA 1989, 1991b) and the guidelines regarding the formulation of site-specific PRGs (EPA 1991a) advocate the use of site-specific information wherever possible. Site-specific information and viable exposure routes will vary with the location, magnitude, and nature of the spill or leak, as the local human populations, regional topology and hydrogeology, and land use. Practical, site-specific considerations as implemented in the EIS/GWM platform are discussed below.

Rather than using point estimates in exposure assessment, the EIS/GWM simulation tools can be used to estimate distributions for exposure assumptions. Use of this methodology does not alter the basic structure of the exposure estimate. However, it does refine the way chemical intakes are calculated in the exposure assessment.

Figure 3 illustrates the overall approach as implemted in the program. The starting point is to establish the statistical characteristics of all pertinent input parameters characterizing a site. Such parameters include: soil properties (soil layers, porosity, hydraulic conductivities, dispersion etc.), chemical properties (adsorption, stoichiometry, etc.), as well as loading/source site-specific conditions. Then, their mean values and standard deviations automatically feed the scientific engines (simulation algorithms) available in the platform.

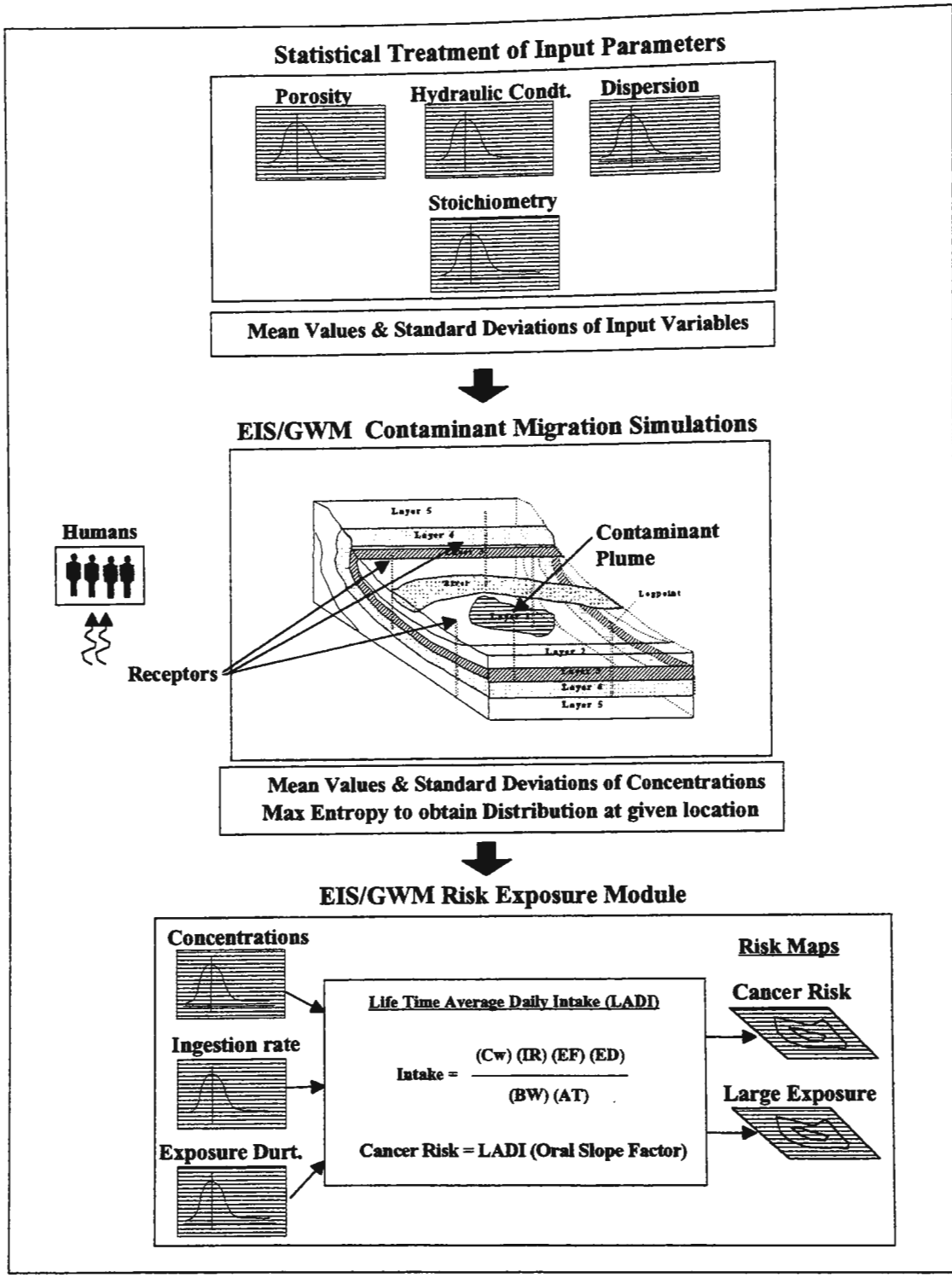

Figure 3. Risk assessment implementation in EIS/GWM.

These algorithms simulate different natural processes that include:

- ground water flow with special features such as slurry walls, geosynthetics and geologic faults;
- Single species contaminant migration processes such as advection (computed from fluxes produced by the flow module), dispersion, chemical reaction (sorption, ion-exchange, chemical decay), and sink/source mixing; and,
- Migration and degradtion of hydrocarbons accounting for oxygen-limited biodegradation occuring at the site.

The outcome of the simulation is the spatial distribution of the mean values and standard deviations of the concentrations throughout the site. The mean values are the conventional point estimates as produced by the corresponding algorithms activated on a given site. A first-order approximation is used to compute the standard deviation of the concentrations "C" assuming that all input are statistically independent.

At this stage we only know the mean and variance of the concentration probability distribution. However, invoking the principle of maximum entropy (Jaynes 1978) the assignment of a concentration probability distribution is that which maximizes the information entropy subject to the additional constraints imposed by the given information (i.e. the mean and variance values). Detailed solutions for a number of cases are given in Goldman (1968), Tribus (1969), Dendrou (1977).

In the EIS/GWM simulation model, the analyst determines a continuous or discrete distribution to describe each random variable. This distribution is defined in terms of the probability density function (PDF) or the cumulative distribution function (CDF). Several distributions are defined by one, two, or more parameters. When running the EIS/GWM simulation model, the computer automatically proceeds to determine the distribution of daily intakes. From this distribution, a specific intake can be selected *(e.g.,* the average or mean intake, median intake, or 95th percentile upper confidence limit on the intake) that, in combination with the appropriate toxicity benchmark concentration, is used to calculate risk.

EIS/GWM simulations can also include correlations between variables (Smith *et al.* 1992). For example, there is a correlation between body weight and ingestion rate. Using strongly correlated variables in deriving an estimate of exposure serves to strengthen the estimate by preventing nonsensical combinations of variables in its derivation.

In most cases, the daily human intake calculated using the EIS/GWM simulation is less than that calculated using point estimates. This is not to suggest the use of the platform because it produces lower estimates, but rather because its estimates can be associated with probabilities. This results in increased confidence in the estimate of intake, thus ensuring increased confidence in public health protection.

CASE STUDY

Site Description

The selected site in this application is an industrial site where BTEX has been released in the groundwater from leaky oil tanks. It is determined that ground water is the medium of concern and off-site residents are the population of concern based on their use of ground water as drinking water source. The site covers an area approximately 4550x4720 meters. An LNAPL fuel has been released into the soil and the shallow confined aquifer as shown in Figure 4. The contaminant plume migrates towards the north, where several drinking water wells are located. These wells are of primary importance to the adjacent municipality and a detailed groundwater study is initiated to predict the extent and migration of the spill in the shallow confined layer which is a subject of the investigation. Samples collected around the perimeter of the spill indicate that free product has not reached the perimeter of the oil tank farm. The relatively uniform throughout the year flow regime with low annual precipitation (4 cm.) corroborates the assumption of a stable piezometric map throughout the duration of the selected scenario analysis.

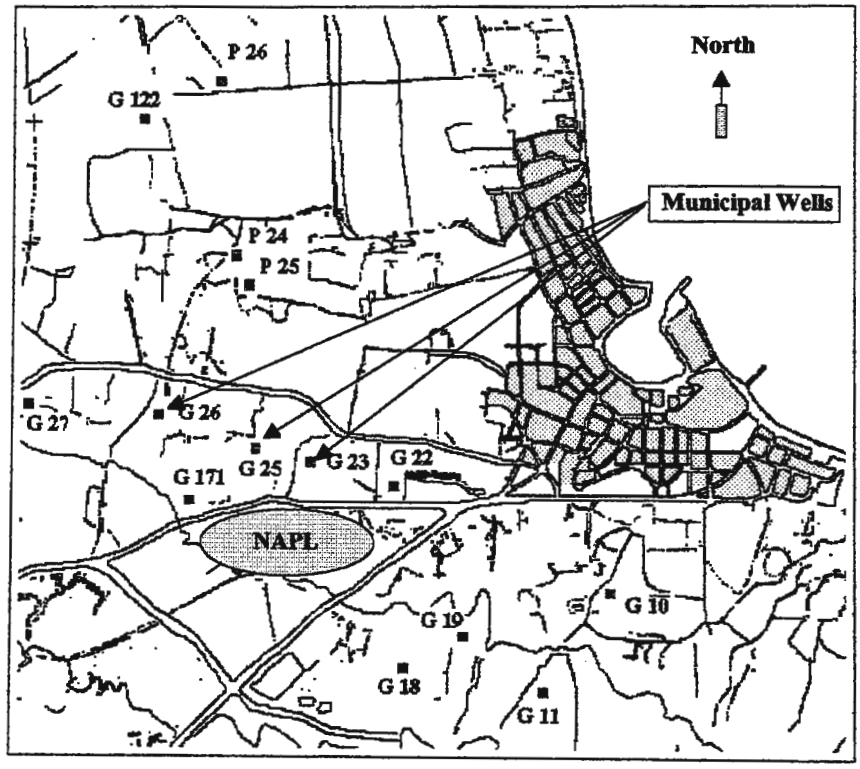

Figure 4. Site layout and location of NAPL contamination.

The objectives of the study are the following:

- Determine the extent of contamination; rate of progression.
- Evaluate the risk of contamination of municipal wellfields.

Groundwater FLOW and Migration Models

The EIS/GWM platform is used to simulate the migration of dissolved-phase contaminants at the vicinity of the oil tank site. This simulation necessitates the use of the groundwater flow (Miflow) and migration (Migra & BioRem3D) models, built on the site-specific data. These data indicate the existence of a relatively shallow layer of medium-grained sand throughout the examined area (Figure 5). The thickness of this aquifer varies between 0 and 20 meters overlaying a relatively impermeable clay layer. The general grid orientation is in the direction of the flow. Several grid discretizations were examined leading to the 48x48 macroelement mesh shown below. Calibration runs for heads involved adjusting hydraulic conductivities so as to match observed piezometric heads (first 100 days of the contaminant migration). A constant source mechanism is retained to specify the initial contaminant plume.

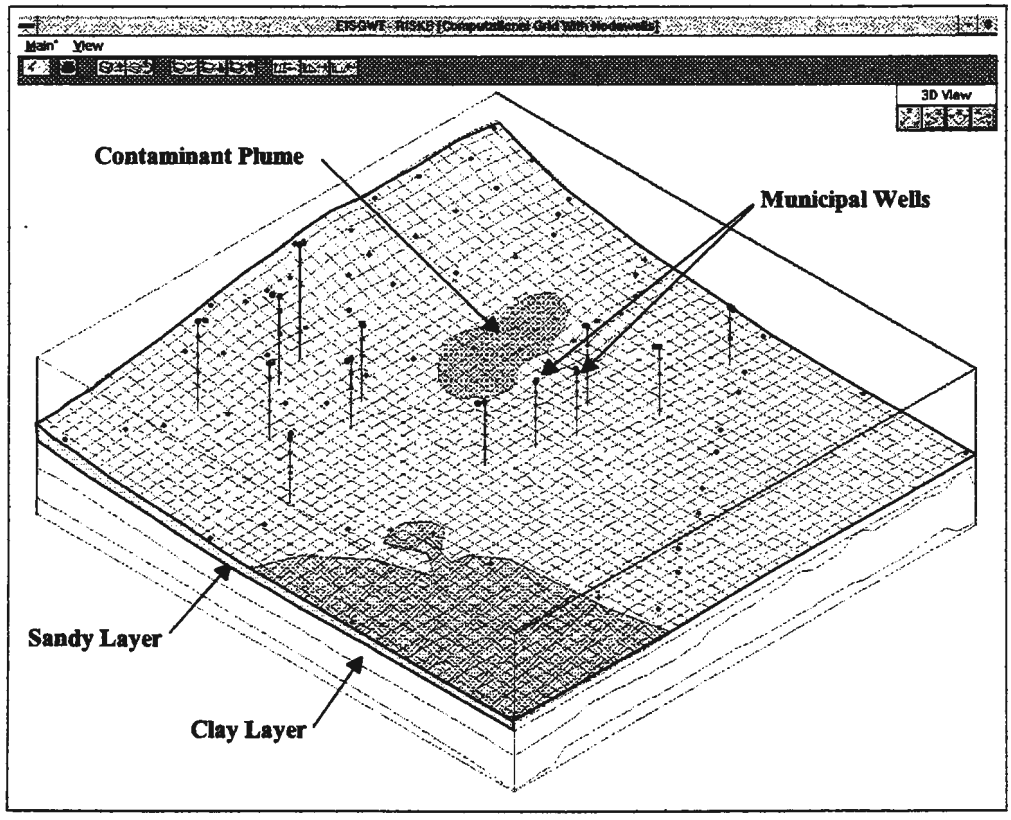

Figure 5. 3D configuration of the geologic strata (soil layers).

A series of sensitivity analyses were made about conductivities, as well as of the advective resolution process, using the MOC method (USGS Method of Characteristics) and the Discrete Element Method. The latter being more efficient is retained for the production runs used for the risk analysis. Among the several grids that were used to discretize the site area the medium grid (100x100 m cells) offered the best cost efficiency ratio. That is the accuracy of the simulation is maintained while the computational burden is kept at acceptable levels.

Calibration of the BTEX plume involved many steps some of which required a sensitivity analysis which included the proper characterization, in order of importance, of the advection mechanism (influenced by the flow regime), dispersion, retardation, decay properties, and other chemical interactions. The following computer runs are retained for the risk assessment study:

File Name	Description	Degrees of Freedom	Computational Module
RISKM	Medium Mesh One Species analysis	6912 Degrees	Migra
RISKB	Medium Mesh Multispecies analysis	6912 Degrees	Biorem 3D (includes biodegradation process)

The results of these simulations are shown in Figure 6 and 7. Figure 6 illustrates the variation of the piezometric heads in the vicinity of the contaminant plume, while Figure 7 shows the extent of the contaminant plume 1000 days after the initial release. As it can be seen, the extent of the contaminant plume has reached the zone of influence of the municipal wells, the "end points" (receptors) in our investigation. To proceed with the risk assessment of the use of the groundwater as a drinking water resource, we need to use the exposure equation to estimate the intake for groundwater. The concentration of BTEX (Cw) in this equation is obtained from the computational modules "Migra" and "Biorem 3D". This equation is now applied to each well located north of the contaminant plume. A summary of the raw values for the concentrations is given below:

Well Number	Results from Migra [ppm]	Results from Biorem 3D [ppm]
G 171	2.15	0.56
G 25	1.52	0
G 23	3.09	0.89
Uncertainty in the Estimates	**Moderate Uncertainty [.5-1.0 ppm]**	**Large Uncertainty [1.5-2.0 ppm]**

Natural biodegradation considerably reduces the concentrations of dissolved BTEX in the groundwater, but their estimates include a large uncertainty that may affect the associated risk to drinking water.

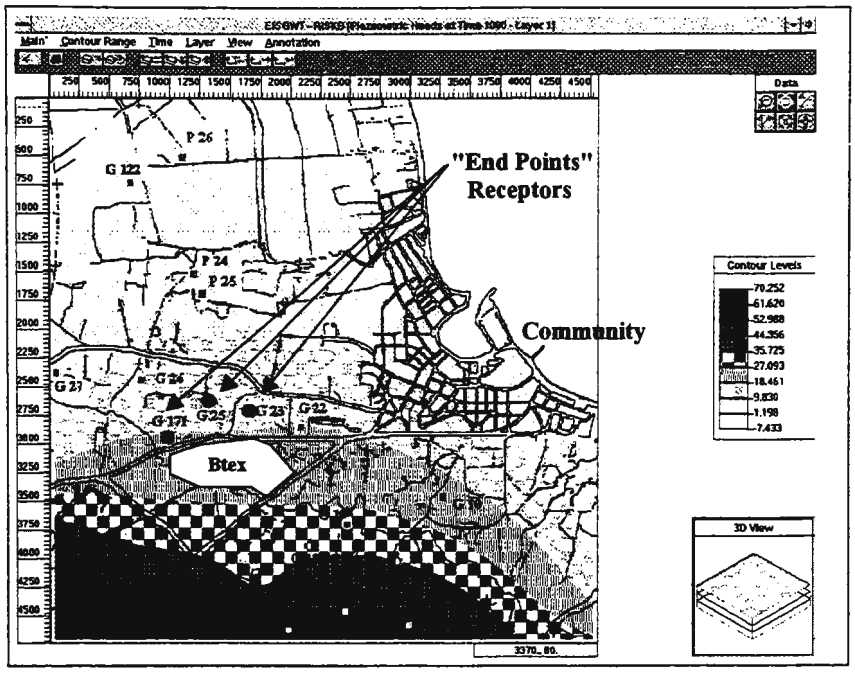

Figure 6. Computed Piezometric Heads.

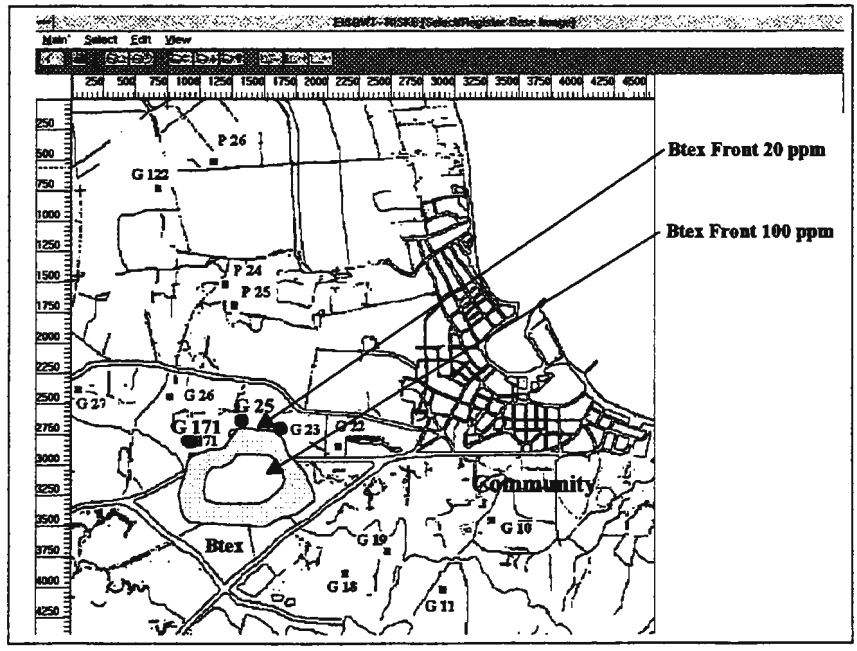

Figure 7. Computed Extent of BTEX Plume (Migra Simulation).

Risk Exposure Study

The deterministic values of the BTEX concentrations (Cw) reported in the previous table will typically result in a point estimate scenario of the benzene ingestion in water. However, to perform an uncertainty analysis a distribution is needed for all the exposure parameters (such as the ingestion rate, the exposure frequency, the exposure duration, the body weigh and the cancer potency factor) and the BTEX concentration at the "end points" (receptors). The distribution of the exposure parameters is obtained from Data bases of laboratory experiments. However, to obtain the distribution of the BTEX from the migration simulation is a more elaborate task. Several options are offered for this implementation as shown in the table below:

Method	Fundamental Principle	Analysis Type & "End" results	Size [Degrees of Freedom]	Number of Runs
Deterministic (Point estimate)	One value estimate	Nonlinear Mean	6,912 DOF	1
Monte Carlo	Multiple estimates for range of probable values	Nonlinear Distribution	6,912 DOF	5,000 to 10,000
Generalized point estimate	Equivalent discrete Probabilities at reaction points	Nonlinear Distribution	6,912 DOF	2,048
Stochastic Finite Element	Karhunen-Loeve expansion	Nonlinear Distribution	37,600 DOF	1
Uncertainty model (proposed model)	Max entropy principle	Nonlinear Distribution	6,912 DOF	1

A quick observation of the resources needed to estimate the BTEX distribution at the "End points" favors the proposed uncertainty model. Indeed, the maximum entropy principle explained in the previous section allows a cost effective evaluation of the BTEX concentration distribution without any penalty on the computational effort. At this stage we can combine all the various distributions to come up with the distribution of the "Cancer Risk" due to the BTEX contamination of this particular site. This is achieved as shown in Figure 8.

First we compute the lifetime average daily dose (LADD) based on the input distribution of the following parameters: the BTEX concentration obtained from the simulation, the ingestion rate, the exposure frequency, the exposure duration, the body weight, the life span and the conversion factor. Then the cancer risk is estimated based on the following equation:

$$CancerRisk = (LADD)(CPF)$$

Where:

LADD=Lifetime Average Daily Dose (mg/kg/day)

CPF= Cancer Potency Factor $(mg/kg/day)^{-1}$

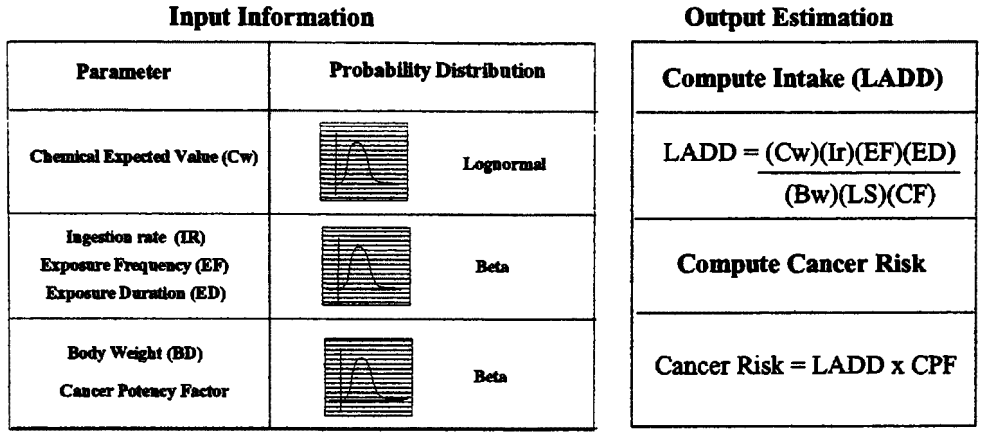

Figure 8. Estimating distribution of human daily intakes.

The input values that are used in this risk assessment study are shown below. For the exposure parameters we assumed a lognormal and beta distributions as the most representative of the laboratory tests.

Parameter	Distribution	Mean	Variance	Min-Max Range
Chemical Concentration	Lognormal	(mg/l)		
Ingestion rate	Lognormal	2.0 l/days	0.25	
Exposure Frequency	Beta	350 days/year		Min=250, Max=365
Exposure Duration	Beta	70 (years)		Min=9, Max=70
Body Weight	Lognormal	70 (kg)		
Cancer Potency Factor(CPF)	Lognormal	0.029 (mg/kg)	0.67	

These parameters are now combined to estimate the cancer risk according to the above equation. A typical set of results are shown in Table 1 for municipal well G 23 (retained "End Point") (see also Figure 7). Several uncertainty models are compared with the conventional point estimate approach proposed by EPA. These models are based on the computed concentration at well G23; the exponential model retains only the mean concentration from the simulation, while the lognormal model retains both the mean and variance of the concentration. Two contaminant migration scenarios are also considered; one which considers advection, and dispersion as the predominant natural processes (implemented in module Migra) and one which also includes biodegradation (implemented in module BioRem3D). A variety of very interesting observations can be made focusing the discussions first on the merits of the two simulation scenarios and then on the advantages of the corresponding uncertainty models.

Table 1. Summary of the results of the risk assessment study for well G 23.

Processing Module	Max Entropy Uncertainty Model	G 23-BTEX Concentration (mg/liter)	Life Average Daily Dose (LADD)	Cancer Risk (Expected Value)	95th Percentile of PDF
Migra (Advection, Dispersion)	Point Estimate	3.1	8.4×10^{-2}	2.4×10^{-3}	-
	Exponential (mean)	3.1	2.5×10^{-2}	2.1×10^{-4}	2.2×10^{-4}
	Lognormal (mean, variance)	(3.1), (0.5)	2.1×10^{-2}	1.9×10^{-4}	2.0×10^{-4}
Biorem (Advection, Dispersion, Biodegradation)	Point Estimate	0.89	2.36×10^{-2}	6.0×10^{-4}	-
	Exponential (mean)	0.89	0.3×10^{-2}	6.2×10^{-5}	1.9×10^{-4}
	Lognormal (mean, variance)	(0.89), (0.3)	0.2×10^{-2}	5.5×10^{-5}	1.6×10^{-4}

Comparing Simulation Scenarios at Well G 23

The discussion is focused on the results of the conventional point estimate procedure. As it can be seen in Table 1, the expected "Cancer Risk" is the highest when the simulation includes only advective and dispersive terms (module Migra). The simulation that includes biodegradation (module BioRem3D) shows a dramatically decrease in the expected cancer risk. In the context of hazardous waste cleanup, site-specific cancer risk between 10^{-4} and 10^{-6} may be deemed acceptable by the appropriate authority. In that respect, when biodegradation is accounted for, the point estimated risks are acceptable. However, this picture is changed when we consider the results based on the distribution of the input simulation parameters. In this particular case for example, little gain is obtained when biodegradation is included. This is due to the high uncertainties associated with the input site dependent parameters of the biodegradation process.

Comparing Uncertainty Models at Well G 23

In general the use of the uncertainty models results in reduced estimated cancer risk. As it can be seen in Table 1, the point estimate of the cancer risk gives 2.4×10^{-3}, while the 95th percentile for the cancer risk based on the exponential model is 2.2×10^{-4}. The lognormal uncertainty model decreases this value even further because the quality of the information is better, since the variance of the computed concentrations is also included in the risk assessment study.

CONCLUDING REMARKS

Aiming at Improving Risk Characterization under EIS/GWM

The basic objective of the risk assessment study under EIS/GWM is to be able to better characterize the risk as our knowledge of the natural processes affecting the contaminant migration improves. Figure 9 illustrates the outcome of the present analysis. It is clear that risk assessment using the conventional statistical approach leads only to an average risk estimate based on in-situ measurements that are lumped together over the entire studied domain. As a consequence, the same risk estimate is applied to all "End Points". The penalty on some of these "end Points" is steep as the high estimated cancer risk may result in a prohibitive remediation cost.

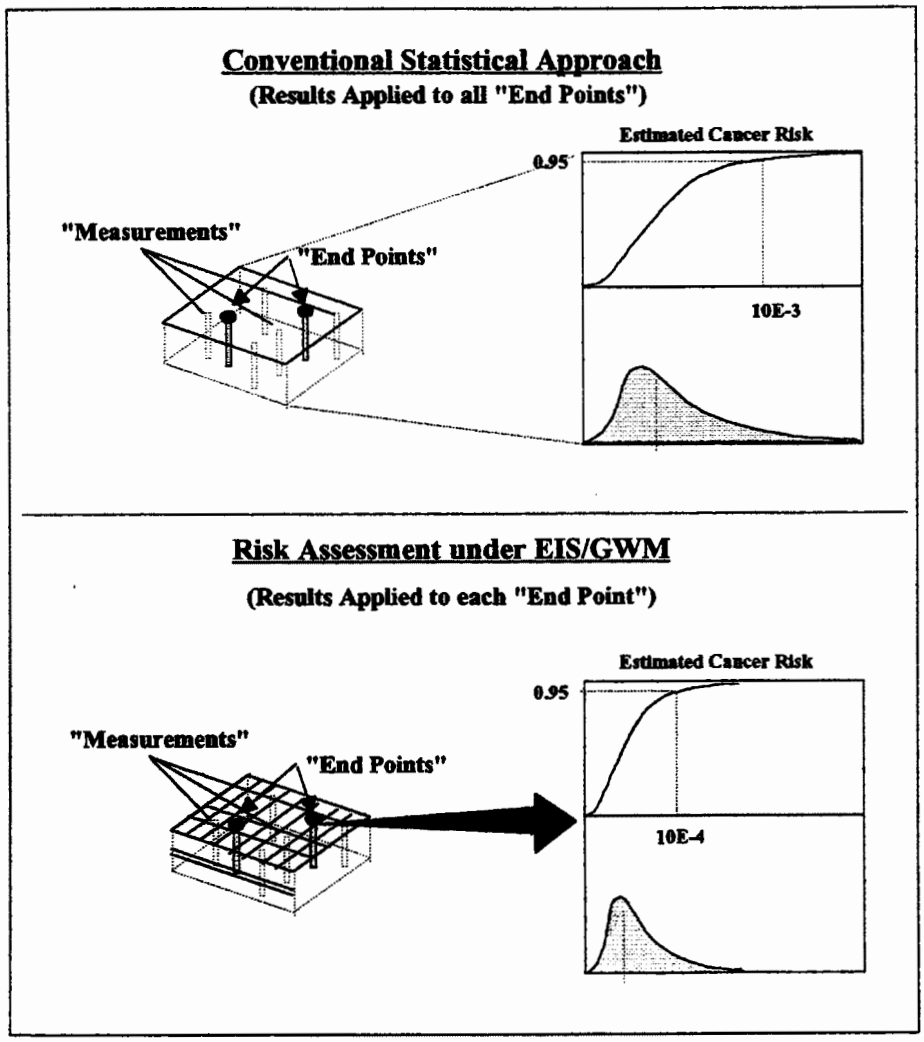

Figure 9. Simulation based risk assessment.

A more pragmatic approach is adopted in this document which improves greatly on the conventional risk evaluation. The improved methodology combines statistics of a site characterization with a variety of numerical models that simulate different physical processes. This results in reducing the inherent uncertainties of the study, narrowing the probability distribution function of the health risk. This approach requires a good understanding of the use of the different models in the overall risk assessment. Otherwise the high uncertainty of the estimated concentrations at "End Points" will again 'flatten' the probability curve resulting in high estimated risk percentiles.

Numerical models designed to describe and simulate environmental systems cover a wide range of detail and complexity: they range from very simple statistical black-box models to the "all-inclusive", multiphase, spatially discretized simulation models offered under the EIS/GWM platform. But even for the most detailed and refined models, macroelements (discrete elements or compartments) require some distribution at a scale larger than that of the size of the sample from the field or experiment. In fact, what models really describe are simplified conceptualizations of the real-world system, which are very difficult to relate directly to the data point samples of these systems. In that respect, models and data operate on two different levels of abstraction and aggregation, and therefore traditional data from a spatial or functional microlevel can hardly be used directly. Instead, from the available data one can try to derive information about the system at the appropriate scale, for comparison with the respective modeling factors. Ideally, the measurements should be made directly at the appropriate level, but some of the more promising techniques in environmental data collection are still in their infancy, at least as far as scientific applications are concerned.

The two elements that will drive the risk based approach in the near future are:

- the introduction and use of scale-dependent statistics; and
- the association of cost with the corresponding target risk reduction level in relation to the uncertainty of that estimate.

Scale-dependent statistics is an aspect of the risk-based remediation approach which must be thoroughly developed. Elements of the statistical theory of scale dependence exist but their application in risk assessment is lacking. As an example, geostatistical kriging as implemented in EIS/GWM can be used to derive 'point' estimates or 'volume' estimates. Depending on the nature of an input parameter to a simulation model (e.g. conductivity, or initial concentration) a point estimate or a volume estimate may be the appropriate statistical inference to use. Similarly, scale must be accounted for at the level of the field or laboratory measuring device.

Finally, cost must be by necessity a key element of the risk based approach: because the marginal rate of return per unit of additional risk reduction will show whether we have reached the level of diminishing returns. When this happens, you need to evaluate the system at a higher level of accuracy (narrow the probability distribution) before further analyzing remedial options.

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INTER-LABORATORY COMPARISON OF QUALITY CONTROL RESULTS FROM A LONG-TERM VAPOR WELL MONITORING INVESTIGATION USING A HYBRID EPA METHOD T01/T02 METHODOLOGY

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ABSTRACT

Analyses of air samples has received a significant amount of attention since the passage of the Clean Air Act (CAA). Of particular interest is the analysis for volatile organic compounds (VOCs) in air. Although the CAA recently has focused a significant amount of attention on the analysis of air samples, a very large, complex air investigation was initiated in 1988 when a small leak in an underground gasoline line was discovered, but not before over a million gallons of gasoline was released to the saturated and unsaturated zones, under and around a major oil terminal in New York State. The facility is located in a generally residential area and as such, the possibility of gasoline fumes migrating to the basements of residents, all of which were utilizing municipal water supplies, was of concern to the facility owners and the local health department.

During 1988 and 1989, the facility owners pro-actively installed several hundred ground water and vapor monitoring wells on the facility and in the nearby residential community. Extensive monitoring of the vapor wells for eighteen VOCs via air sample collection using calibrated personal sampling pumps on multi-media Tenax/Ambersorb sorbent tubes followed by direct thermal desorption GC/MS analytical techniques (EPA T01/T02 hybrid) was conducted on the vapor monitoring wells over the last 7 year period. As a fairly low analytical action limit of 10 nl/L of benzene was established based on conservative health considerations, the facility owners contracted the primary author to design, implement and oversee the quality assurance program such that data quality was evaluated on a real-time basis.

During the aggressive remediation and weekly vapor well monitoring that has occurred since early 1988, a significant amount of performance data has been generated by two commercial laboratories and one regulatory laboratory and has been independently validated. This paper presents a comparison of the QC results generated since 1988, such as inter- and intra-laboratory duplicates/triplicates, surrogate spike recoveries and double-blind performance evaluation results between the three laboratories over the seven year period. Based on these performance data, the hybrid EPA T01/T02 hybrid appears to represent an acceptable alternative to the more recently commercially adopted EPA T014 (e.g., Summa Canister) methodology for the analysis for VOCs in air.

INTRODUCTION

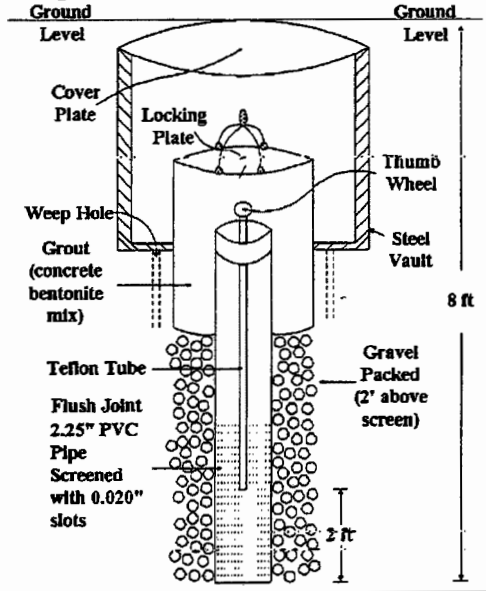
In 1987, a gasoline leak occurred at a storage facility of a large petroleum distributor located in New York State. It was estimated that over one million gallons of gasoline was released to the saturated and unsaturated zones under and around a petroleum terminal from a hole in an underground supply line on the petroleum distributor's property. Approximately 110 vapor monitoring wells were installed in and around the potentially impacted residential community. In addition, approximately 200 water monitoring wells were also installed around the facility and in the surrounding community.

An initial survey of the impacted area revealed that one of the water monitoring wells contained seven (7) feet of gasoline floating product.[1] Public health was of concern due to the possibility of toxic gasoline fumes entering the basements of the potentially impacted community.

Approximately, 470,000 gallons of gasoline were recovered during the first three years of the clean-up of this spill[1]; however, the continuous monitoring of the remaining fuel would require additional time and effort. Due to the long term monitoring (estimated 5 - 10 years) of the vapor wells, "normal", frequent indoor air quality sampling was not feasible due to the inconvenience that would be placed upon the home owners surrounding the facility. The alternative sampling design that was established involved an outdoor soil vapor monitoring well program. The soil vapor monitoring wells were installed in and around the potentially affected residential area. This type of a program allowed accessibility at any time and enable the soil vapors to be tested at typical basement depth.

The vapor wells were constructed by blending existing vapor probe technology with a length of ⅜" outside diameter Teflon® tubing (at basement depth) with a thumb-wheel fitting capable of a leak tight seal for the organic sampling tubes (see Figure 1).[1,2]

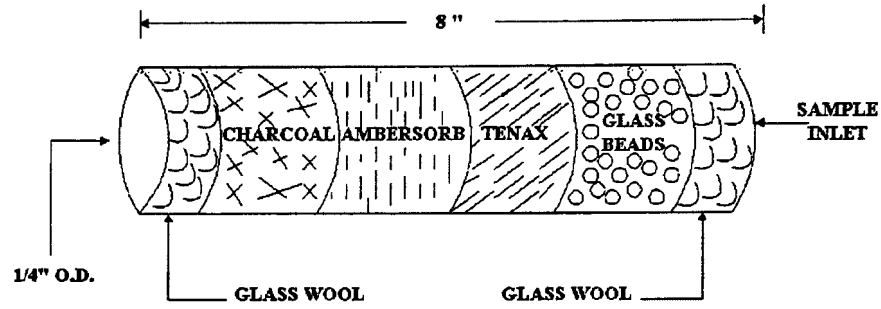
Figure 1
Vapor Monitoring Well Construction



EXPERIMENTAL

Approximately 25 - 30 vapor wells were sampled on a weekly basis. Multi-layer sorbent tubes[2] were employed as the collection vessels for this investigation.[3] The sorbent tubes were constructed of Pyrex® glass (20cm length × 6mm O.D. and 4 mm I.D.). These tubes contained sequential layers of glass beads, Tenax, Ambersorb XE-340 and charcoal absorbants which were held in place with a glass frit and glass wool (see Figure 2).[1]

Figure 2
Sorbent Tube Design



Before each sampling round, the sorbent tubes were conditioned by the analytical laboratory. This conditioning involved a purge with ultra high purity helium (60 mL/min) at a temperature of approximately 310°C for twenty minutes. After the 20 minute conditioning period, the tubes were continuously purged until room temperature was achieved. A surrogate compound, 4-Bromofluorobenzene (BFB) was added to each conditioned tube just prior to shipment to the field sampling team. Each tube was placed in a storage container and shipped in a cooler to the field sampling team.

Sample collection employed the use of individual personal pumps. The pumps were programmed to obtain an air volume sample of approximately 1.0 Liter. The flow rate for these pumps were typically around 50 mL/min. The analytical design consisted of a Multi Tube Desorber (MTD), a concentrator, and a Gas Chromatograph/Mass Spectrometer (GC/MS). Eighteen volatile organic target compounds (Table 1) were investigated.

Table 1
Target Volatile Organic Compounds

benzene	1,2,4-trimethylbenzene	trichloroethylene
toluene	*m*-dichlorobenzene	tetrachloroethylene
m-xylene	*p*-dichlorobenzene	1,2-dichloroethane
o-xylene	*o*-dichlorobenzene	1,2-dibromoethane
p-xylene	*p*-diethylbenzene	ethylbenzene
1,3,5-trimethylbenzene	1,1,1-trichloroethane	naphthalene

The analytical laboratories involved in the analysis of these samples were required to follow strict quality assurance/quality control (QA/QC) procedures. All analytical procedures had to meet the requirements as stated in a quality assurance project plan (QAPP) which was prepared during the design phase of the investigation. Due to the possible public health concern, the laboratories were required to electronically transmit preliminary analytical results to the QA oversight contractor within 7 calendar days after sample receipt. Complete data packages were submitted by both the two commercial laboratories for rigorous third-party data validation as these data were used as the basis for the risk assessments/remedial decisions.[4,5]

Two commercial laboratories were involved in the analysis of the vapor well sorbent tubes. The sampling schedule was established such that one commercial laboratory would receive samples every other week. Having two laboratories involved in the project allowed flexibility in the scheduling of sampling events. In situations where one laboratory was experiencing difficulties in meeting the analytical schedule, the other laboratory was usually available to meet the project's needs. Additionally, Suffolk County's Department of Health Services Air Pollution Laboratory served as a reference laboratory and provided regulatory oversight for the commercial laboratories involved.

A rather extensive analytical database was maintained for all the sampling events (field and performance) that were conducted for this investigation. The database that was designed allowed the project team to monitor trends in levels of the target compound in various ways. Some of the trends observed over the duration of the sampling events are summarized and discussed in the Results and Discussion Section.

Periodically, performance evaluation (PE) samples were prepared by the Suffolk County laboratory and issued to project laboratories. Known concentrations of target compounds were spiked onto conditioned sorbent tubes and issued to the two commercial laboratories as blind PE samples. The results of these PE samples were issued by the Suffolk County laboratory to the QA oversight contractor and reviewed against the "theoretical" values. A summary of one such round of PE samples is summarized and discussed in the Results and Discussion Section.

Additionally, split sampling events between the Suffolk County laboratory and the commercial laboratories were conducted as an additional measure of performance of the commercial laboratories. These split sampling events involved the collection of simultaneous field samples that were issued to the commercial laboratories as well as Suffolk County's laboratory for analysis. An evaluation of the results of a split sampling event is also discussed in the Results and Discussion Section.

As a way of monitoring the analytical procedure, a surrogate compound, BFB, was added to each sampling tube prior to shipment to the field for use in sampling. The percent recoveries of BFB were reviewed and evaluated to ensure that the analytical technique was properly followed by the laboratories and that problems in the sampling and analysis did not occur (i.e. leaks occurring during the thermal desorption of the samples for GC/MS analysis). A summary and evaluation of typical BFB recoveries observed during the investigation are also discussed in the Results and Discussion Section.

RESULTS AND DISCUSSION

The ongoing monitoring of the vapor wells demonstrated that, in general, the concentrations of the target compounds decreased as a function of time. As shown in Figures 3, 4, and 5, the average concentrations of benzene, toluene, ethylbenzene and xylenes decreased as the number of months in which the wells were monitored increased. The statistics associated BTEX in VW-12 are presented in Table 2. The average concentration of benzene observed in this particular vapor well was 4.0 nl/L over the six years of sampling.

Table 2 - BTEX Statistics in VW-12 over Time

	Benzene	*Toluene*	*m,p-Xylenes*	*o-Xylene*	*Ethylbenzene*
Minimum	0.5	0.5	0.5	0.5	0.5
Maximum	40.7	44.0	4.0	1.7	1.3
Mean	4.0	3.7	1.1	1.0	1.0
Median	1.5	1.5	1.0	1.0	1.0
Std. Dev.	7.8	6.4	0.5	0.2	0.1
Range	40.2	43.5	3.5	1.2	0.8
n	70	70	70	70	70

During the months of June, 1989 through May, 1990, elevated levels of BETX were observed in VW-12 as shown in Figure 4. The statistics associated BTEX during these months in VW-12 are presented in Table 3. The average concentration of benzene observed in this particular vapor well during these months was 10.9 nl/L as opposed to the average concentration of 4.0 nl/L that was observed over the six years of sampling.

Table 3 - Statistics for BETX in VW-12 during June 1989 - June 1990

	Benzene	*Toluene*	*m,p-Xylene*	*o-Xylene*	*Ethylbenzene*
Minimum	1.5	1.5	1.0	1.0	1.0
Maximum	40.7	44.0	4.0	1.7	1.3
Mean	10.9	9.5	1.4	1.1	1.0
Median	6.3	7.3	1.0	1.0	1.0
Std.Dev.	12.7	10.4	0.8	0.2	0.1
Range	39.2	42.5	3.0	0.7	0.3
n	19	19	19	19	19

In general, seasonal trends were not observed as shown in these figures. Also, as shown in Figure 5, occurrences of elevated benzene levels were observed periodically in the latter months of the investigation. These occurrences (when greater than 10 nl/L), were confirmed/negated through the analysis of a split sample by the County's laboratory. If a split sample was not available for analysis, resampling of the monitoring well in question was immediately initiated, and analysis of the resampling event was conducted by the County's laboratory and the other project laboratory that did not report the initial positive results. In all such instances, the vapor well result in question was negated through split sample analysis and/or resampling.

The results of a blind PE sampling event is presented in Figure 6. These PE samples were prepared by the Suffolk County laboratory and issued as PE samples (single blind) to one of the project laboratories. The commercial laboratory results were in agreement with both the theoretical concentration and county laboratory's concentration for every compound of interest with the exception of *o*-dichlorobenzene and naphthalene. These two compounds were observed at elevated concentrations by the commercial laboratory. Additional PE samples were provided to the commercial laboratory, since these two compounds did not fall within the acceptance range (0% - 30% difference - acceptable, 31% - 50% - borderline acceptable, and > 51% not acceptable) around the theoretical concentration. The analysis of these additional PE samples by the commercial laboratory was acceptable.

The results of split sampling events for VW-1, VW-8 and VW-104 are presented in Figures 7, 8 and 9, respectively. In general, the commercial laboratories compared well to each other and to the regulatory laboratory. Variations in specific compound concentrations were observed in some PE/split sampling events; however, these instances were usually corrected through additional sampling and analysis or routine laboratory maintenance and/or corrective actions.

The surrogate compound, BFB, was used to monitor the analytical technique. The percent recoveries of BFB, from the analytical laboratories, were reviewed and evaluated to ensure that the analysis of project samples was in control. This surrogate compound ensured that problems in the sampling and analysis did not occur (i.e. leaks occurring during the thermal desorption of the samples for GC/MS analysis). Typical BFB recoveries that were observed for this project are presented in Figure 10 and a statistical interpretation of these recoveries is presented in Table 4.

Table 4 - Statistics for BFB Percent Recoveries

	BFB
Minimum	60
Maximum	137
Mean	103
Median	101
Std. Dev.	19
Range	77
n	34

CONCLUSIONS

Overall, the vapor well monitoring program that was instituted for this project performed very well. The design of the program was such that the monitoring wells were accessible to the field sampling team at any time and the homeowners' daily routines were not disrupted due to sampling events.

Concentrations of the analytes of concern were monitored on a timely basis. During the life of the project, over 9500 vapor monitoring wells were sampled and analyzed. Approximately 2.0% of these vapor wells contained benzene above the 10 nl/L action level. Also, approximately 7.4% of the vapor monitoring wells tested had on some occasion exhibited benzene at a level greater than the laboratory's analytical detection limit.

As demonstrated in Figures 3, 4 and 5, BTEX concentrations decreased over time and seasonal variations in vapor well concentrations were not observed. This demonstrated and well-documented decrease in vapor concentration has led to a revised monitoring schedule in which vapor well are now sampled and analyzed on a quarterly basis instead of the weekly basis that was initially instituted for this project.

Performance Evaluation samples and split samples were used to assess project laboratory performance. As seen in Figures 6 through 9, laboratory performance on PE samples as well as split samples, were, in general, acceptable. Variations in specific compound concentrations were observed in some PE/split sampling events; however, these instances were usually corrected through additional sampling and analysis or routine laboratory maintenance and/or corrective actions.

Finally, the QC measures that were instituted for this soil vapor well monitoring program were effective in monitoring the quality of the data that was used as a basis for risk assessment/remedial decisions. The surrogate compound, BFB was effective in monitoring the laboratory analysis conditions. Recoveries of this compound outside a 50 - 150% window usually provided indication that either (1)the laboratory incorrectly spiked the sorbent tubes before they were issued to the field sampling team or (2) a leak occurred during the analytical process and analytes were lost. As seen in Figure 10, BFB recoveries throughout the investigation were typically within the 50 - 150% recovery window.

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Average Monthly BTEX Concentration (nl/L) for VW-12
Concentration (nl/L)
0
5
10
15
20
25
30
35
40
45
See Blown -up Area
Feb-88
Mar-88
May-88
Jun-88
Jul-88
Aug-88
Sep-88
Feb-89
Mar-89
Apr-89
May-89
Jun-89
Jul-89
Aug-89
Sep-89
Oct-89
Nov-89
Dec-89
Jan-90
Feb-90
Mar-90
Apr-90
May-90
Jun-90
Jul-90
Aug-90
Sep-90
Oct-90
Nov-90
Dec-90
Jan-91
Feb-91
Mar-91
Apr-91
May-91
Jun-91
Jul-91
Aug-91
Sep-91
Oct-91
Nov-91
Dec-91
Jan-92
Feb-92
Mar-92
Apr-92
May-92
Jun-92
Jul-92
Aug-92
Sep-92
Oct-92
Nov-92
Dec-92
Jan-93
Feb-93
Mar-93
Apr-93
May-93
Jun-93
Jul-93
Aug-93
Sep-93
Oct-93
Nov-93
Dec-93
Jan-94
Feb-94
Mar-94
Apr-94
Month
Benzene
Toluene
m,p-Xylene
o-Xylene
Ethylbenzene

FIGURE 3

FIGURE 4

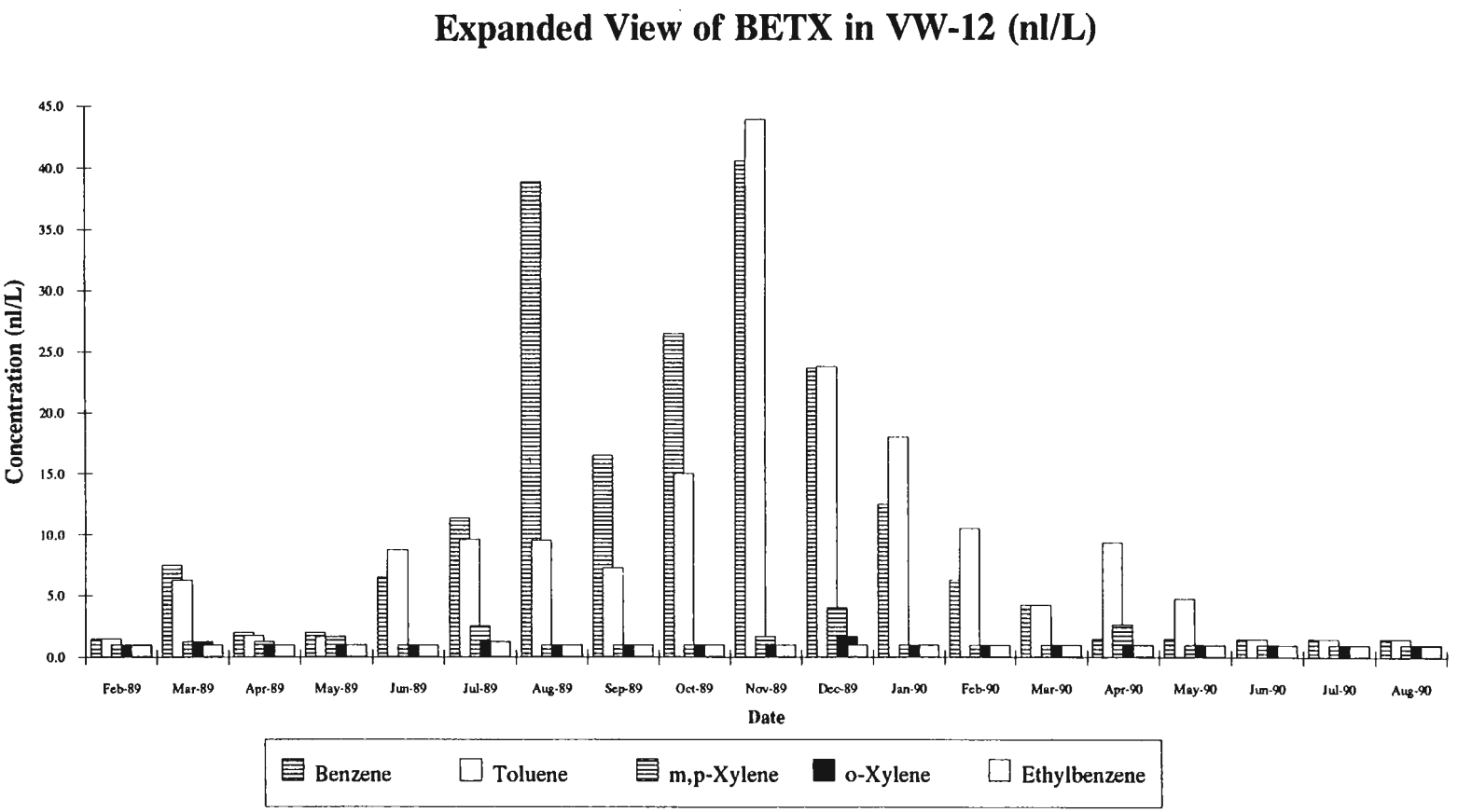

Expanded View of BETX in VW-12 (nl/L)
Concentration (nl/L)
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Feb-89
Mar-89
Apr-89
May-89
Jun-89
Jul-89
Aug-89
Sep-89
Oct-89
Nov-89
Dec-89
Jan-90
Feb-90
Mar-90
Apr-90
May-90
Jun-90
Jul-90
Aug-90
Date
Benzene
Toluene
m,p-Xylene
o-Xylene
Ethylbenzene

FIGURE 5

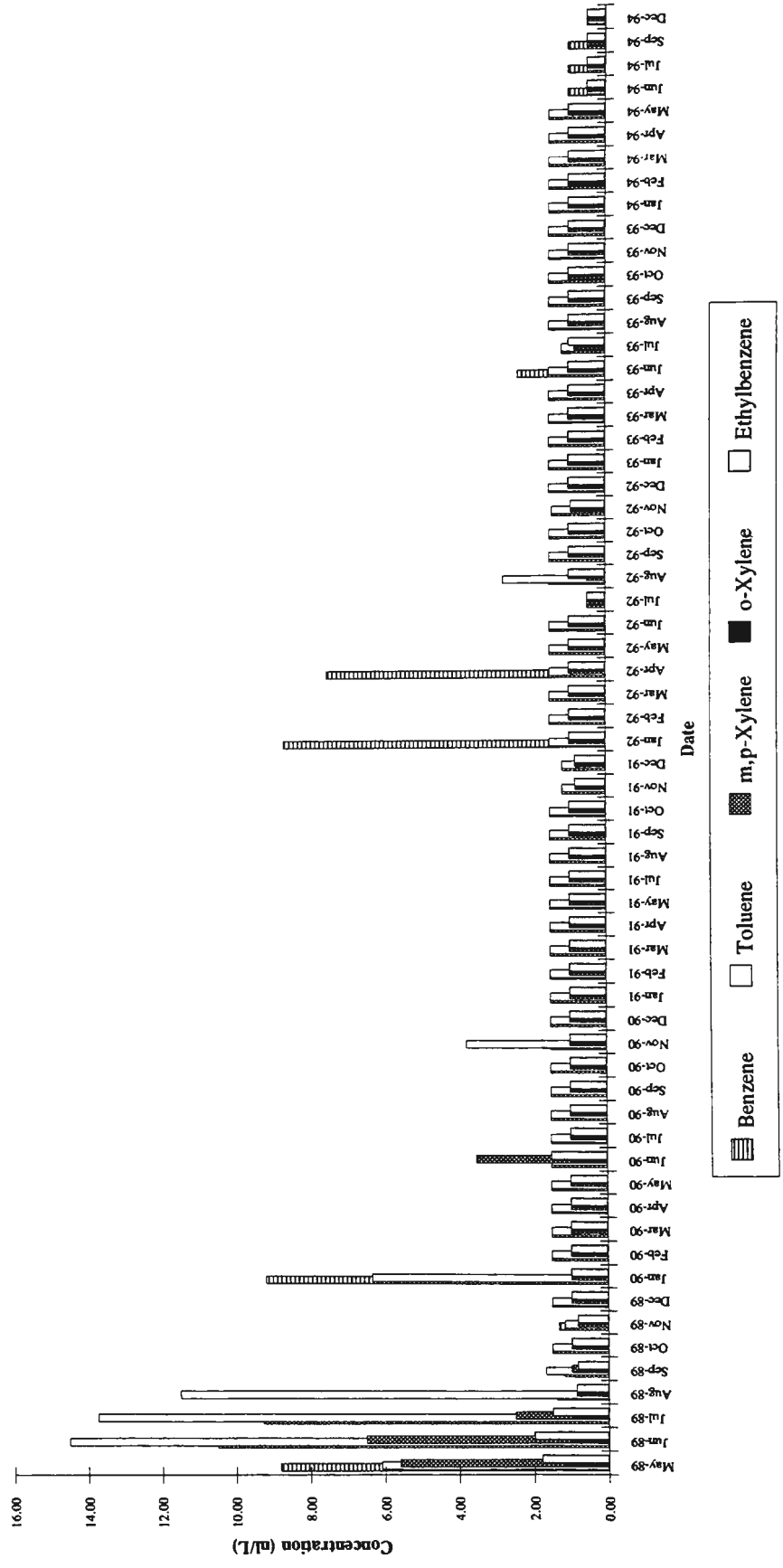

Average Monthly BTEX Concentration (nl/L) for VW-99
Concentration (nl/L)
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
Date
May-89
Jun-89
Jul-89
Aug-89
Sep-89
Oct-89
Nov-89
Dec-89
Jan-90
Feb-90
Mar-90
Apr-90
May-90
Jun-90
Jul-90
Aug-90
Sep-90
Oct-90
Nov-90
Dec-90
Jan-91
Feb-91
Mar-91
Apr-91
May-91
Jul-91
Aug-91
Sep-91
Oct-91
Nov-91
Dec-91
Jan-92
Feb-92
Mar-92
Apr-92
May-92
Jun-92
Jul-92
Aug-92
Sep-92
Oct-92
Nov-92
Dec-92
Jan-93
Feb-93
Mar-93
Apr-93
Jun-93
Jul-93
Aug-93
Sep-93
Oct-93
Nov-93
Dec-93
Jan-94
Feb-94
Mar-94
Apr-94
May-94
Jun-94
Jul-94
Sep-94
Dec-94
Benzene
Toluene
m,p-Xylene
o-Xylene
Ethylbenzene

FIGURE 6

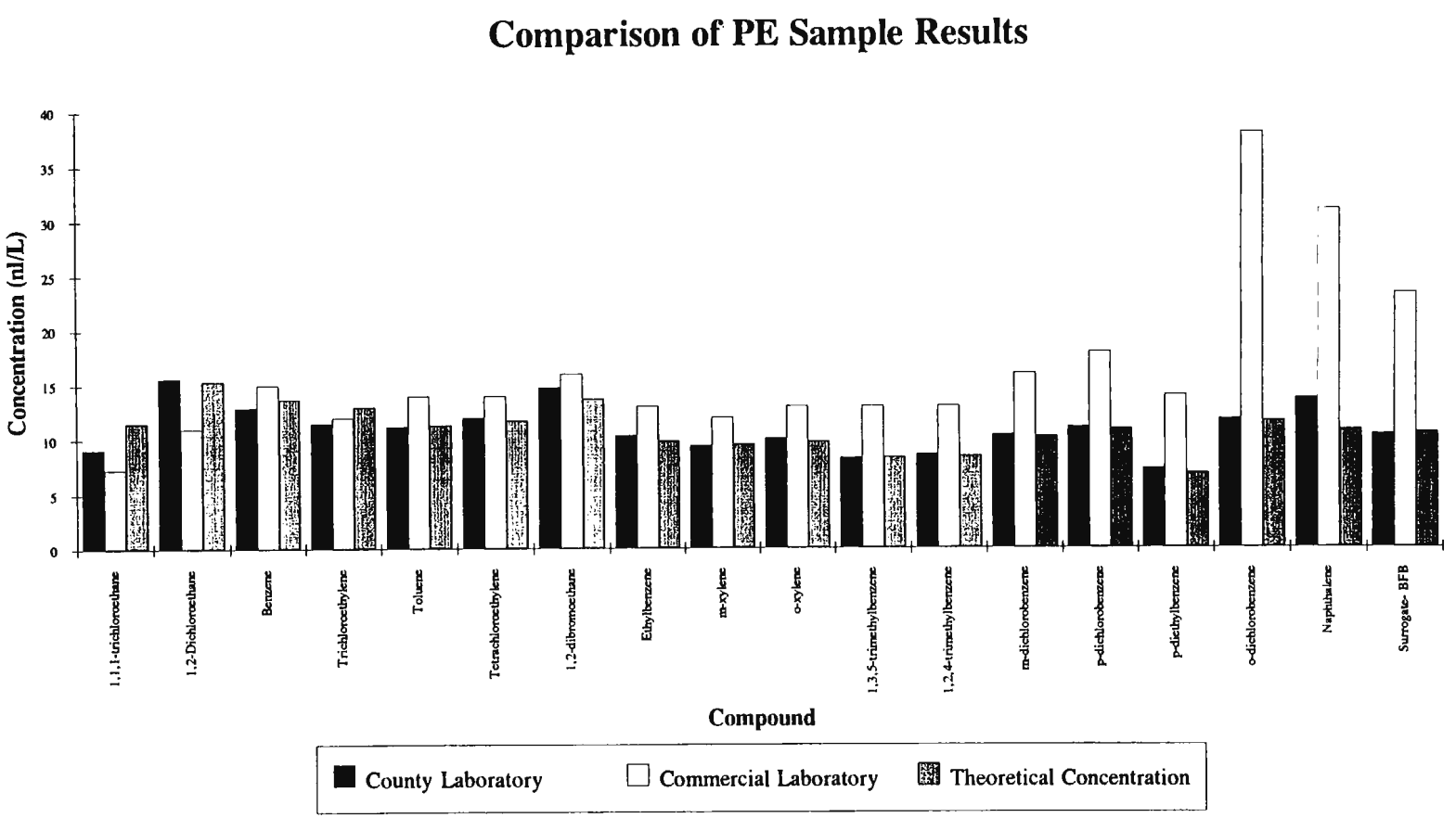

Comparison of PE Sample Results
Concentration (nl/L)
0
5
10
15
20
25
30
35
40
1,1,1-trichloroethane
1,2-Dichloroethane
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene
1,2-dibromoethane
Ethylbenzene
m-xylene
o-xylene
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene
p-dichlorobenzene
p-diethylbenzene
o-dichlorobenzene
Naphthalene
Surrogate- BFB
Compound
County Laboratory
Commercial Laboratory
Theoretical Concentration

FIGURE 7

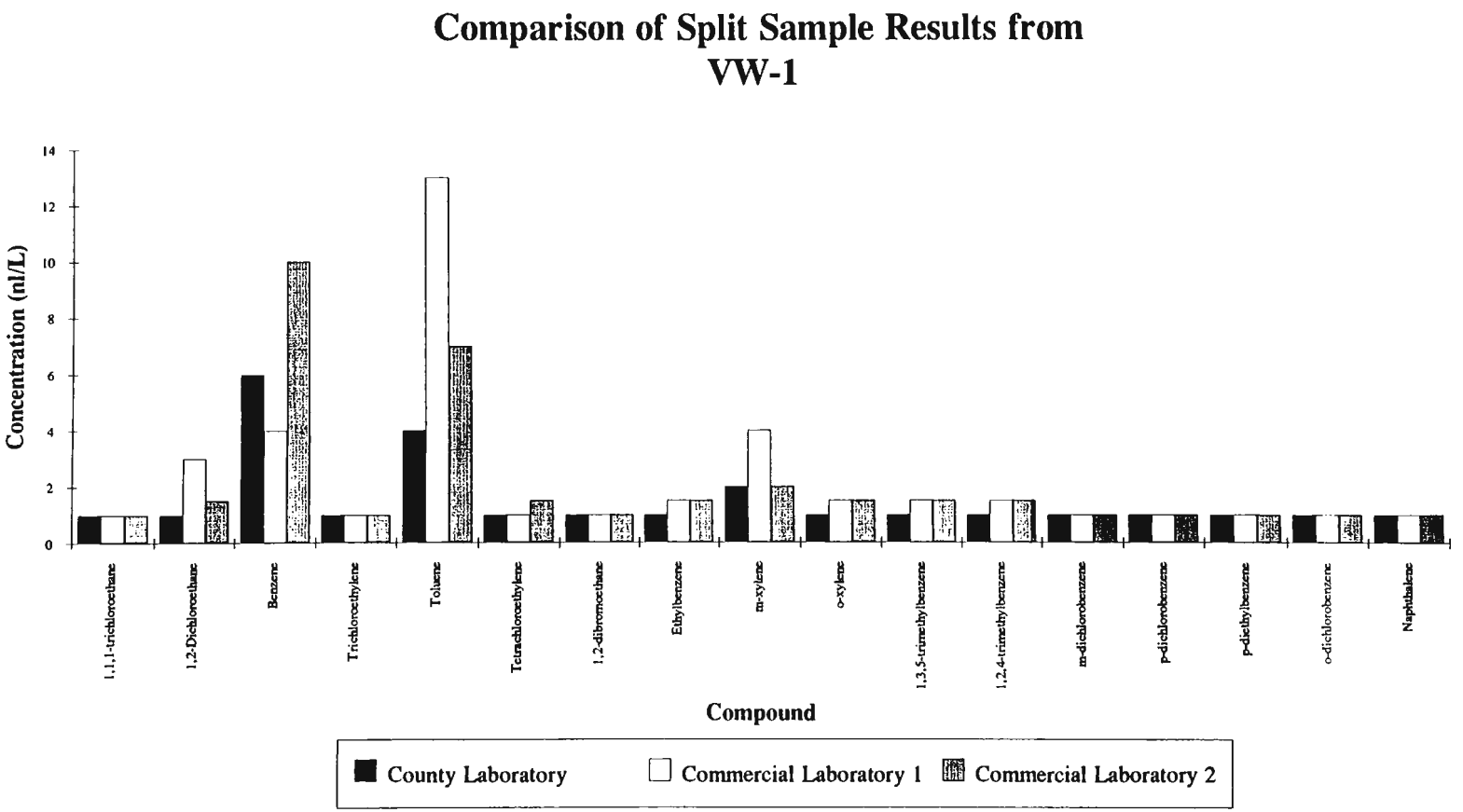

Comparison of Split Sample Results from VW-1
Concentration (nl/L)
0
2
4
6
8
10
12
14
1,1,1-trichloroethane
1,2-Dichloroethane
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene
1,2-dibromoethane
Ethylbenzene
m-xylene
o-xylene
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene
p-dichlorobenzene
p-diethylbenzene
o-dichlorobenzene
Naphthalene
Compound
County Laboratory
Commercial Laboratory 1
Commercial Laboratory 2

FIGURE 8

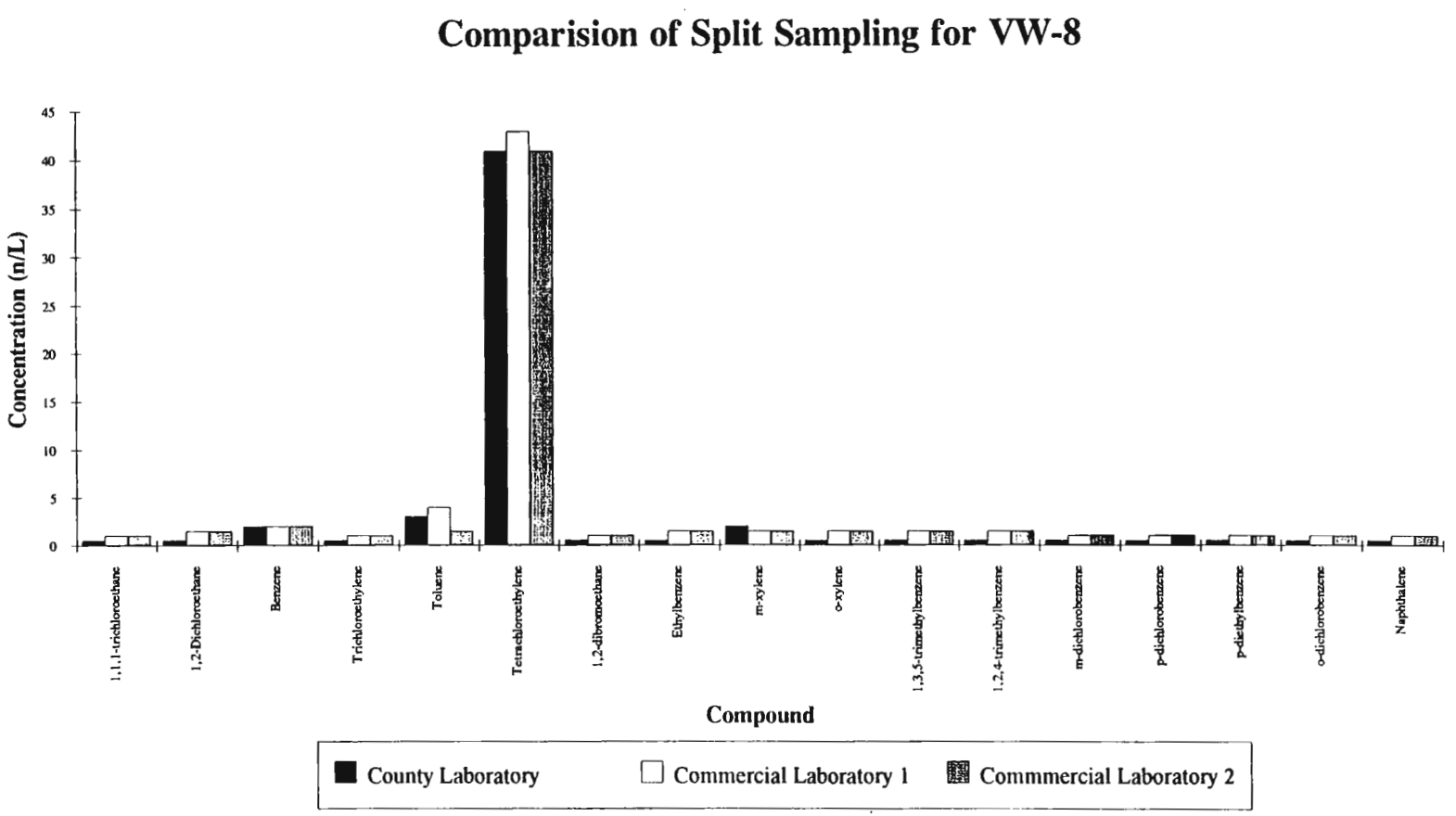

Comparision of Split Sampling for VW-8
Concentration (n/L)
45
40
35
30
25
20
15
10
5
0
1,1,1-trichloroethane
1,2-Dichloroethane
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene
1,2-dibromoethane
Ethylbenzene
m-xylene
o-xylene
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene
p-dichlorobenzene
p-diethylbenzene
o-dichlorobenzene
Naphthalene
Compound
County Laboratory
Commercial Laboratory 1
Commmercial Laboratory 2

FIGURE 9

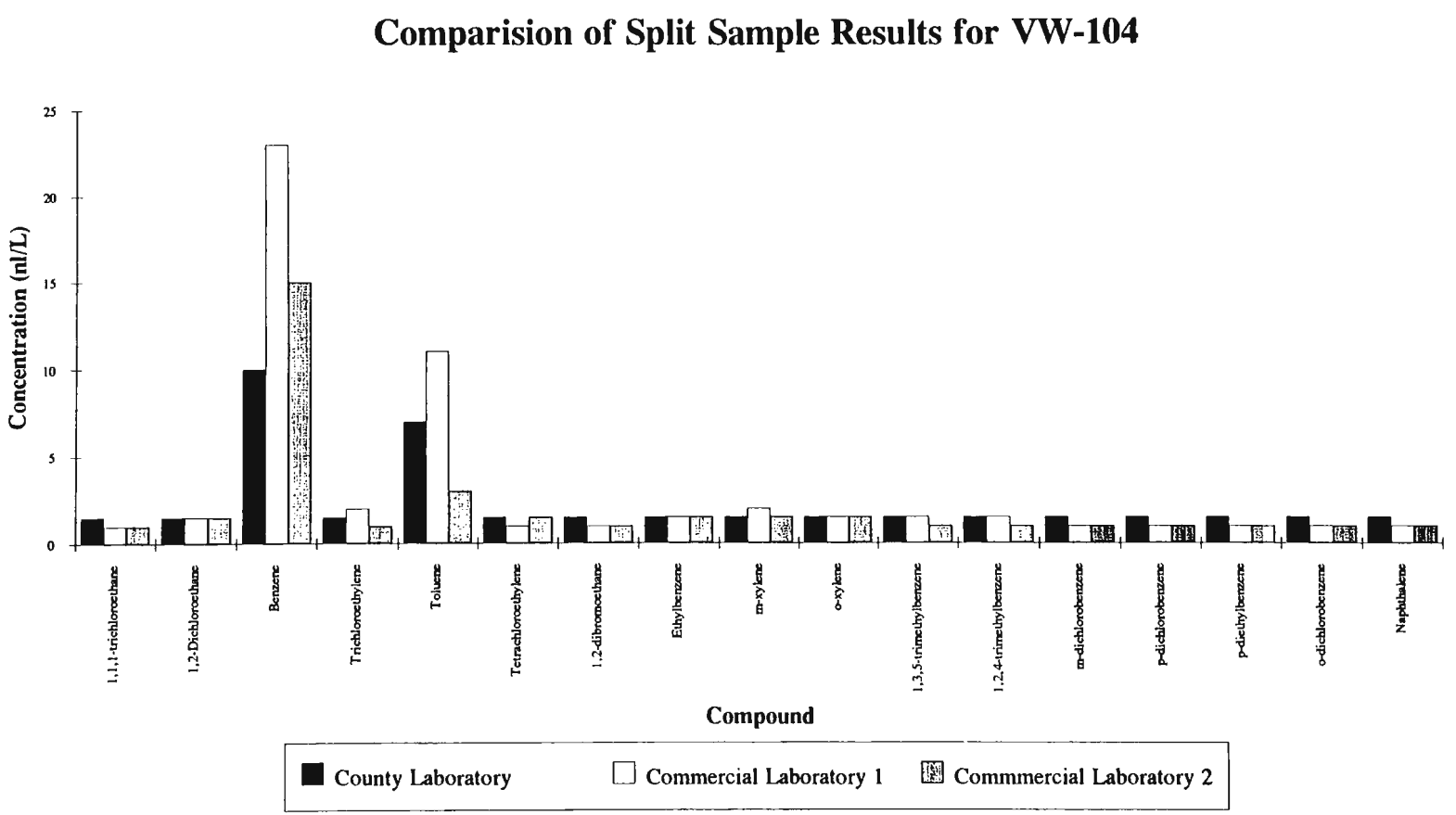
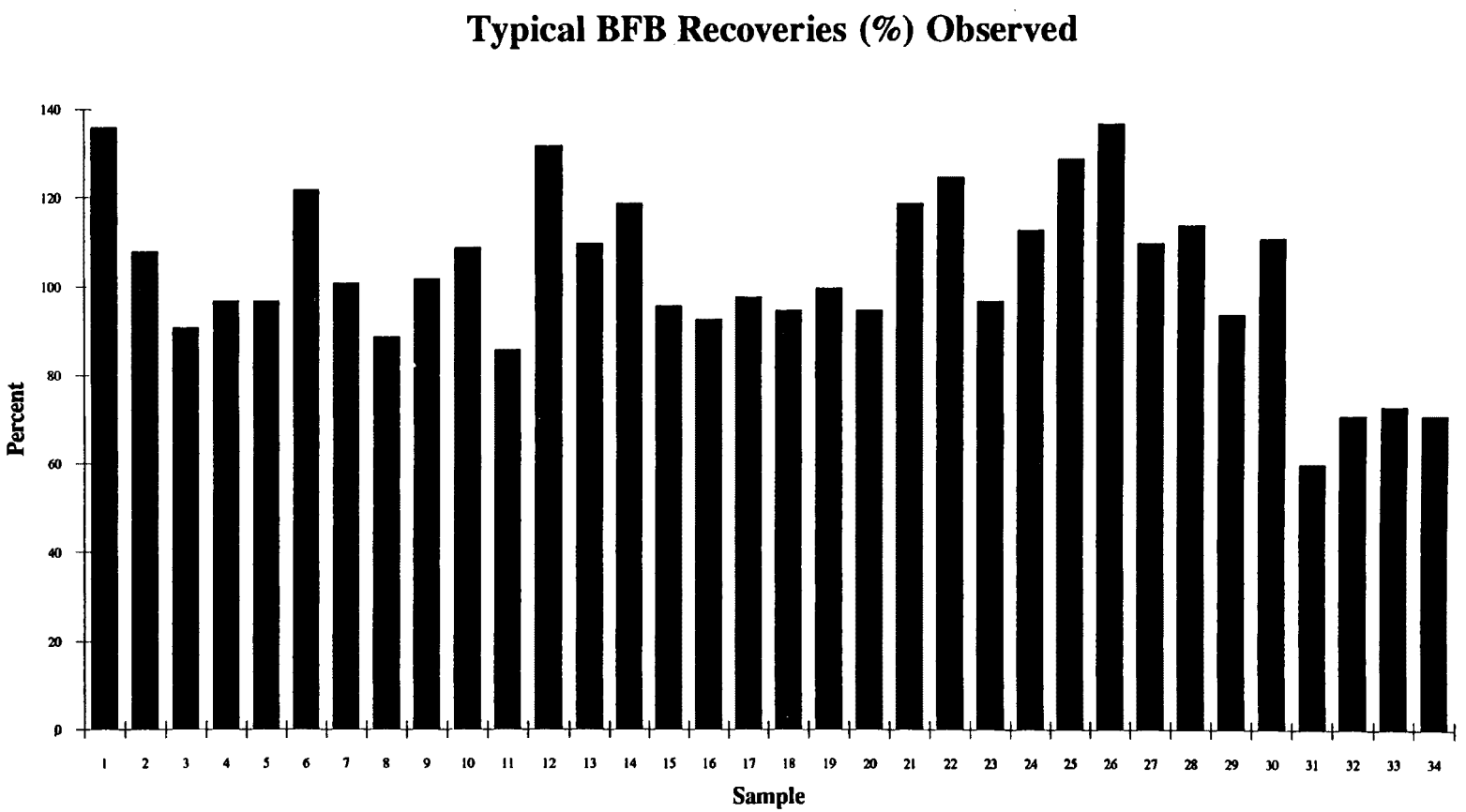

Comparision of Split Sample Results for VW-104
Concentration (nl/L)
25
20
15
10
5
0
1,1,1-trichloroethane
1,2-Dichloroethane
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene
1,2-dibromoethane
Ethylbenzene
m-xylene
o-xylene
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene
p-dichlorobenzene
p-diethylbenzene
o-dichlorobenzene
Naphthalene
Compound
County Laboratory
Commercial Laboratory 1
Commmercial Laboratory 2

FIGURE 10


Typical BFB Recoveries (%) Observed
Percent
0
20
40
60
80
100
120
140
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
Sample

General

68

CHARACTERIZING HAZARDOUS WASTES: REGULATORY SCIENCE OR AMBIGUITY?

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ABSTRACT

Proper waste characterization is one of the cornerstones of the RCRA program and its regulations. A waste generator needs to determine if his waste is hazardous or not. All future actions and liabilities regarding the waste flow from that initial determination. The costs of making an incorrect determination can be staggering in terms of potential waste clean up costs and possible civil or even criminal penalties.

Waste characterization should be based on good science and not be ambiguous. It should be a straight forward, simple and objective process. Unfortunately, it is not. Too much of the process is subjective. Even where objective tests are possible, parts of the tests are poorly defined and lead to confusion by the regulated public and the testing laboratories. These poorly defined aspects or "gray areas" need clarification from EPA. This paper will identify a number of problems with the waste characterization methods and regulations, and will suggest possible steps that the waste generator can take to reduce his liability until EPA takes some of the guess work out of this important process. Until then, all waste generators need to be aware of these potential problems so that they can take steps to minimize their liability.

INTRODUCTION

Proper classification of a waste material is extremely important for the waste generator. The waste generator needs to know if his waste is hazardous or not. Classification of a waste as hazardous or non-hazardous is the initial step determining which road the generator must follow in the handling, labeling, transportation and disposal of that waste. This difference can mean savings of thousands, even millions of dollars to the generator, and can substantially impact the generators long term liability. The penalty for not properly characterizing a waste can be huge. It includes increased costs for handling, treatment or disposal of the waste, plus the potential liability that may arise from clean up costs at a Superfund site, or it may arise from civil or even criminal sanctions from the regulators.

Generators are always responsible for their wastes, but the requirements under Subtitle D (for non-hazardous wastes) are substantially less than those under Subtitle C (for hazardous wastes). In addition, liability from mishandling hazardous wastes is much greater than for non-hazardous wastes. Furthermore, the public's interest and concern are much greater for hazardous wastes than for non-hazardous wastes.

EPA attempted to minimize confusion when they devised the RCRA regulations and promulgated the waste classification rules in 1980. These rules stated that wastes were only considered hazardous if they were "listed," or if they failed to pass any of four "characteristic tests". A waste was either on the list or it wasn't. It either passed the characteristic test, or it failed . This approach looked to be very objective, and to many, it was very black or white. Unfortunately as more wastes have been subjected to these rules,

it has become evident that these rules are not clear or objective. Instead, they contain a great deal of "gray."

Since 1980, EPA has attempted to deal with some of the gray, by adding notes or memos to the RCRA Docket, redescribing what they really meant on the RCRA Hot Line, and in a few cases, officially clarifying specific parts of the regulations through the normal rule making process. Unfortunately, there are still many issues to be dealt with, and EPA has put most of these aside due to budgetary constraints.

A federal judge recently described the regulations that relate to waste characterization as, ..."a sea of ambiguity."[1] This judge later vacated his preliminary finding[2] when the plaintiff abandoned its theory and dismissed the case, but the comment still seems appropriate.

Here, we define a "gray area" as a part of the regulations or test methods that are unclear or ambiguous. The characteristic regulations are described in Part 40 of the Code of Federal Regulations (CFR), Section 261.2. We can identify "gray areas" in each part of these regulations.

REPRESENTATIVE SAMPLES

Wastes are are often complex mixtures of chemicals and other materials. Physically and chemically they can be difficult to work with. Often they are very difficult to accurately analyze or characterize. The first part of the process requires that we obtain a sample of the waste for analysis, and here is where we encounter our first gray area.

The regulations require that we test a "representative sample" of the waste. This is defined in 40 CFR, Section 260.10 as, "A *representative sample* means a sample of a universe or whole (e.g., waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole."

This definition has two distinct problems. First, we do not know how much waste constitutes the "universe or whole," and second, we do not know how to determine the "average" properties.

We do know that wastes are almost never homogeneous. Essentially, all wastes are mixtures that are heterogeneous or even extremely heterogeneous. As a result, the average property is likely to be different for different amounts of the waste. The average for a scoop of the waste will be different from a drum, or a pile or a day's production of the waste. The average for the top of a pile may well be different from that at the bottom of the pile. Without knowing the size of the universe, we can not make accurate comparisons between samples or against a regulatory standard.

The waste characteristics measure attributes of a waste. These attributes are not additive, and therefore, they can not be averaged. For example, a waste that flashes at 20°C is no more hazardous than a waste that flashes at 50°C. The average is not a waste that flashes at 35°C. The Ignitability test results in a yes or no answer. How do we average yes and no? Is the average a maybe?

Another example is Corrosivity which is determined from the pH of a sample. However, pH is a logarithmic property which technically can not be averaged. Multiple factors effect the pH or flash point or leaching potential of a waste. These factors vary to differing degrees through out a heterogeneous waste, and therefore they influence the attribute to differing degrees. This assures that the values will not be additive nor averagable.

Another consequence of the concept of average property is the fact that "average" represents a range of actual values. If the average value is near the regulatory limit, then some of the actual values are likely to be above the regulatory limit. Technically, half of the actual values can be above the regulatory limit and the average will still not exceed the limit. If we can expand or contract our universe to include more values above the limit, then we definitely have a violation. If we can expand or contract the universe to include more values below the limit, then we do not have a violation.

Unreliable results are often obtained because there is not a clear understanding of what constitutes a representative sample or detailed guidance has not been given on how to properly sample and subsample a waste. Sometimes, efforts made in the field to collect a representative sample are defeated in the laboratory when proper guidance is not given. For example, some laboratory personnel have been known to scoop a subsample for testing only from the top of the container. The resulting values may be high, low or even non-detect, but they are not likely to be representative of the entire sample in the container. Other laboratory personnel selectively remove rocks or other material from the subsample and then do not correct their result for this change. This situation will lead to erroneously high values. Both situations illustrate the importance of double checking a laboratory's results. Waste generators need to be aware of these potential problems. When their waste appears to be near the regulatory limit, it can be especially important to them to have a third party assure that these types of errors are not being made.

There are also a number of "gray areas" in the individual characteristic tests and regulations and we will highlight a few.

CHARACTERISTIC OF IGNITABILITY

The only test for ignitability applies only to liquids. However, liquid is not defined and is subject to misinterpretation especially as to how it relates to sludges, semi-solids, semi-liquids, free liquids, etc. In addition, aqueous solutions containing less than 24 percent alcohol by volume are excluded. Aqueous solutions and alcohol are not defined. The regulation writers sought to exclude alcoholic beverages, but there are many ways to describe an aqueous solution and there are many different alcohols besides ethanol.

When the waste is not a liquid, there are no tests prescribed; only subjective descriptions that are open to misinterpretation. For example, an ignitable solid is described as burning so "vigorously and persistently that it creates a hazard." This can encompass a wide variety of situations, and the degree of hazard will depend upon where the waste is burned.

CHARACTERISTIC OF CORROSIVITY

Again we encounter the term "aqueous" without a clear definition. pH was chosen as the indicator of corrosivity, but pH can only be accurately measured in dilute aqueous

solutions. Suspended solids, oils and water soluble organics all interfere with the test. Solids were excluded from this classification, but what about pastes, semi-solids, semi-liquids, etc. Do we consider only free liquids or not?

EPA recently clarified one important part of this characteristic[3], and that is the explicit requirement to measure the pH at 25 ± 1° C when the pH is greater than 12.0. This clarification was necessary because pH is very sensitive to temperature changes at the high end of the pH scale, and widely differing values are obtained unless the temperature is controlled. EPA should be commended for clarifying this issue which could have had a negative impact on thousands of users of lime and other highly alkaline materials throughout the country.

CHARACTERISTIC OF REACTIVITY

For the most part, the characteristic of reactivity is the classic example of subjective regulations. Of eight different properties, only one has an objective test associated with it, and even that test has problems. The problems with measuring Reactive Cyanide and Sulfide have been described elsewhere.[4] The measurement problems also reflect on the theoretical basis for the recommended guidelines for cyanide and sulfide. It is important to note that the guidelines of 250 mg/kg for cyanide and 500 mg/kg for sulfide have never been formally adopted through the rule making process and are still subject to challenge.

In all fairness, developing reliable, objective tests for reactive wastes is not an easy task. EPA has made some efforts to develop a few more objective tests, but this work has been put aside due to budgetary constraints. However, more work needs to be done in this area, and EPA should address the issue of characterizing a waste that results from a mixture of a small amount of "reactive " material with a large amount of non-reactive material. Where does one draw the line?

CHARACTERISTIC OF TOXICITY

This characteristic does in fact have an objective test called the toxicity characteristic leaching procedure or TCLP. It should be kept in mind that the values obtained from the TCLP are not inherent properties of the waste, but are instead, attributes. Consequently, the amount extracted is dependent upon the conditions of extraction. If two laboratories do not provide exactly the same conditions or use exactly the same procedure, then their results will differ. The TCLP is a lengthy procedure with numerous opportunities for error. Again, waste generators need to be aware of these potential problems. When their waste appears to be near the regulatory limit, it can be especially important to them to have a third party assure that errors are not being made.

SUMMARY

As we discussed earlier, wastes by their very nature are often complex mixtures of various materials. Physically and chemically they are difficult to work with and difficult to accurately characterize. The current regulations are flawed, and better guidance is needed from EPA on both sampling and analysis. Guidance on how to deal with the situation where representative sampling is not possible or where the characteristic tests do not work for one reason or another would also be helpful.

Until additional guidance is forthcoming, the waste generator needs to be alerted to the "gray areas" in these regulations. When in doubt or especially when the results appear to be close to the regulatory limit, the generator should get a third party opinion. When these "gray areas" are encountered, the generator should consider challenging the classification of a waste. Such challenges will encourage the adoption of better science and less ambiguity in these important regulations.

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THE MISUSE OF THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

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ABSTRACT

The Toxicity Characteristic Leaching Procedure (TCLP) was developed to estimate the mobility of certain organic and inorganic contaminants in a municipal landfill and to determine if these wastes should be classified as "hazardous". However, many regulators, environmental consultants, and industry environmental managers are inappropriately applying the TCLP to determine potential leaching to groundwater of a variety of contaminants in soils and sediments at a variety of non-landfill sites. The TCLP is misused in two ways: it is applied to incompatible chemistries (*e.g.*, performing TCLP to determine cyanide leaching from soil) and it is used for incompatible site scenarios (*e.g.*, using TCLP to determine leaching of contaminants at sites that are not equivalent to the municipal landfill model). The effect of misusing the TCLP is that regulators and decision makers will misinterpret results, and incorrectly predict the potential for impact to groundwater of the contaminants. The TCLP is a test that should be limited to determining if a waste should be considered a RCRA-regulated waste. For other settings, such as at Superfund and state-lead sites, alternatives to using the TCLP in the determination of potential impact to groundwater, such as mathematical models to estimate mobility using site-specific parameters, are also discussed.

INTRODUCTION

Under Subtitle C of the Resource Conservation and Recovery Act (RCRA), hazardous wastes are evaluated using four characteristics: corrosivity, ignitability, reactivity, and leaching potential. The Toxicity Characteristic Leaching Procedure (TCLP) was developed to test the leaching potential of toxic constituents in a municipal landfill under specific landfill conditions. The TCLP Final Rule (Hazardous Waste Management System: Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions, *Federal Register*, Vol. 55, No. 61, March 29, 1990) lists the 39 compounds that are regulated based on the TCLP test. Method 1311 in *SW846* (July 1992) is the EPA-approved TCLP method. The TCLP thereby replaced the Extraction Procedure (EPTOX) leach test formerly required under RCRA.

The TCLP was designed to simulate leaching of an industrial waste dumped in a municipal (sanitary) landfill, therefore, acetic acid was chosen as the extraction fluid because it is a major component of typical municipal landfill leachates. However, the TCLP scenario may not be applicable to contaminated soils at sites that do not fit the

municipal landfill scenario. At such sites, organic acids may not be present, and therefore, leaching tests that use organic acids may selectively solubilize certain compounds or elements from the contaminated soil (in the laboratory TCLP test) whereas this would not occur in the environment. Elements such as lead are especially susceptible to incorrect classifications in contaminated soils where mobility using a TCLP test would classify the soil as a hazardous waste but the environmental site conditions would not be conducive to leaching.

The dilution and attenuation factors (DAFs) developed for organic compounds under the TCLP scenario were based on a database of municipal landfills. The equations used to determine the compound-specific DAFs simulate the transport and attenuation of contaminants as they travel through a landfill, to the underlying groundwater, and then to a drinking water well exposure point. Unlike the organic TCLP constituents, the inorganic regulatory limits for TCLP metals are not derived from DAFs modeled for a municipal landfill scenario. Regulatory levels for metals were set as ten times the Drinking Water Standards, rather than a subsurface fate and transport model to calculate constituent-specific DAFs. Therefore, exceedances of TCLP leachate results for metals, especially for non-landfill sites, must be interpreted with caution since no fate and transport related process were considered for the development of the regulatory levels.

The TCLP has been used incorrectly by regulators to evaluate potential impact on groundwater due to leaching from contaminated soils for a number of years. A Leachability Subcommittee established by EPA's Science Advisory Board (SAB) acknowledged some of the problems with the test and stated that in most cases of inappropriate use, "the justification given was that it is necessary to cite standard and approved methods." This paper discusses examples of the inappropriate use of the TCLP, in terms of incompatible chemistries and sites. It also recommends the use of an alternate leachate test, Synthetic Precipitation Leaching Procedure (SPLP), and site-specific modeling.

INCOMPATIBLE CHEMISTRIES

The TCLP was developed to assess potential groundwater contamination for a specific set of environmental contaminants including 8 metals, 11 volatile organic compounds (VOCs), 12 semivolatile organic compounds (SVOCs), 6 pesticides, and 2 herbicides. Extensive research and method development studies were performed during the development of the TCLP procedure for these specific compounds and analytes. Use of the TCLP for some chemicals that were not included in the method development or in the final TCLP rule constitutes "misuse", and may not provide technically valid results.

An example of the inappropriate use of TCLP by a regulatory agency because the method is incompatible with the chemistry of the analytes of concern is discussed below. The Record of Decision (ROD) for a site in New York (1) where cyanide and fluoride were to be analyzed on soils beneath excavated material, required the use of a TCLP leachate test and cleanup goals were to be set based on these TCLP results. In this example, the ROD required the TCLP procedure to be modified such that the pH of the extraction

fluid was adjusted to background overburden groundwater pH conditions. There are several potential problems with analyzing cyanide in a TCLP leachate. In addition, no method study was undertaken to validate the TCLP method for cyanide and fluoride.

Cyanide exists in the environment in many forms that have different mobility, stability, and toxicity. Most environmental regulations require the analysis of "total cyanide" as a measure of the potential impact of cyanides as a health threat at contaminated sites. This is a very conservative approach, as "total cyanide" refers to all cyanide compounds that can be classified as simple or complex. The simple cyanide compounds dissociate easily under acidic conditions and are present in aqueous solutions as HCN and CN^-, which are the most toxic forms of cyanide in water and in the air. Some complex cyanides, such as the iron-cyanide complexes, are very stable in soils and are not toxic due to their extremely low human bioavailability (2). Simple cyanides exist most typically in aqueous solutions as HCN rather than CN^- because the pH of most natural waters is lower than the pK_a of molecular HCN.

In order to maintain the integrity of the sample from the time of sampling to the time of analysis, and prevent loss of the simple cyanides, aqueous samples are preserved with sodium hydroxide (NaOH), which increases the pH and also converts the HCN (which is easily lost to the atmosphere) to CN^-. During the TCLP extraction procedure, the pH is maintained in an acetic acid buffer solution at 4.93. This acidic pH releases any cyanide that was not tightly bound (simple cyanide complexes) in the soil sample. The TCLP extract is maintained in this acidic buffer until the time of analysis. Without method development to determine the accuracy of cyanide recovery, or techniques to minimize the loss of cyanide during the laboratory testing, the TCLP extraction method should not be used for determination of cyanide because the most toxic forms of cyanide are lost during the procedure. At best, the TCLP is expected to produce cyanide results that are biased low; at worst, the TCLP results in false negative results for cyanide in the leachate.

An alternative procedure to assess the potential leaching of cyanides to groundwater is the SPLP. The SPLP, Method 1312 (September 1994), is a leach test that uses an extraction fluid modeled after the pH of the precipitation in the region of the US where the soil is located. The SPLP does not use acetic acid. Instead, it uses an unbuffered extraction fluid of sulfuric and nitric acids (Extraction Fluids #1 and #2). However, the SPLP procedure also allows for a deionized water leach, in place of the acidic extraction fluid, to determine cyanide and volatiles leachability (Extraction Fluid #3). A deionized water extraction fluid provides more technically sound results for cyanide in the leachate because the simple cyanides are not lost upon introduction to the extraction fluid. Further, if it is important to obtain a laboratory test result for the potential of cyanide leaching from contaminated soils in an acidic environment, a zero headspace extractor, similar to that used for the determination of VOCs, may be used to prevent the loss of the volatile cyanide species in reaction with the acidic extraction fluid. Method development and validation would need to be undertaken to verify that this is a viable alternative.

As another example, the use of TCLP at sites in which organic acids are not the dominant leachate form can result in an incorrect classification of a soil as "hazardous" due to the reaction of the contaminant in question with the acetic acid extraction fluid of the TCLP. Lead is a prime example of this phenomenon. In an interlaboratory comparison study, conducted in 1988 by RTI for OSW (3), the TCLP Method 1311 consistently leached more lead from soil than the SPLP method. Results from the study showed that for soil samples with total lead concentrations ranging from 2000 to 30,000 mg/Kg, the TCLP leached lead at levels ranging from 2.0 to 375 mg/L whereas the SPLP leachates contained lead ranging from nondetect values (detection limit was 0.1 mg/L) to 19 mg/L (3). These are significant differences in the leachate potential based upon the chemical reaction of the extraction fluid with the site soils.

INCOMPATIBLE SITES

In addition to the analytical chemistry related issues with the TCLP discussed above, another major problem with the TCLP is how these results are being used by regulators at hazardous waste sites. At a number of sites (under non-landfill conditions) across the nation, TCLP test results have been used by regulators as a measure of potential for impact to groundwater with little or no consideration given to site-specific conditions. This has led to remediation of soils (in most cases, excavation and off-site disposal) that exceed the TCLP standard, even though in a number of cases these soils did not pose a threat to human health or the environment. The following example illustrates this problem.

At the South Cavalcade Superfund site in Houston, a former wood-preserving and coal-tar distillation facility, the selected remedy required excavation and treatment of all soils that either: 1) exceeded the risk-based cleanup goal or 2) exceeded the regulatory TCLP levels (leaching-based cleanup goal) (4). The primary contaminants of concern at the site included benzene, 3- to 5-ring polycyclic aromatic hydrocarbons (PAHs), and metals – arsenic, chromium, and lead. Benzene degrades very rapidly in the environment and the large ring PAHs and lead bind readily to any organic material present in soils. As a result, benzene concentrations in the leachate might be degraded to acceptable levels by the time the leachate reaches the water table, and the PAH compounds and lead may not reach the water table in a reasonable time frame (travel time could be on the order of a few hundred to thousand of years, depending on the distance to the water table), hence having no impact on the groundwater. Thus, the use of the leaching-based cleanup standard at this site cannot be justified because exceedance of the TCLP regulatory level in a vadose zone soil sample does not necessarily mean that groundwater will be impacted. Further, basing remedy decisions on exceedance of TCLP regulatory levels can easily result in unnecessary remediation.

As the above example shows, TCLP results should not be used to evaluate potential impact on groundwater at non-landfill sites because this approach does not account for contaminant properties (*e.g.*, mobility and degradation) and site-conditions (*e.g.*, lack of acetic acid from municipal waste and other site-specific soil conditions) which dictate the fate and transport of contaminants in the subsurface and determine the potential impact on groundwater. The best approach for assessing potential for impact to groundwater would be to use a combination of leaching tests and transport models.

ALTERNATE APPROACH

The first step of our approach consists of using the SPLP test to determine leaching potential under laboratory conditions. These SPLP results would be compared to a compliance concentration equal to the maximum contaminant level (MCL) times a universal or generic DAF. The universal DAF would account for different soil types and other variables, such as depth to groundwater, similar in concept to that of Chiang *et al.* (6). If the SPLP concentrations exceeded this compliance concentration of the universal DAF times the MCL, a site-specific model would then be developed.

The site-specific modeling would consist of two parts:

1) Estimation of a site-specific soil/water partition coefficient (K_d).

2) Estimation of contaminant concentrations incorporating the effects of contaminant dispersion, retardation, and degradation as the leachate migrates through the vadose zone and subsequently mixes with groundwater.

The data needed for defining the soil/water partition coefficient (K_d) depend on the chemicals of concern. If organics are of interest, the organic content of soil, often referred to as fraction organic carbon (f_{oc}), is needed to estimate the soil/water partition coefficient (K_d); if metals are of concern, the metal concentration present in soil and the metal concentration expected to be present in the aqueous form in the leaching liquid (*i.e.*, rainwater) is needed to estimate the soil/water partition coefficient (K_d). The SPLP, rather than the TCLP, is recommended to estimate the metals concentration expected to be present in the leaching fluid since this test more closely simulates field conditions at non-landfill sites.

The soil/water partition coefficient, estimated either using the f_{oc} (for organics) or the SPLP (for metals), would then be used as input to a transport model to estimate leachate concentrations as a function of depth and evaluate the potential for impact to groundwater.

The main advantage of this approach is the improved accuracy and increased reliability in predicting potential impact to groundwater.

Replacing the leaching test with a model was also recommended in a 1992 EPA workshop to assess the potential impact of oily wastes in the environment, because it was recognized that the TCLP does not accurately represent the disposal scenario of oily wastes in a landfill.

CONCLUSIONS

The TCLP is an appropriate tool only where it is truly applicable. Site-specific models should be used to assess potential leaching of contaminants that are not compatible with the TCLP test or at sites that are not comparable to a municipal landfill management disposal scenario. Thus, we recommend:

- The TCLP should be used only for the scenario for which it was developed, *i.e.*, for municipal landfill scenario and for specific chemicals of concern with chemistries which are compatible with the acetic acid fluid leach and with the specifics of the method techniques.

- Use SPLP and/or modeling for other sites to generate the best estimate of mobility of contaminants to groundwater and potential threat to human health.

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THE SYNTHETIC GROUNDWATER LEACHING PROCEDURE (SGLP): A GENERIC LEACHING TEST FOR THE DETERMINATION OF POTENTIAL FOR ENVIRONMENTAL IMPACT OF WASTES IN MONOFILLS

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ABSTRACT

The toxicity characteristic leaching procedure (TCLP) is often used in a generic manner for the prediction of leaching trends, although the intent of this test was for the prediction of leaching under codisposal conditions in sanitary landfills. The application of acidic conditions to predict field leaching that can occur under a wide range of conditions may lead to false prediction of leaching trends. Additionally, conditions imposed on leaching systems by inappropriate leaching solutions may alter the distribution of redox species that would be found in the field. In some cases (with reactive wastes), 18 hours, as specified in the TCLP and other short-term leaching tests, may be an insufficient equilibration time.

A generic test of leachability called the synthetic groundwater leaching procedure (SGLP) and a long-term leaching (LTL) procedure, developed at the Energy & Environmental Research Center (EERC) at the University of North Dakota, have been used to predict leaching under field conditions. Specific uses have included characterization of coal ash disposed of in monofills and prediction of mobility of selenium in mined areas. In many applications, the SGLP has demonstrated trends widely different from TCLP and other commonly used leaching protocols. In the case of coal ash, the trends indicated for leaching by the SGLP show much different trends than TCLP. These differences can be explained by the fact that many commonly used leaching tests impose conditions on samples different from those in a field environment and, thus, bias data in a manner leading to inappropriate interpretation for environmental impact. Elements most often affected include arsenic, boron, chromium, vanadium, and selenium. Long-term leaching using the LTL procedure is used for waste materials that may undergo hydration reactions after disposal upon contact with water. The implication for the usefulness of these tests is magnified by the increase in reactive wastes that will be produced using advanced combustion systems to comply with the Clean Air Act Amendments. These materials, which are almost always reactive, behave much differently under field conditions than would be predicted using the TCLP or other short-term leaching procedures. At the present time, the SGLP test along with long-term leaching is being used in a number of states, including Minnesota and Indiana, for determination of the environmental impact of coal conversion solids. The test has been written up in draft form for consideration by the American Society for Testing and Materials (ASTM) as a standard for leaching of coal ash.

INTRODUCTION

Waste materials are of general concern to all, and the potential for environmental harm through disposal is real. Because of this, the proper testing of materials to evaluate the potential for environmental harm must be carried out in a manner that is scientifically valid, defensible, accurate, precise, and relevant to the disposal conditions anticipated. Often materials are subjected to the toxicity characteristic leaching procedure (TCLP) (1), and for the most part, some waste materials can be at least partially evaluated for their potential environmental impact. It is recognized that nearly any disposed material has the potential to generate leachate with characteristics different from local groundwater, but this does not always imply degradation of the environment. Some waste materials disposed in environments where local sediments produce groundwater of relative high ionic strength may generate leachates from the infiltration of rainwater that are of higher quality than native groundwater. These waste materials are of little concern, and it is the potentially problematic substances on which proper testing is imperative.

A limitation of the TCLP that appears to be often overlooked is that the application for which it was intended was the evaluation of leaching under codisposal conditions in a sanitary landfill. Numerous materials are highly unlikely to be disposed of in sanitary landfills, and under expected monofill disposal, are highly unlikely to encounter an acidic environment. Rather, an alkaline environment would be maintained for long-duration leaching because of the nature of these wastes. While numerous other waste streams could also be considered, coal combustion solid residues (CCSRs) will be the focus of this paper, because of the high volume and mass of CCSRs and because most residues from lower-rank coals or from advanced combustion processes will be alkaline in nature (either because of inherent properties or alkaline additives used to scrub acid gases for emission reduction).

Many coal combustion solid residues have physical, chemical, and mineralogical characteristics advantageous for utilization and can be marketed for a wide variety of engineering applications in construction and other industries. Despite their potential for use, high volumes of these materials are disposed of every year throughout the United States. With the enactment of the 1990 Clean Air Act Amendments, coal combustion solid residues may change in character (as combustion methods change) and will certainly increase in volume. The use of advanced combustion processes and scrubbers for acid gas reduction will provide an alkaline nature to many residues and will certainly affect trace element distribution and mobility. The quantity of these materials requiring disposal is expected to increase dramatically as coal combustion and environmental systems change to meet new regulations. The environmental disposal practices for these materials are important issues impacting the coal mining and utility industries, regulatory agencies, electric utility ratepayers, and the general public.

Regulatory agencies, the coal mining industry, and the utility industry agree that the environmental issues of clean air and water are of the highest priority when considering disposal/utilization of coal conversion solid residues and other by-products. Regulatory approaches must be adequate to safeguard the environment while minimizing the economic

burden on industries that must, in turn, pass that cost on to consumers in the form of increased rates for electricity. Comprehensive and appropriate scientific information is essential to make the difficult, but necessary, decisions regarding the disposal or utilization of these highly complex solid materials.

Chemical, physical, and mineralogical characterization of wastes are all important in formulating a plan for scientifically based disposal. This paper is a discussion of protocols for the leaching characterization of waste materials to determine potential for environmental impact.

EXPERIMENTAL

Numerous investigations of the leachability of trace elements from coal combustion solid by-products have been conducted at the Energy & Environmental Research Center (EERC) using several leaching procedures. The primary objectives of these investigations can be summarized as follows:

- Identify trace elements of environmental significance, to include currently regulated trace elements and others present at significant total concentrations
- Determine the total amounts of all identified trace elements
- Measure and compare the leachability (mobility) of the identified trace elements using several leaching tests

The materials included as examples in this report are two CCSRs, a low-rank coal fly ash and a solid scrubber residue from a duct-injection demonstration project to control stack gas emissions of sulfur and nitrogen acid gases. These solid residues were subjected to a comprehensive chemical characterization scheme that met the objectives listed above. These were as follows:

- Qualitative screening for identification of elements present.
- Quantitation of total concentrations of selected elements in the bulk sample and determination of mineral phases present.
- Leaching of the solid by the selected leaching procedures, determination of concentrations of all selected elements in resulting leachates, and identification of mineral phases present in leached solids.

The qualitative screening was performed by proton-induced x-ray emission (PIXE). PIXE was used to identify elemental constituents (from sodium through uranium) present in the material. The purpose of the screening was to identify all elements of interest either from the standpoint of potential toxicity or from the standpoint of scientific interest.

The results of the screening procedure were used to select elements of interest for the various studies used as examples in this paper. Table 1 is a list of both Resource Conservation and Recovery Act (RCRA) elements and non-RCRA elements of interest included in these studies. The RCRA elements are arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Several of the RCRA trace elements were not identified as present by the screening procedure and are not typically found in coal combustion solid by-products, but were included in this study for completeness. Boron and molybdenum were also included since they are elements that are often concentrated in coal combustion solids and are not always identified by PIXE at low concentrations.

Other materials referred to in this report were also subjected to the same screening protocols. Because of space limitations, only elements of interest that illustrate differences in results from various leaching procedures are discussed, as well as examples to show the need for long-term leaching, which is not addressed by the regulatory leaching tests.

Following the qualitative screening and identification of elements to be included in the investigation, total concentrations of the identified elements were determined in the original

TABLE 1

Elements of Interest Identified by PIXE

Element	Type[1]
Ag	1
As	1
B	2
Ba	1
Cd	1
Cr	1
Cu	
Hg	2
Mn	
Mo	2
Ni	
Pb	1
Se	1
Sr	
Zn	

[1] Type 1 indicates RCRA elements. Type 2 indicates elements of high interest in coal conversion solid residues.

solid material. Appropriate sample dissolution techniques were used for different groups of analytes. Sample dissolutions were performed in duplicate, and resulting solutions were analyzed by atomic absorption (AA) or inductively coupled argon plasma (ICAP) spectrophotometric techniques as appropriate. Mercury was analyzed by cold-vapor generation with AA detection. Matrix-matched standards were used to calibrate instruments, and standard laboratory quality control methods were employed, including sample duplicates and analyte spike recoveries. Major and minor constituents were determined in addition to the identified trace elements. These constituents provide standard information important in the classification of these material types for utilization and required for interpretation of the mineralogical characterization. The major and minor elemental constituents shown in Table 2 are reported as percent oxides. Trace elements have been reported as elemental concentrations. This reporting format is only a convention specified by the American Society for Testing and Materials (ASTM). The results do not indicate actual oxides present in the materials, but rather the total concentrations of these elements expressed as oxides. It has been widely

TABLE 2

Major, Minor, and Trace Bulk Chemical Analyses

Major/Minor Constituents	Duct-Injection Solid, %	Fly Ash, %	Trace Elements	Duct-Injection Solid, μg/g	Fly Ash, μg/g
SiO_2	17.3	49.7	Ag	140	0.6
Al_2O_3	8.73	22.1	Cd	< 0.1	12
Fe_2O_3	7.84	17.5	Ba	350	600
CaO	32.6	1.77	Cr	58	150
MgO	0.58	0.94	Hg	0.9	0.6
Na_2O	4.27	0.45	Se	9.1	2.2
K_2O	0.47	2.22	As	140	54
P_2O_5	0.17	0.16	Pb	39	140
TiO_2	0.42	0.91	B	400	340
BaO	0.04	0.07	Mo	28	11
MnO_2	0.02	0.04	Ni	50	220
SrO	0.03	0.04	Cu	39	91
Moisture	0.80	0.31	Zn	130	460
LOI[1]	9.02	3.39	Br	110	ND[2]
SO_3	16.6	0.25	Cl	8530	ND

[1] Loss on ignition.
[2] Not determined.

reported that relatively low percentages of the elemental concentrations of these elements actually are present in simple, pure oxide forms. Most coal combustion solid by-products contain an amorphous or glassy phase and numerous and diverse crystalline phases.

The final step of the laboratory investigation was to characterize several leaching procedures, with subsequent analysis of the resulting leachates. A summary of the procedures used for the leaching (trace element mobility) characterization are as follows:

- The TCLP (U.S. Environmental Protection Agency [EPA], 1986) is the EPA regulatory leaching procedure, through the RCRA, for the determination of the hazardousness of wastes. Land disposal of materials identified as hazardous by this leaching procedure is prohibited by the EPA. The TCLP has also been adopted by many state regulatory agencies to provide leaching information on solid wastes (not hazardous) which are not federally regulated. This test uses end-over-end agitation and a 20-to-1 liquid-to-solid ratio with an 18-hour equilibration time. Two leaching solutions are specified for use with this test. Leaching Solution #1 is an acetate buffer prepared with 5.7 mL of glacial acetic acid per liter of distilled deionized water and adjusted to pH 4.93 with 1 N sodium hydroxide solution. Leaching Solution #2 is an acetic acid solution prepared by diluting 5.7 mL of glacial acetic acid to one liter with distilled deionized water. This solution will have a pH of 2.88. The TCLP specifies a test to determine the alkalinity of the waste to be leached which, in turn, determines what leaching solution should be used. More-alkaline materials utilize Solution #2, while less-alkaline materials are leached with Solution #1. Both leaching solutions were used in this leaching characterization, although by definition, leaching Solution #2 would have been chosen according to the test protocol for nearly all of the alkaline materials being discussed in this report. The choice of leaching solution is based on the results of a determination of the alkaline nature of each solid residue.

  The use of both leaching solutions allows comparisons to be made between the waste forms and also provides an interesting comparison between the materials with respect to the acid leachability of each element tested.

- The synthetic groundwater leaching procedure (SGLP) (2) was developed as a generic leaching test to be applied to materials to simulate actual field leaching conditions.

  Since the TCLP was designed to simulate leaching in a sanitary landfill under codisposal conditions, it is not appropriate to evaluate leaching of coal conversion by-products in typical disposal or utilization scenarios. To provide more appropriate and predictive information for coal conversion by-products and other unique materials, a leaching test was developed using the same basic protocol as the TCLP, but allowing for the appropriate leaching solution chemistry. Test conditions are end-over-end agitation, a 20-to-1 liquid-to-solid ratio, and an 18-hour equilibration

time. The leachate used for this project was distilled deionize water. For certain predictive applications, this solution may not be totally appropriate since mercury, for example, would be highly influenced by the presence of chloride because of the formation of an extremely stable mercury chloride complex. Local, site-specific factors, such as the presence of significant halide concentrations or other geochemical factors likely to influence trace element mobility, would have to be considered in any real disposal setting. For our work on many research projects, the most likely source of water would be rainwater, thus prior mineralization would not be a consideration. Additionally, because of the extremely alkaline nature of the samples included in this report and their high acid-neutralization capacity beyond the simple high pH, acidity from the impact of varying acid precipitation concentrations was not considered to be an important factor (although, as with every imaginable factor would, no doubt, have influenced results to some small degree). The purpose of this test was to provide data not influenced by the presence of acetate ion or the initial acid impact when sample and leaching solution were mixed.

- A long-term leaching (LTL) procedure, also using distilled deionized water, was included to identify effects associated with any mineralogical changes that may occur in the waste forms upon long-term contact with water. Separate samples were analyzed after 18 hours, 48 hours, 1 week, 4 weeks, and 12 weeks. It has been found previously that, on long-term contact with water, certain coal conversion solid waste materials form secondary hydrated phases with mineralogical and chemical compositions different from any of the material in the original ash (3). In another research project, it was demonstrated that the formation of these hydrated phases was often accompanied by dramatic decreases in solution concentrations of oxyanionic species such as borate, chromate, selenate, and vanadate (4). Ettringite formation has been implicated in this phenomena. The decrease in the concentrations of these elements would not be predicted from the results of short-term leaching tests.

RESULTS AND DISCUSSION

The results of laboratory investigation are summarized in four separate figures for clarity in the presentation of data. Some LTL results have been omitted, where concentrations were below the lowest level of quantitation (LLQ), to simplify interpretation of these data and to emphasize the change in leachate concentrations of elements with time. In these cases, the absolute concentration value is of less scientific significance than trends in concentration.

Figures 1 and 2 show elemental concentrations for all of the RCRA elements in leachates from the three leaching solutions. The SGLP, TCLP leaching Solution #1, and TCLP leaching Solution #2 represent a series of increasing acidity, thus, the TCLP #1 is less acidic than TCLP #2, and the SGLP leaching solution is essentially neutral. The measured concentration for each element is compared with the RCRA limit as well as with the maximum theoretical concentration. This maximum concentration is calculated by using the results of bulk chemical analysis for each element, assuming total dissolution of each analyte at the 20-to-1 liquid-to-solid ratio used in the leaching protocols. This allows comparison of RCRA limits and leachate concentrations with a calculated worst-case scenario (maximum calculated concentrations), assuming total dissolution of analyte.

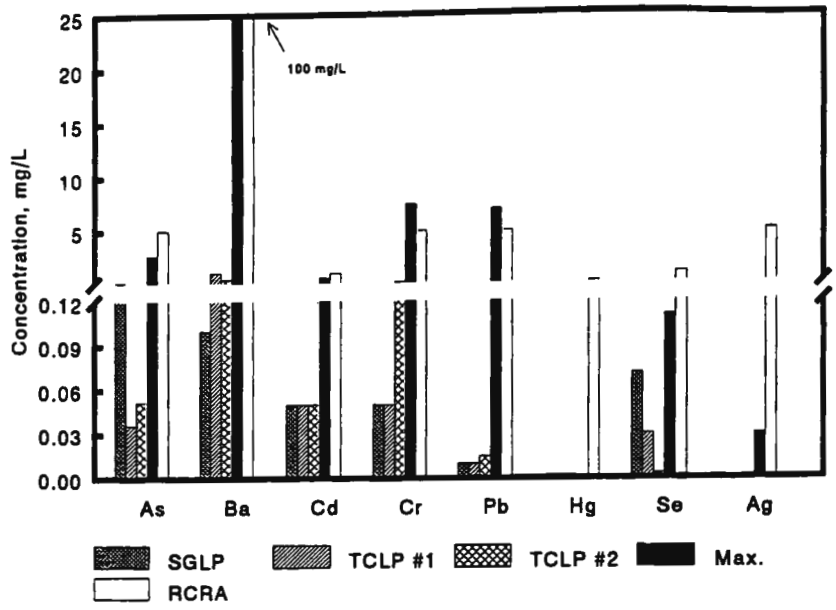

Figure 1. Fly ash SGLP and TCLP (RCRA elements). (Reprinted with permission from Elsevier Science.)

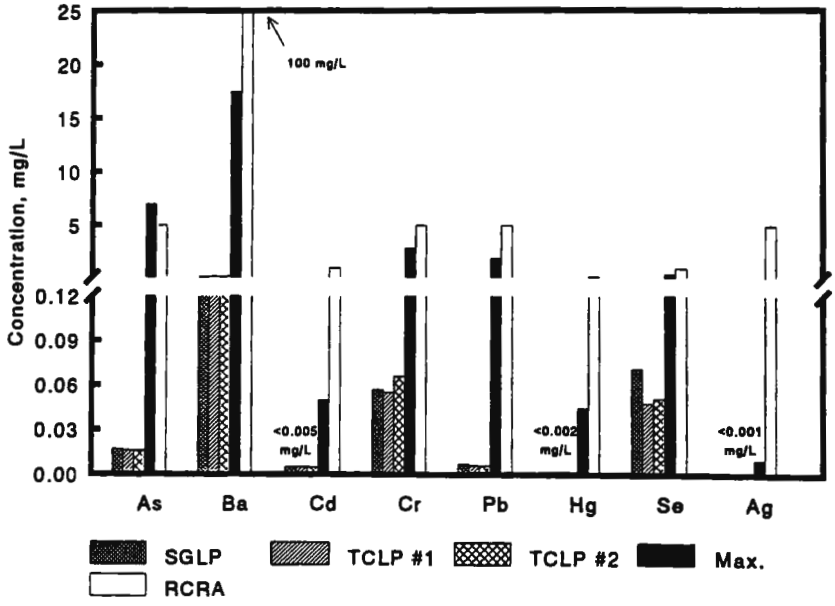

Figure 2. Duct-injection ash SGLP and TCLP (RCRA elements). (Reprinted with permission from Elsevier Science.)

A general conclusion that can be drawn from these figures is that the leachability of most of the RCRA elements present in these samples is extremely low. It can be seen that mobile analytes, as represented by leachate concentrations, are always a fractional portion of that available and are often several orders of magnitude lower than theoretical calculated amounts.

Figures 3 and 4 contain similar information on the non-RCRA as that for the RCRA elements in previous figures; however, in these figures, the comparison is with respect to the maximum calculated value only since RCRA limits do not exist. This concentration is calculated assuming that the total mass of trace elements as determined from the bulk analysis had dissolved. The non-RCRA elements were chosen for the purpose of scientific evaluation of the various leaching tests.

Greater differences in leachability of trace elements for the various leaching solutions were shown with the fly ash selected than with the duct-injection residue. This is often the case for the less-alkaline materials like this low-calcium fly ash, where acidity of leaching solution has more control over final pH than for the strongly alkaline materials, where final pH is essentially controlled by the large amounts of alkaline materials available.

Figures 5 and 6 show information on the change in concentrations during LTL tests of RCRA elements, measured at above the LLQ. As before, the levels are compared against the RCRA limit for each element. The y-axis for concentration has been split for more meaningful

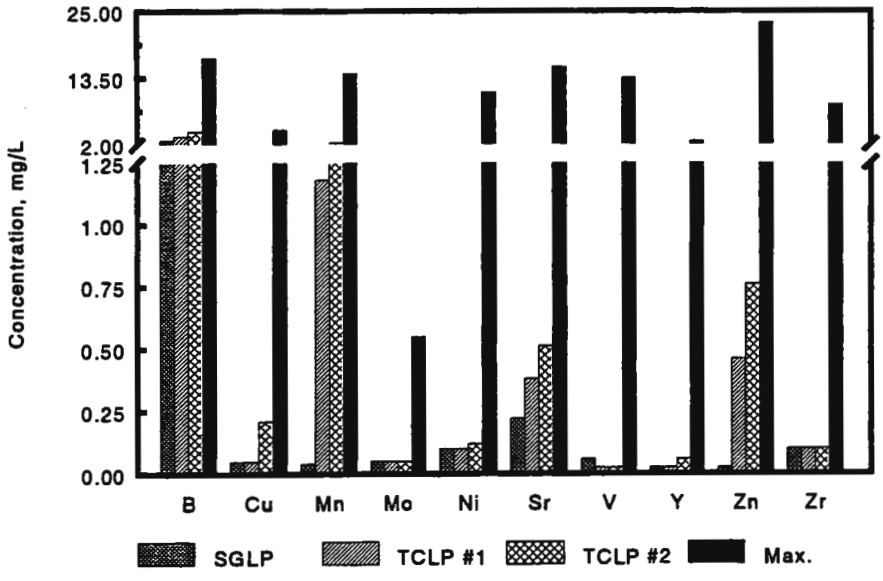

Figure 3. Fly ash SGLP and TCLP (non-RCRA elements). (Reprinted with permission from Elsevier Science.)

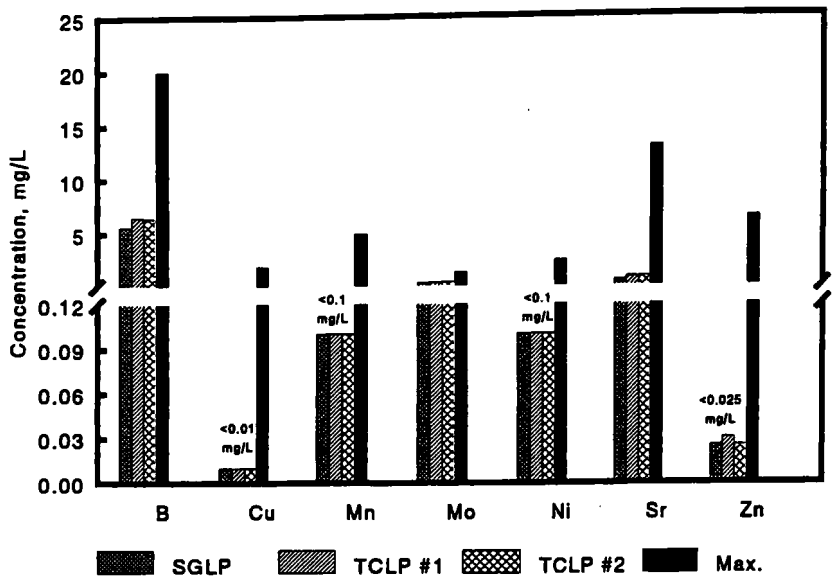

Figure 4. Duct-injection ash SGLP and TCLP (non-RCRA elements). (Reprinted with permission from Elsevier Science.)

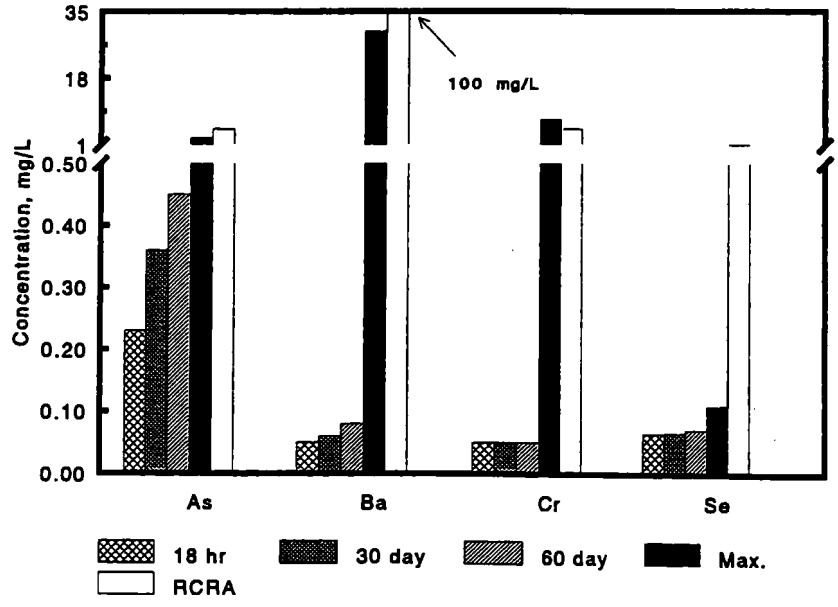

Figure 5. Fly ash LTL (RCRA elements). (Reprinted with permission from Elsevier Science.)

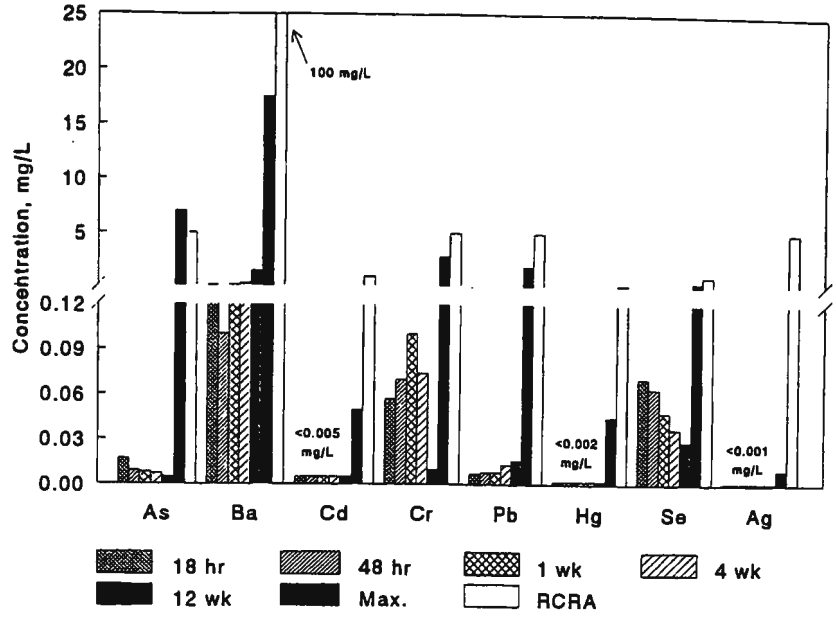

Figure 6. Duct-injection ash LTL (RCRA elements). (Reprinted with permission from Elsevier Science.)

representation of very low and relatively high concentrations. Additionally, it should be noted that the RCRA limit for barium is actually 100 mg/L, as noted in the chart, which extends the overall range for all elements to between 6 and either 25 or 35 mg/L, as required by the leachate composition of each sample.

The important information in these figures are in the trends of solubility with respect to time rather than actual concentrations. It can be seen that the behavior of arsenic, chromium, and selenium in the duct-injection ash are anomalous with respect to the expected gradual increase with time. In the case of these elements, the formation of new mineralogical phases is most likely responsible for the decrease in leachate concentration over time. It has been shown in another research project that the formation of ettringite can be accompanied by the fixation of a number of elements (4). Arsenic, chromium, and selenium can be immobilized by incorporation into an insoluble ettringite phase. Normal leaching with a gradual increase in leachate concentration with respect to time was seen for the fly ash. This material, because of its low alkalinity, was not expected to form ettringite or ettringitelike phases that could affect oxyanion concentrations. Additionally, most of the RCRA elements in the fly ash leachate were below the detection limits and are not shown on the graph.

Figures 7 and 8 compare LTL leachate concentrations for non-RCRA elements versus time and include the calculated maximum concentrations of elements in the leachate, assuming total dissolution of trace elements, as determined from the bulk analysis.

Anomalous behavior is seen for molybdenum concentrations in fly ash leachate and for boron concentrations in duct-injection ash leachate. These trace elements can be immobilized in

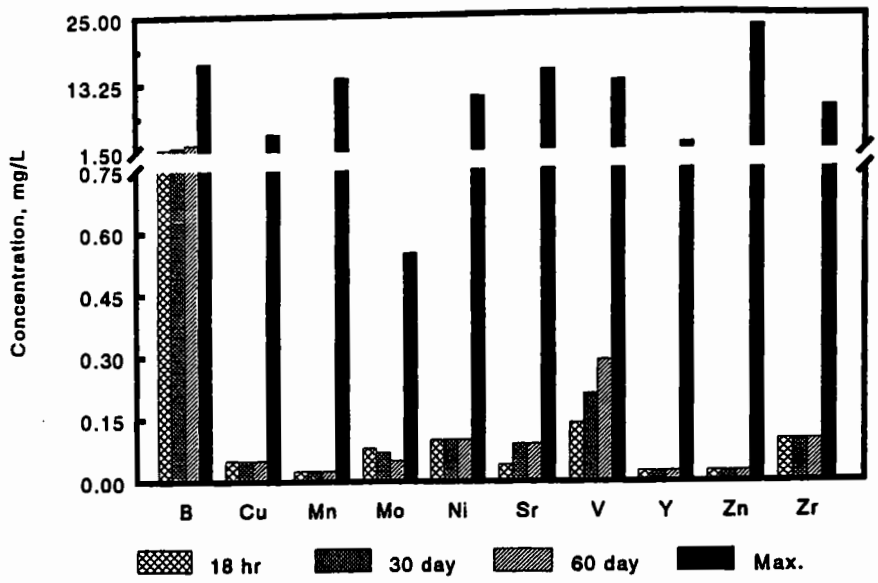

Figure 7. Fly ash LTL (non-RCRA elements). (Reprinted with permission from Elsevier Science.)

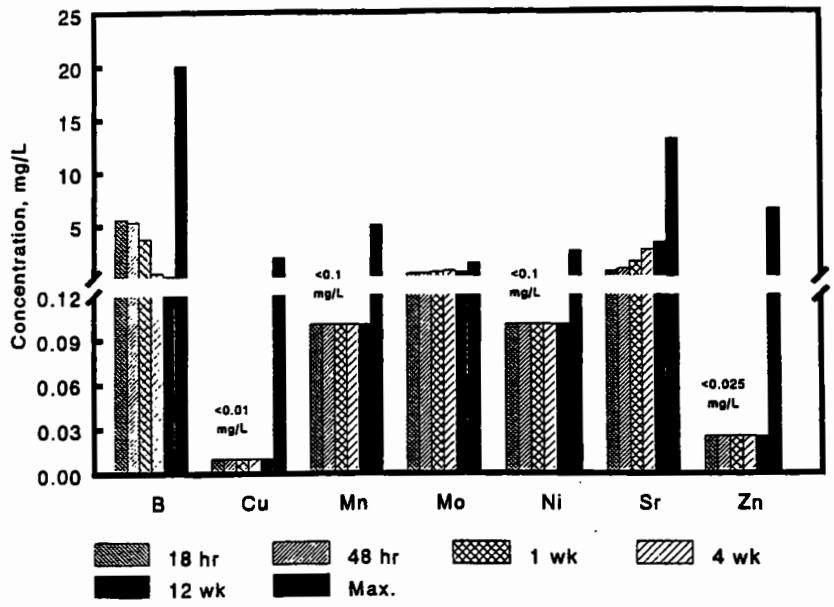

Figure 8. Duct-injection ash LTL (non-RCRA elements). (Reprinted with permission from Elsevier Science.)

ettringite phases as seen with RCRA elements (Figure 7). Several other elements show a gradual increase in concentration that indicates their presence in moderately soluble phases which gradually dissolve or release trace elements on long-term contact with water.

SUMMARY

The characterization of a waste material for disposal must include a complete study consisting of chemical, mineralogical, and often physical characterization. Site characterization and the effects of potential interactions of leachate with the environment are essential parts of any complete study designed to evaluate potential for environmental impact of a waste material.

Long-term leaching results indicate the importance of this test in appropriate circumstances primarily because of the unpredictability of results for individual elements between different solids. Additionally, LTL most closely represents the environmental scenario most wastes are likely to encounter, whereas multiple pore volumes of leaching solution in contact with the solid over an 18-hour period are highly unlikely to occur. Despite the inconvenience of having to wait for months for results, LTL should be performed as a part of the environmental impact evaluation if the potential to exceed RCRA limits exists.

Trace element mobility (leachability) in coal combustion solid by-products can be characterized for individual materials and not for generalized categories of these materials. Therefore, each specific disposal project requires appropriate material characterization based on the distinct and specific attributes of that material.

An acidic leaching solution does not constitute a "worst-case scenario," as applied to the TCLP leaching of coal conversion solids or any other material. Leaching procedures and solutions must be carefully chosen and evaluated to provide reliable information and to be scientifically valid. A regulatory testing scheme should include flexibility to adopt a short-term leaching procedure allowing the use of appropriate leaching solutions and/or long-term leaching tests when necessary. It may not be appropriate to attempt and model a worst-case scenario in a laboratory procedure since this represents the use of science to demonstrate a "case" rather than to accurately characterize a sample.

There are currently no laboratory leaching tests available that provide an accurate prediction of absolute leachate concentrations of trace elements in field settings. Thus, leachate concentration trends, as provided by LTL results, and comparisons of leachable amounts versus total amounts of analyte in LTL, provide the best scientifically useful and valid information currently available from laboratory tests. Empirical results of short-term leaching can be very misleading and are often being misapplied for the formulation of decisions impacting our environment.

Absolute containment of a waste and its leachate is impossible even in the best engineered disposal facility. Thus, since escape of leachate is inevitable, slow controlled release of trace elements is essential to ensure low, nontoxic leachate concentrations that can be re-equilibrated in the environment. Toxicity with respect to most trace elements is a function of concentration and not identity, thus release is not necessarily undesirable. Since disposal is forever,

scientific thought about disposal must consider the long term and be realistic in terms of what actually constitutes a hazard.

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SUGGESTED MODIFICATION OF PRE-ANALYTICAL HOLDING TIMES - Volatile Organics in Water Samples

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ABSTRACT:

The current political climate for environmental programs dictates that quality control/quality assurance requirements be cost effective, reduce error, improve quality, or otherwise add value to data collection. Current holding time requirements, especially in the case of volatiles in water, are a prime example of minimal improvement in environmental data reliability at inordinately high costs to both regulators and the regulated community. Through the development and validation of a holding time model, this paper describes a concept of "practical reporting times" and suggests alternative approaches for implementation. These include the extension of pre-analytical holding times for volatile organics in appropriately preserved (i.e., no headspace and pH 2) water samples to 28 days. Based on common data delivery schedules, e.g., 30-day submission, this functionally eliminates the current regulatory requirement. A second aspect of the modification of regulatory requirements is the definition of a mechanism for further extension based on analyte- and sample-specific demonstration of acceptable stability. The activities summarized in this paper were designed by a steering committee with representation from across U.S. Environmental Protection Agency (EPA) Program and Regional Offices, the Department of Energy (DOE - Office of Environmental Management), and the Department of Defense (DOD). The work was performed at Oak Ridge National Laboratory (ORNL).

BACKGROUND:

Pre-analytical "Holding Times" for environmental samples were initially based on the reasonable concept that chemical and physical characteristics may change during each of the many steps from sampling through analysis. In response to the need to limit degradation or loss in water samples, holding times were arbitrarily set and specified in 40CFR Part 136 (1979). Unlike most technical and legislative aspects of environmental programs, this requirement has never been significantly updated. Actually, its impact has been expanded beyond the initial application to many additional regulatory programs and environmental media (1,2,3). There is widespread skepticism in the environmental community of the technical basis for the requirement. However, the complexity of the organizational structure sustaining it is a daunting obstacle to change. Table 1 lists the Environmental Protection Agency (EPA) Offices that explicitly or implicitly (e.g., included within method guidance) maintain the regulatory status. Table 2 summarizes the legally mandated requirements.

table 1

MANDATED HOLDING TIMES FOR VOCs

Program / Reference	Holding Time (Days) - 4C storage	
	pH adjustment	no pH adjustment
SDWA - 40CFR 141		
Halocarbons	14	pH adjustment required
Aromatics	14	pH adjustment required
CWA - 40CFR 136		
Halocarbons	14	14
Aromatics	14	7
RCRA (TCLP, Delisting) - 40CFR 261		
Halocarbons	14(a)	14(a)
Aromatics	14(a)	14(a)

(a) for TCLP Characterization, the sample must be extracted in 14 days and than analyzed within 14 days of the TCLP extraction

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table 2

EPA PROGRAMS that PROPOSE / CONTROL / MODIFY / APPROVE VOC Holding Times

* Office of Emergency and Remedial Response (OERR-Superfund)
* Office of Solid Waste (OSW-RCRA)
* Office of Water (OW- Drinking Water/Wastewater - CWA)
* Office of Prevention, Pesticides, and Toxic Substances (OPPTS - Pesticides/TSCA)
* Office of Air and Radiation (QAR - Stationary / Ambient)

HISTORY:

Since the mid-1980's various Interagency groups (US EPA, DOE, and DOD) have funded various projects to evaluate options and clarify analyte-specific holding time considerations. Table 3 lists physical characteristics of various target analytes to illustrate the diversity across the volatile organic analytical fraction. Initial holding time investigations centered on ways to bring chemistry into the interpretation of analytical results. Risk assessment may be questioned as a relatively inexact estimate or interpretation of technical variables, but at least the disciple recognizes that not all chemicals behave identically. The basic studies supporting several subsequent publications were presented at the 3rd, 4th, and 5th Annual Waste Testing and Quality Assurance Symposium and were again discussed during a special session at last year's Symposium (4-6). In addition, several EPA and DOE groups have published summary studies interpreting and expanding various aspects of the data sets. These are readily available elsewhere, and beyond the scope of this presentation (7-10).

table 3

Physical Constants for Selected Volatile Organic Chemicals (VOCs)

COMPOUND	DENSITY (gm/ml)	BOILING POINT (degrees C)	VAPOR PRESSURE (mm of Hg)
Bromomethane	1.68	3	1250
Chloroform	1.48	61	160
Trichloroethene	1.46	87	60
Styrene	0.906	145	5
Benzene	0.877	80	76
Toluene	0.867	110	22

CURRENT STATUS:

Based on last year's special session and subsequent Interagency discussions, EPA's Analytical Operations Branch provided DOE with data (results only) from historical holding time studies which were sent to Oak Ridge National Laboratory for assessment. The purpose has been to use this data, supported by a limited verification study, to demonstrate applicability of a model developed at ORNL that defines a "practical reporting time (PRT)." Table 4

table 4

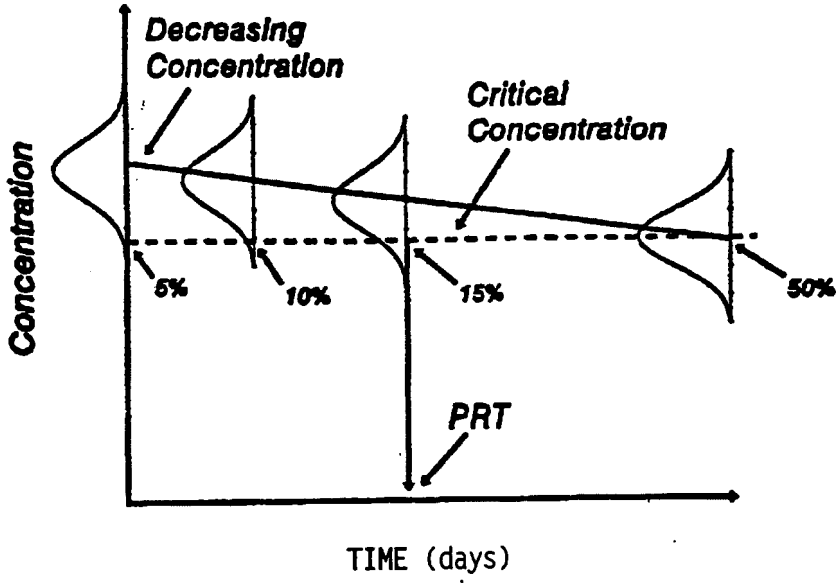
. PRT values compared with other holding time studies in aqueous matrices.

	ORNL 4C no preservative			ORNL 4C NaHSO4			EPA 4C no preservative
Compound	Distilled water	Groundwater	Surfacewater	Distilled water	Groundwater	Surfacewater	Sewage water
Acetone				≥112	≥112	≥112	31
Benzene	≥112	102	62	42	≥112	34	≥90
Bromodichloromethane							≥90
Bromoform	≥112	≥112	51	≥112	≥112	≥112	≥90
Bromomethane				≥112	≥112	≥112	
2-Butanone				≥112	≥112	≥112	23
Carbon Disulfide				31	39	34	68
Carbon Tetrachloride	≥112	≥112	96	57	≥112	≥112	19
Chlorobenzene	≥112	≥112	65	≥112	≥112	54	≥90
Chloroethane				≥112	≥112	≥112	
Chloroform	≥112	≥112	57	≥112	≥112	≥112	≥90
Chloromethane				≥112	≥112	≥112	
Dibromochloromethane							≥90
1,1-Dichlorethane	≥112	≥112	55	≥112	≥112	≥112	≥90
1,2-Dichloroethane							≥90
1,1-Dichlorethene	≥112	≥112	80	≥112	51	≥112	≥90
1,2-Dichloroethene							≥90
1,2-Dichloropropane	≥112	≥112	85	41	≥112	45	≥90
Ethylbenzene	≥112	19	13	≥112	≥112	≥112	≥90
2-Hexanone				≥112	≥112	≥112	28
Methylene Chloride	≥112	≥112	71	19	22	40	≥90
4-Methyl-2-Pentanone				≥112	≥112	≥112	54
Styrene	≥112	0	10	≥112	≥112	≥112	79
1,1,2,2-Tetrachloroethane	9	≥112	≥112	49	≥112	40	≥90
Tetrachloroethene	≥112	≥112	55	≥112	≥112	≥112	81
Toluene	≥112	67	56	≥112	≥112	≥112	≥90
1,1,1-Trichloroethane							≥90
1,1,2-Trichloroethane	≥112	≥112	87	≥112	≥112	26	≥90
Trichloroethene	≥112	≥112	53	36	≥112	33	≥90
o-Xylene/Xylene total	≥112	80	≥112	≥112	≥112	≥112	≥90

summarizes suggested holding times developed through application of the model for both data sets. Specific details of the statistical approach are beyond the scope of this presentation and published elsewhere (11). Generally, the model specifies the length a sample can be held with reasonable assurance the analyte concentrations have not changed significantly. The value of the approach is that the key terms (significant change and reasonable assurance) are user variable and user defined. Risk of error is quantitative and consistent with currently available draft data quality assessment guidance.

The ability to assess analyte-specific contributions to variability contributed by holding times, especially for samples analyzed beyond currently specified limits, is critical for accurate data interpretation, e.g., data validation. Empirical data from historical and more recent studies have determined the appropriate degradation (loss) model (e.g., zero order, first-order, log-term, etc) providing analyte-specificity to the statistical approach. Figure 1 demonstrates the PRT for a linear decreasing concentration, approximately 80% of the cases reviewed.

figure 1



Practical reporting time (PRT) for an analyte with a linear decreasing concentration

Processing the EPA data through the model verified that at the level of assurance defined as acceptable (85% confidence in identifying a 15% change), there was minimal loss in data reliability from holding time extension. Loss / degradation does occur (e.g., carbon tetrachloride in this particular data set) and is extremely variable. Table 4 summarizes the results of the data analysis (n=150 analyte pairs for the ORNL studies and n ranged from 79 to 86 for the EPA data set). The results are dependent upon many chemical, physical, and biological factors. There is clearly no universal correct answer for all analytes in all samples. However, the approach described here is technically defensible because it recognizes analyte variability and because it provides a mechanism to assess changes (degradation).

Understanding and managing variability is preferable to arbitrary black and white decisions that are currently required. The possibility of minimal loss, especially of infrequently found analytes, is a sacrifice that is a cost-effective tradeoff worth making given the value added by the approach described here. This is a preferable to maintaining an entire system based on the worst case situation. The approach described here will introduce a risk-based system that supports quantification and management of sample-specific variability consistent with interagency interests and Congressional direction.

A generally recognized need in the modification of current holding time requirements is separation of contractual issues from technical considerations (9th Annual Waste Testing and Quality Assurance Symposium). Current Superfund Guidance (12) attempts to address this problem by relying on data validator judgement to interpret effects and define the impact of analyses performed beyond current limits (for soil and water). This is not a solution for a consistent, documented, defensible process; however it clearly points out the need for a defined procedure to quantify analyte-specific effects and to actually provide the necessary guidance for interpretation.

PROPOSAL(S) FOR MODIFICATION OF CURRENT REQUIREMENTS:

The first aspect of proposed modification is a simple extension of maximum holding time to 28 days for water samples properly collected, preserved, and stored (e.g., no headspace and acidified to pH <2). This functionally separates technical and contractual requirements assuming current, typical data delivery schedules of approximately 30 days. This approach is simple and technically more justifiable.(reliability and cost) than current requirements. It is immediately applicable to many routine monitoring data collection activities and essentially all of the regulated community.

A second, more complex aspect of the proposed modification is to define a procedure for site- and analyte-specific stability studies to extend holding times beyond 28 days for specific matrix and analyte combinations, especially for large scale or long term projects (e.g., DOE's mixed waste programs requiring radiochemical screening prior to sample shipment for hazardous chemical analysis). This would allow program decisions to determine an appropriate, cost-effective approach for a wide variety of environmental investigation and monitoring programs. In addition, the approach effectively defines and meets data needs consistent with current EPA guidance and future requirements (13-15).

CONCLUSION

Recently several encouraging factors have pushed the identification and implementation of more effective environmental data collection activities. These include:

The current EPA emphasis stressing scientific input into the decision making process of environmental programs(16,17)

Distribution of several Quality Assurance guidance and requirements documents covering data collection aspects (e.g., Data Quality Objective planning and Data Quality Assessment).(13-15)

Recognition that environmental decisions are never without risk and variability / error can be managed but not eliminated. A related aspect is the acceptance of laboratory or measurement uncertainty as a potentially minor contribution to overall uncertainly in estimating site conditions(18).

Questions about cost versus increased knowledge from traditional quality control parameters, e.g., duplicated matrix spikes (19).

The emphasis on performance based methods criteria to replace earlier generations of method adherence philosophy, not directly related to decision criteria.

Role of Environmental Monitoring Methods Council to integrate diverse requirements across EPA programs, e.g., Offices of Water and Solid Waste and Superfund.

This initial set of proposals is a first attempt to establish a process for cooperative efforts to identify changes in environmental data collection activities that can improve the decision making process for both regulators and the regulated community. Additional potential topics include polychlorinated biphenyls in water and soil and volatile organics in soil.

In the current budget climate, it is essential to assure that research is tied directly to regulatory concerns to efficiently focus on relevant problems, facilitate distribution of information, and enhance the rate of acceptance of technical advances. Environmental research is relevant only when it is accepted and directly applied to real data collection projects and environmental decisions. This particular project was selected as an informal pilot partly because, consistent with the DQO process, it required minimal new data. This has obvious advantages in cost, but also in the reduction of time required to complete the study . However, the primary reason for selection was (perhaps inappropriately) simplicity. Adopting this proposal will result in essentially no negative impact on environmental decisions. However, decisions may be made with a better perspective on the inherent uncertainty of environmental data collection activities. This isn't a sacrifice, but a necessary recognition of reality. The primary potential benefit from the suggested changes is significantly more cost-effective data collection supporting environmental decisions. The following is a brief summary of potential areas for cost reduction:

* Effective analytical "batch sizing" for analytical laboratories can improve the efficiency of sample processing. For example, single or very small batches require up to 300% increase in actual analyses to meet quality control requirements. Extensions of holding times would significantly increase analytical batch sizes dropping the routine percentage of QC samples from potential >40% to <20%.

* "Required" instrumentation/personnel for analytical demand, a standard contract feature, would be reduced (e.g., two instruments necessary instead of three contractually "required").

* Relief from holding times as a "functional" sampling schedule driver. For example, often sampling is limited to half day activities to accommodate overnight shipment to remote laboratories. Alternatively, sampling days could be extended followed by "bulk sample" shipment. This could easily result in a "5-day" sampling program being completed in two days with resource and time reductions carried on through the entire data collection process.

The adoption of the modifications suggested in this presentation will have essentially no adverse effect on reliability of environmental data. The only effect would be to significantly reduce program costs and improve the technical understanding of environmental conditions. Current plans are to introduce the approach through the Quality Assurance Management Staff (QAMS) the EMMC as a mechanism for entry across boundaries. Draft sections consistent with the EPA's methods format have been submitted for consideration as a section in SW-846 (19)

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SECONDARY WASTE MINIMIZATION IN ANALYTICAL METHODS*

by

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SECONDARY WASTE MINIMIZATION IN ANALYTICAL METHODS

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ABSTRACT

The characterization phase of site remediation is an important and costly part of the process. Because toxic solvents and other hazardous materials are used in common analytical methods, characterization is also a source of new waste, including mixed waste. Alternative analytical methods can reduce the volume or form of hazardous waste produced either in the sample preparation step or in the measurement step.

We are examining alternative methods in the areas of inorganic, radiological, and organic analysis. For determining inorganic constituents, alternative methods were studied for sample introduction into inductively coupled plasma spectrometers. Figures of merit for the alternative methods, as well as their associated waste volumes, were compared with the conventional approaches. In the radiological area, we are comparing conventional methods for gross α/β measurements of soil samples to an alternative method that uses high-pressure microwave dissolution. With the alternative method, liquid waste was reduced by a factor of nine (200 mL/sample), dry active waste was reduced by a factor of two, and analysis time was reduced by a factor of three. Preliminary measurements using alternative on other matrices (i.e., oils, greases, sludges), and for the use of alternative, nonhazardous solvents for the preparation of soils indicate additional reduction in waste volumes is possible. For determination of organic constituents, microwave-assisted extraction was studied for RCRA regulated semivolatile organics in a variety of solid matrices, including spiked samples in blank soil; polynuclear aromatic hydrocarbons in soils, sludges, and sediments; and semivolatile organics in soil. Extraction efficiencies were determined under varying conditions of time, temperature, microwave power, moisture content, and extraction solvent. Solvent usage was cut from the 300 mL used in conventional extraction methods to about 30 mL. Extraction results varied from one matrix to another. In most cases, the microwave-assisted extraction technique was as efficient as the more common Soxhlet or sonication extraction techniques.

INTRODUCTION

The U.S. Department of Energy (DOE) will require a large number of waste characterizations over a multi-year period to accomplish the Department's goals in environmental restoration and waste management. Estimates vary, but two million analyses annually are expected.[1] The waste generated by the analytical procedures used for characterizations is a significant source of new DOE waste. Success in reducing the volume of secondary waste and the costs of handling this waste would significantly decrease the overall cost of this DOE program.

Selection of appropriate analytical methods depends on the intended use of the resultant data. It is not always necessary to use a "high-powered" analytical method, typically at higher cost, to obtain data needed to make decisions about waste management. Indeed, for samples taken from some heterogeneous systems, the meaning of "high accuracy" becomes clouded if the data generated are

intended to measure a property of this system. Among the factors to be considered in selecting the analytical method are the lower limit of detection, accuracy, turnaround time, cost, reproducibility (precision), interferences, and simplicity. Occasionally, there must be tradeoffs among these factors to achieve the multiple goals of a characterization program. The purpose of the work described here is to add "waste minimization" to the list of characteristics to be considered. In this paper we present results of modifying analytical methods for waste characterization to reduce both the cost of analysis and volume of secondary wastes. Although tradeoffs may be required to minimize waste while still generating data of acceptable quality for the decision-making process, we have data demonstrating that wastes can be reduced in some cases without sacrificing accuracy or precision.

APPROACH

A typical characterization includes the following sequential steps: planning, sample collection, sample transport, sample preparation (including separations), measurement, data analysis, and reporting. Opportunities for waste minimization exist in the planning stage and in the sampling process. However, we have taken the preparation, separation, and measurement steps as our prime targets because these laboratory-based processes involve chemicals, sometimes hazardous ones, and typically generate significant volumes of waste. Furthermore, we have data to show that the waste volume can be significantly reduced by applying emerging new technologies. We have chosen to review the analytical procedures in three areas -- sample injection for inorganic analysis, dissolution of waste samples for radiochemical analysis, and sample preparation for analysis of organic constituents.

SAMPLE INTRODUCTION FOR INORGANIC ANALYSIS

With the promulgation of SW-846 Update II,[2] many of the regulated elements present in environmental and waste samples may be determined by using inductively coupled plasma (ICP) atomic emission spectroscopy, ICP-mass spectrometry (ICP-MS), or a combination thereof. Although these measurement techniques are often capable of achieving instrument detection limits of micrograms per liter or better, normal ICP sample introduction -- continuous pneumatic nebulization (CPN) of a sample solution -- utilizes only 1 to 10% of the sample uptake. The remaining portion of the consumed sample goes directly to laboratory waste, thereby creating a secondary waste stream that would be considered corrosive by standards in the Resource Conservation and Recovery Act, and could also be toxic or mixed radioactive waste. Despite the poor efficiency of the pneumatic nebulization process, dissolution or digestion is the preferred means of preparing bulk solids for ICP analysis. Our objective in this project is to identify and evaluate high-efficiency alternatives for solution introduction that will reduce or eliminate this particular secondary waste stream.

Graphite furnace atomization, hydride generation, and nebulization can all be used to introduce dissolved analytes into an ICP.[3] In the case of furnace atomization and hydride generation, the efficiency with which the analyte is introduced depends in large part upon the chemical properties of the element. The utility of these techniques varies considerably among groups in the periodic table. Solution nebulization, which is a physical means of analyte transport, works well for a broad range of elements and, thus, for a broad range of applications; however, the inefficiency of solution nebulizers was, until recently, the major source of ICP waste. However, development of the direct injection nebulizer (DIN),[4,5] which utilizes 100% of a sample solution by nebulizing it directly into the base of the ICP, has allowed analysts to reduce or eliminate ICP waste.

We compared solution analyses using DIN and CPN. Table 1 summarizes the equipment used and operating conditions. Use of the flow injection (FI) manifold was critical because it facilitated reductions in sample uptake and rinsing between samples. The impact of these reductions is also shown in the last two rows of Table 1. Note that the duration of each spectral integration and the number of repeat integrations were identical for the two systems. The 33% improvement achieved in analysis time using FI-DIN was due principally to the excellent rinseout characteristics of the FI-DIN system. Better rinseout also contributed to the 50% reduction in per sample waste volume; however, the lower consumption of the FI-DIN system was also a factor.

Table 1. Equipment and operating conditions used in this work.

	Continuous pneumatic nebulization	**Flow-injection direct-injection nebulization**
ICP-mass spectrometer	PlasmaQuad II+ with high performance interface (Fisons Instruments, Winsford UK)	
Nebulizer	V-groove (Fisons)	Microneb 2000 (CETAC, Omaha NE)
Spray chamber	Scott double-pass (Fisons)	none
Primary solution pump	Minipuls 3 peristaltic pump (Gilson, Middleton WI)	Model S1100 HPLC pump (CETAC)
Solution consumption (mL/min)	1.0	0.06
Injection loop (mL)	none	0.5
Analysis time (min/sample)	7.5	5.0
Waste volume (mL/sample)	7.1	3.4

Tables 2 and 3 compare important analytical figures of merit that were obtained using each of the sample introduction systems. The data in Table 2, which are based upon nine blank analyses carried out over two days, indicate that the instrumental detection limits achieved with each system are quite similar. However, neither system obviates blank limitations as shown by the comparatively poor detection limits for Ni and Pb. The blank limitations for Ni and Pb also appear to affect the precision of Ni and Pb determinations in dilute aqueous standards and two representative aqueous laboratory wastes (Table 3); however, determinations made using both systems appear to agree well in most instances, even where precision is poor.

The data we have collected thus far suggest that significant reductions in waste volume and analysis time are realized, with little or no compromise in analytical figures of merit, when FI-

DIN is used in place of CPN for ICP-MS analyses. These results should also be directly applicable to ICP atomic emission spectroscopy. As we continue to examine the FI-DIN system, we intend to make further comparisons of long-term figures of merit, while also studying the susceptibility of FI-DIN sample introduction to common ICP-MS interferences, i.e., polyatomic ion spectral interferences and sensitivity suppression by matrix elements. We will also examine means of further reducing waste and analysis time by means of different flow injection protocols, i.e., smaller injection loops, shorter rinse times, and changes in valve and pump switching logic.

Table 2. Comparison of ICP-MS 3σ detection limits.

	Instrument detection limit (μg/L)	
Element	**FI-DIN**	**CPN**
Ni	1	0.5
Cd	0.05	0.05
Pb	0.8	0.6
U	0.01	0.003

Table 3. Comparison of analyte concentrations determined in nine ICP-MS analyses.

		Analyte concentration (mg/L)			
Sample	**Method**	**Ni**	**Cd**	**Pb**	**U**
10 mg/L Std	FI-DIN	10.1 ± 0.9	10.2 ± 0.1	12 ± 1	10.14 ± 0.04
	CPN	10.2 ± 0.3	10.02 ± 0.09	9.7 ± 0.2	9.4 ± 0.2
Waste sol'n # 37	FI-DIN	0.8 ± 0.2	1.31 ± 0.01	1.8 ± 0.3	3.24 ± 0.03
	CPN	0.79 ± 0.05	1.34 ± 0.03	1.58 ± 0.06	3.06 ± 0.09
Waste sol'n # 40	FI-DIN	0.38 ± 0.03	0.0656 ± 0.0005	0.77 ± 0.06	0.613 ± 0.006
	CPN	0.37 ± 0.09	0.073 ± 0.008	0.72 ± 0.07	0.57 ± 0.02

SOIL DISSOLUTION FOR RADIOCHEMICAL ANALYSES

Dissolution is a vital aspect of sample preparation for environmental radiochemical analyses of soils. The traditional laboratory techniques[6,7] of high temperature fusion and prolonged acid digestion are time consuming. In addition, they both generate large quantities of secondary wastes and fume hood emissions. Microwave technology has previously had limited application in the radiochemical laboratory because of constraints on sample size resulting from vessel pressure limitations. However, newer microwave systems incorporating closed vessels can

withstand pressures up to 10 MPa (1500 psi). Thus, larger sample sizes can be accommodated. We have achieved shorter processing times and reliable sample digestion while dramatically reducing secondary wastes.

We have used gross α/β measurements to compare the performance of alternative procedures for sample preparation: (1) a high-pressure microwave system and (2) a traditional procedure that uses a hot plate for digestion by repetitive acid treatment. A variety of soil types of potential interest to DOE were selected for testing, including a National Institute of Standards and Technology reference soil from the Rocky Flats Plant (SRM 4353) and several environmental and contaminated soils from selected DOE sites (labeled Con1, Con2, and Con3). Paired, two-tailed *t*-tests indicate no significant differences at the 95% confidence interval in the measurements on samples prepared from the hot plate and microwave digestion procedures for these soils; representative data[8] are shown in Table 4. In addition, the microwave procedure demonstrated good reproducibility and low blank values. In comparison to the traditional hot plate method, the acid volumes required for the microwave procedure are a factor of 20 lower, the analyst time for sample processing is a factor of 2.5 lower, and the sample turnaround time is a factor of 16 lower.

Because reactivity increases as pressure increases, these high-pressure microwave systems may make it possible to use alternative, nonhazardous solvents to leach certain contaminants from soils for analysis. We have also investigated replacing strong, corrosive acids with milder, nonhazardous complexing agents for removing plutonium from soils. While these complexing agents have been successful for the extraction of contaminants such as plutonium, as shown in Table 5, the reagents fail to totally break down the sample matrix and, therefore, are not applicable to matrix constituents such as U and Th.

Table 4. Gross α/β analyses by hot plate and microwave digestion methods.

	Alpha (pCi/g $\pm 2\sigma$)		Beta (pCi/g $\pm 2\sigma$)	
Soil type	**Hot plate**	**Microwave**	**Hot plate**	**Microwave**
SRM 4353	15 ± 5	18 ± 5	14 ± 4	11 ± 3
Fernald	9 ± 7	9 ± 5	<6	10 ± 3
Mound	22 ± 9	13 ± 7	16 ± 6	19 ± 4
Con1	320 ± 34	354 ± 35	31 ± 7	32 ± 7
Con2	174 ± 26	191 ± 26	22 ± 7	23 ± 7
Con3	183 ± 26	202 ± 27	27 ± 8	38 ± 8

Table 5. Alternative solvents for high pressure microwave digestion of soils. Soil utilized was 1 g of SRM 4353 "Rocky Flats Soil #1." Accepted value is 0.217 ± 0.016 pCi ^{239}Pu/g.

Solvent specifications	^{239}Pu activity (pCi/g ± 2σ)	Chemical recovery (%)
20 mL 1M citric acid	0.214 ± 0.020	67
20 mL 1M sodium citrate	0.237 ± 0.025	56
10 mL 2M citric acid	0.180 ± 0.044	59
10 mL 1.5M sodium citrate	0.124 ± 0.029	33
10 mL 4M tartaric acid	0.257 ± 0.055	55
10 mL 1.5M sodium tartrate	0.218 ± 0.040	68
10 mL 1M Na_2CO_3-0.1M EDTA	0.201 ± 0.014	45
20 mL 1M Na_2CO_3-0.1M EDTA	0.174 ± 0.032	36
10 mL 2M Na_2CO_3-0.1M EDTA	0.183 ± 0.044	55
20 mL 2M Na_2CO_3-0.1M EDTA	0.189 ± 0.039	62
20 mL 1M citric acid + 1 mL H_2O_2	0.238 ± 0.041	50
10 mL 2M citric acid + 1 mL H_2O_2	0.209 ± 0.037	58

MICROWAVE-ASSISTED EXTRACTION OF ORGANIC COMPOUNDS

Standard U.S. Environmental Protection Agency (EPA) methods for the extraction and analysis of semivolatile organic compounds (SVOCs) (also called the "base/neutral/acid fraction") in soil and solid waste samples typically use over 300 mL of hazardous solvents, such as methylene chloride. Microwave assisted extraction (MAE)[9,10,11,12] has the potential to reduce the amount of solvent required to 30 to 50 mL. We have studied the extraction of SVOCs from soil, sediment, and sludge samples using SW-846 Method 8270B[2] for measurement and the MAE technique for preparation of samples. In most cases, the MAE results compare favorably with the conventional extraction techniques while simultaneously allowing for reduced solvent usage.

To test the extraction of all Method 8270B SVOCs, these materials were spiked onto a blank soil (Environmental Resource Associates) and extracted at various temperatures. Three solvents were used: methylene chloride, a 50:50 mixture of methylene chloride:acetone, and a 50:50 mixture of hexane:acetone. With the spiked samples, no obvious trends were seen between extractions carried out at 40, 80, and 120°C. At 40°C, increasing the extraction time from 5 to 20 minutes increases the extraction yields; however, at 80 and 120°C this trend is not observed.

No dependence of recoveries on the microwave power setting was observed. Sample water content tends to decrease extraction efficiency for the acetone-containing solvents while increasing the extraction of polar compounds with methylene chloride. Table 6 gives the recoveries of semivolatile organic compounds by class for sonication extraction, Soxhlet extraction, and MAE with four different solvent compositions.

Table 6. Comparison of the recoveries of SVOCs using alternative extraction techniques.

Semi-volatile compound class	Compounds in class	Average percent recovery					
				Microwave-assisted extraction			
		Sonication extraction	Soxhlet extraction	CH_2Cl_2	$CH_2Cl_2 + H_2O$[a]	CH_2Cl_2 + acetone	Hexane + acetone
Alkylphenol	5	67	56	68	69	70	72
Halophenol	10	72	78	79	76	78	82
Nitrophenol	4	46	64	56	76	70	76
Phthalate	6	110	97	97	76	70	74
PAH	20	86	84	82	90	87	93
Halocarbon	13	60	70	70	81	78	82
Ether	6	72	75	72	79	77	80
Ketone	2	67	74	70	84	81	81
Sulfonate	2	66	76	24	73	69	63
Alcohol	1	69	73	72	70	71	71
Carboxylic acid	1	13	61	17	38	41	37
Pyridine	2	1	36	0	54	19	24
Amide	2	57	75	56	85	84	86
Nitrosoamine	5	64	70	60	77	77	83
Aromatic amine	12	41	57	49	71	56	54
Hydrazine	1	73	70	69	79	76	78
Azoamine	1	18	78	20	78	88	96
Nitroamine	5	84	88	86	101	95	96

[a]Water is 10% by weight of sample.

More complete data are available elsewhere.[13] Direct comparison with an 18-h Soxhlet extraction procedure using methylene chloride gives very similar results for methylene chloride:water, methylene chloride:acetone, and hexane:acetone. Methylene chloride MAE extractions yield similar results to sonication extractions with methylene chloride. Neither MAE nor sonication with methylene chloride is as efficient as the Soxhlet and MAE procedures with other solvents. A number of compounds are not extracted efficiently (particularly strongly polar materials such as benzoic acid and some amines and pyridines). However, this inefficiency is observed with both MAE and traditional extraction techniques.

The MAE extractions were carried out on soil CRM103-100 (Lot No. RQ103), which contains 15 certified compounds. This PAH-containing soil sample (Fisher Scientific/Resource Technology Corporation) is from a Superfund site located in the western United States. Extraction times of 5, 10, 20, and 40 minutes and temperatures of 40, 80, and 120°C were tested. The optimum time/temperature combination was found to be 20 minutes at 120°C. Under these conditions, the average percent recovery for the certified compounds in the reference material is 90% of the certified values with methylene chloride solvent, 113% with methylene chloride:acetone, and 109% with hexane:acetone. When 10% by weight of water is added to the solid before extraction, the methylene chloride extraction efficiency goes up to 100%, while the other two solvents decrease to around 80%. Addition of sodium sulfate does not improve yields. Experiments with different microwave power settings showed no clear trends.

Recoveries of SVOCs with MAE extraction on two quality control standards (Environmental Resource Associates) were comparable to those for most compounds extracted by traditional techniques. The low recoveries observed could be an indication of either a problem with the MAE technique or a lack of sample stability. Extraction of PAHs from a certified American Petroleum Institute separator sludge (CRM101-100, Fisher Scientific/Resource Technology Corporation) gave compound recoveries well within certified prediction intervals. Extraction of PAHs from NIST SRM 1941a, however, only yields an average recovery of about 50% of the certified value.

SUMMARY

We have investigated alternative methods for sample preparation and analysis that minimize the production of secondary wastes. Performance data on samples of interest have shown that these alternative methods yield results of comparable quality to those obtained for traditional methods. Our work has demonstrated that flow injection coupled with direct injection nebulization (FI-DIN) is less wasteful than conventional sample introduction techniques, yet critical analytical figures of merit (precision, accuracy) are uncompromised. Significant reductions in waste volume from radiological analysis have been achieved by preparing samples with a high-pressure microwave system. In addition, we have demonstrated that alternative, non-toxic solvents can be used for radiological analyses without compromising extraction efficiency. Recoveries of semivolatile organic compounds from soil, sediment, and sludge using microwave-assisted extraction compare well with those using traditional extraction techniques. Solvent usage and, thus, waste produced are decreased by an order of magnitude with microwave-assisted extraction.

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TEN SURE WAYS TO INCREASE INVESTIGATION AND CLEANUP COSTS

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ABSTRACT

Due to the interdisciplinary nature of environmental investigations, they present a unique challenge to scientists and engineers engaged in these activities. Indeed, environmental professional are often encouraged or even pressured to take actions which may test the limits of their experience and training. This can present interesting opportunities and is a large part of the allure of the environmental field. However, it also encourages a rigid adherence to "standard" procedures and provides opportunities for the misapplication of scientific principles which are beyond the individual's experience. This, in turn, increases the cost of environmental investigations and cleanup projects.

This paper will examine ten of the most common data collection and interpretation problems the author has identified in providing "second opinions" on more than two hundred environmental investigation work plans and reports. It will include a brief description of each problem, case studies to illustrate, and recommendations on how to avoid or overcome the problem. The paper should provide a useful guide for facility managers and regulators who are tasked with reviewing and authorizing environmental investigations. It may also be helpful for consultants, contractors, and others involved in planning and implementing these investigations.

INTRODUCTION

Nearly everyone involved in environmental remediation projects seems to feel that the costs are too high. Some blame the lawmakers for creating unnecessary administrative burdens in the legislation. Others blame the regulators for promulgating complex regulations with unnecessary bureaucratic procedures. Still others blame the legal system for taking advantage of the complexities. While the topic makes for stimulating conversation, those of us who are most directly affected -- the environmental professionals who work for industry, regulatory agencies, and consulting or contracting firms -- are seldom in a position to do much about the problem. Still, we complain with increasing levels of frustration about circumstances which are largely beyond our control.

While we may have little influence over the processes through which environmental projects are conducted, we often have significant control over the costs. Regardless of whether the administrative and legal components of a particular regulatory program are overly complex and largely unnecessary, the fact remains that the largest portion of the funds expended on a typical environmental investigation or remediation project goes to contract field and laboratory services. And most of the participants in a typical project have at least some influence over the scope of these activities.

This paper explores how our training, attitudes, preferences, and prejudices influence the cost of environmental investigations and of the decisions that ultimately determine the cost of the final remedy. As the title suggests, the paper describes ten issues often encountered in environmental projects which may have a dramatic impact on the investigation and cleanup costs. These issues are related more to the way we think about environmental investigations than to our choice of sampling or analytical techniques.

THE CAUSES

It is not a goal of this paper to explore the causes of the various actions that might lead to increased investigation and cleanup costs. Still, the subject is of more than academic interest to those who are ultimately responsible for the success or failure of a particular project. To the extent we are able to understand and influence the causes, we are obviously better equipped to control the costs. Consequently, the subject deserves at least some mention. Conveniently, the majority of the activities that have the most dramatic impact on investigation and cleanup costs also seem to have one or two common causes.

Many appear to be related to the differences or, more properly, to the investigator's failure to recognize the differences between the methods of inquiry that are appropriate in a theoretical or academic setting, versus those that are more properly used in the applied sciences. As students, we are taught that science is a process of discovery. We learn about the most significant achievements in our particular field of endeavor and we are encouraged to expand this knowledge base for the benefit of humankind. But few scientists leave college with any real understanding of how to apply their knowledge outside of an academic setting; this type of training seems to be reserved for engineers and technicians. As a result, scientists are tempted to borrow techniques from the academic world and to apply these methods to virtually any problem they encounter in the "real world." Unfortunately, these two worlds operate under different

priorities. And, these differences are often manifested as increased costs.

The second most common cause seems to be related to the extent to which environmental science is distinct from other scientific specialties. Due to the interdisciplinary nature of the environmental field, environmental investigations present a unique challenge to scientists and engineers engaged in these activities. Indeed, environmental professionals are often encouraged or even pressured to take actions which may test the limits of their experience and training. This can present interesting opportunities and is a large part of the allure of the environmental field. However, it also encourages a rigid adherence to "standard" procedures and provides opportunities for the misapplication of scientific principles which are beyond the individual's experience. This, in turn, increases the cost of environmental investigations and cleanup projects.

THE PROBLEMS

Inappropriate Statements of Objectives. Every investigation that has the potential to lead to costly cleanup actions should begin with a clear statement of objectives to provide a target for the sampling approach. Put simply, the sampling objectives are a statement of the problem that must be solved or, in scientific terms, the hypothesis the investigator intends to test. Unfortunately, the majority of sampling plans fail to accomplish this simple task. Failure can usually be traced to one of two problems. Either the author of the plan is confusing the "what" or "how" of the sampling activity with the "why," or he really doesn't understand the objectives of the study. In the first case, the stated objectives may read something like this:

> "The objective of this study is to drill a monitoring well network around the landfill and to sample the wells quarterly for heavy metal contaminants."

Here we are told "what" will be done, but given no indication as to "why" the study is being conducted. The goals of the study are not provided.

On the other hand, an investigator who knows what a statement of objectives should look like, but who doesn't really understand the objectives of a particular study, might say:

> "In this study, we will determine whether contamination is present by collecting and analyzing ground-water samples, using statistical methods to compare background values with the area of suspected contamination."

This is a far more subtle problem. To most technical people not familiar with the project, this may seem to be an entirely acceptable statement of objectives. We are told that the study is intended to determine if contamination is present. However, that may or may not be the real objective of the study. In other words, the goal of the investigator may not necessarily be the goal of the program. At best, the objective stated in the second example is probably only a part of the program objective, which may be something like:

> "To determine whether releases of hazardous wastes or constituents have entered the environment at levels above the federal Maximum Contaminant Levels (MCLs) for drinking water supplies."

If so, the investigator who adopts the more generic objective of comparing sampling data to background levels may be doing his client/employer a disservice, since it is entirely possible for a constituent to be present above background levels but below the applicable MCL. Therefore, a properly crafted statement of objectives should clearly establish the decision criteria that will later be used to determine whether the investigation is a success.

Failing to Recognize the Role of Experimentation. Once we have an appropriate statement of objectives, the next step is to design an investigation to achieve these objectives. In its most basic form, this involves engineering the circumstances to test an hypothesis which has been developed from observation. This process is usually called the scientific method.

Scientists are taught that objectivity is the most fundamental precept of the scientific method. They must be prepared to take failure in stride. When one approach does not prove fruitful, the scientist learns from her mistakes and tries again using a different approach.

But those who oversee environmental investigations conducted pursuant to a legal or regulatory requirement do not often respond well to failure. They have deadlines to meet, "beans" to count, budgets to account for, and other projects waiting to begin. These factors impose severe limitations on the extent to which the investigator should feel free to experiment. In short, experimentation should be confined to the project objectives. The investigator should use proven methods to answer a particular question or set of questions, leaving the use of innovative research techniques to the academic community. Unfortunately, the investigation process offers abundant temptations to turn even the simplest projects into significant scientific works.

A few years ago, a client was convinced by an eager contractor to try a new and improved analytical method that promised to provide lower detection limits, albeit at a much higher cost. The client viewed the method as an opportunity to demonstrate to the regulators that the company was environmentally proactive, that their policy was to exceed the regulatory requirements. As expected, the regulators agreed to the new approach, provided that a substantial number of verification samples would be analyzed using the traditional method, further increasing the cost.

The method exceeded expectations. It provided detection limits in the parts per trillion range for constituents that would not normally be detected below a few parts per billion using conventional techniques. But the client will not be receiving any awards for innovation. Instead, he will be spending additional money conducting a risk assessment to demonstrate that the constituents -- which could probably be found at the same levels in the polar ice caps if anyone cared to look -- do not pose a threat to human health or the environment.

Failing to Consider Site-Specific Factors. While the researcher who operates in a laboratory environment seeks to control all of the conditions of the experiment, the investigator must work with what he has been given. This situation can certainly make the investigation more complex, but it has the advantage that we can use the available information to eliminate some alternatives, thereby reducing the scope of work and the associated costs.

Unfortunately, many investigators fail to recognize site-specific factors when selecting sampling locations, field methods, or analytes. They lament their inability to control every aspect of the situation, while failing to recognize the corresponding advantages. They take a formula approach to all similar investigations.

A few years ago, a company in the metal finishing business decided to sell surplus property that had been used for a small electroplating operation. A prospective buyer hired an environmental contractor to determine whether the property had become contaminated as a result of the industrial activities. At the time, the typical approach to such investigations was to begin with a "phase I" audit of the industrial activities to determine whether a sampling investigation was warranted and, if so, to identify prospective sampling locations. However, this particular contractor was in the sampling and remediation business and, apparently, had no interest in conducting any of these preliminary activities. The

contractor ignored the available site-specific information and proceeded directly to a sampling program.

In the absence of any historical information to help select appropriate sampling locations, the investigators simply divided the site into a grid and obtained shallow soil samples at the intersection of each grid line. They were not equipped to sample within the building, so they further limited their sampling locations to those grid intersections on the remainder of the property. Most of this area was occupied by an asphalt parking lot.

Without the benefit of historical information on past chemical management practices, they elected to analyze the samples for a wide range of constituents. The result was that nearly every one of the shallow soil samples obtained from beneath the asphalt parking lot was found to contain petroleum constituents. As a result, the contractor's report to their client recommended a multi-million dollar cleanup, at a property that was on the market for approximately $800,000. A more careful review of the data revealed that the samples had contained pieces of asphalt pavement which was the source of the petroleum constituents.

Using Random Sampling Inappropriately. The investigators in the previous example should have used the available information to select biased sampling locations and appropriate analytes. Unfortunately, many inexperienced scientists and engineers mistakenly believe that one must obtain only random samples in order to ensure the integrity of the data. Presumably, the goal is to reduce the influence of the investigator's expectations on the outcome of the investigation. This is certainly a valid concern, and random sampling is an essential component of most environmental investigations. But it must be used appropriately. It is reasonable to assume that a sufficient number of random samples will provide data which are representative of the population/area as a whole. However, when the "population" is not correctly defined, random sampling can unnecessarily add to the investigation costs and can even be used to intentionally deceive in a properly crafted study.

A few years ago, I attended a workshop in which EPA personnel were to learn how to oversee environmental sampling investigations. Following several days of lectures, the participants were divided into groups and asked to design a sampling strategy to determine whether contaminants had entered the soil surrounding a concrete container storage pad. The workshop leader asked my group, in confidence, to design a strategy that would be unlikely to achieve the desired results.

An experienced investigator would probably have suggested that several random samples be obtained from biased locations which the investigator felt were most likely to have been impacted by a release. These locations would have been selected based on runoff patterns and evidence of staining or loss of the integrity of the concrete pad. This program might also have been supplemented with random samples obtained from the general vicinity.

Our proposed approach was limited to random sampling around the perimeter of the pad. I presented this approach to the audience, stressing the scientific "validity" of random sampling. After I finished my pitch, the workshop leader asked the participants to critique the approach. Not one of the more than 100 regulators could find a flaw in our strategy. To the consternation of the leader, they generally agreed that ours was a valid approach, despite that fact that not one of our random samples happened to be located in one of the areas most likely to have been impacted by a release.

Collecting Too Many Samples. Before the advent of the personal computer, the scientific method served as an outline for experimental design. It encouraged the investigator to collect as much data as were necessary to support or refute a specific hypothesis. However, the computer enables investigators to screen large quantities of data in search of hypotheses. This encourages investigators to collect large quantities of data. Needless to say, those who pay the bills do not often view this as a change for the better.

About seven years ago, I attended a workshop to find out more about the application of geostatistics to environmental investigations. Geostatistics have been used for many years to characterize ore deposits and for other traditional geological investigations. They include a variety of techniques, most of which are based on the premise that the characteristics of interest vary spatially. Since environmental data, including chemical data, are usually consistent with this premise, I expected to acquire some valuable new tools that would help me in my work. I was especially hopeful, given that the instructors were consultants who claimed to specialize in using geostatistics for environmental investigations of industrial sites.

It was a three-day program. The morning of the first day consisted of an overview of geostatistical tools. We were told that one of the best uses of geostatistics is to help design sampling programs. The first step is to obtain real data using random data collection techniques. A sampling strategy is then developed by using geostatistical tools to evaluate these data.

Since many environmental investigations begin and end with the collection of random data, I immediately began to question whether this approach would be cost-effective. The bad news came later the same day when we learned that, for a simple ground-water investigation, the instructors recommended installing a preliminary monitoring well network consisting of between 50 and 100 wells placed at equal intervals on a grid. In theory, data obtained from these wells would be used to design a permanent monitoring well network.

At the time, most simple ground-water investigations employed far fewer than 50 wells [new direct sampling techniques developed over the past few years have overcome some of the obstacles, making this method more attractive]. The simple fact that most customers of investigation services are unwilling to pay the cost of such an extensive preliminary effort, forces the investigator to pursue more cost-effective alternatives. Not the least of these is the use of professional judgement in lieu of random sampling techniques, as discussed previously.

Using Inadequate Quality Control. Assuming the investigator has a clear statement of objectives and has designed a sampling strategy to collect the right kind and amount of information to achieve the objectives, the next step is to make sure the data are of sufficient quality. Fortunately, most investigations conducted pursuant to a regulatory requirement are driven by a variety of guidance documents that specify minimum acceptable quality control procedures. However, far too many investigators seem to feel that these procedures do not apply when the investigation is not immediately subject to regulatory scrutiny. In addition, some regulators apparently feel that investigations conducted by, or on behalf of the regulatory agency should not be subject to the same level of control.

The most disturbing example in the authors experience occurred during a Sampling Visit conducted as part of the RCRA Facility Assessment of an industrial facility in the northeast. Facility representatives watched in disbelief as a contractor acting on behalf of the regulatory agency poured fuel into a gasoline-powered auger as it sat in the borehole, then later obtained a sample from that same boring to be analyzed for petroleum constituents.

Using Inappropriate Decision Tools. Assuming the investigation is well planned, carefully executed, and properly documented, the next step is to examine the data to determine whether it supports the objectives. This process typically involves the use of a decision criterion. Perhaps the most common approach is to compare the data to some

reference, such as a regulatory standard, background samples, or, in the case of naturally-occurring substances, the "normal" range of concentrations for the constituent in the medium of concern. Each of these methods can provide valuable insights, but the investigator must be careful to recognize that each method has limitations. Problems most often arise when the investigator allows his expectations to influence how he uses these decision tools.

A few years ago, representatives of a state regulatory agency visited one of our client's facilities and obtained soil samples to determine if an abandoned landfill on-site should be added to the National Priority List. The investigation was flawed from the outset. The strategy was to compare soil samples obtained from two areas: one within the landfill and one from a nearby "background" location. Unfortunately, the regulators elected to sample within the upper few inches of the soil surface, even though they had been told that the landfill was covered with a one-foot thick, natural clay cap comprised of soil from an undisturbed, wooded area of the facility. Consequently, one would not expect that they would find any indication of contamination.

But that minor obstacle did not deter this sampling team. They simply adopted an innovative way of analyzing the data: the democratic method. Basically, their reasoning went something like this. The background samples, by definition, represent the normal range of concentrations one would expect to find in soil samples from this area [begging the question]. Therefore, they concluded, if any of the samples from the landfill area exceed the highest reading from the background area, the landfill must be contaminated. The greater the number of samples that exceed background, the worse the contamination.

It seemed like a sure-fire approach, but they still had to look long and hard to find a problem at this particular site. Eventually, they discovered that barium was slightly higher in some of the landfill samples than in any of the "background" samples. Even though they had no reason to suspect that barium would be present in the landfill, and the levels were well within the natural variation in soils, the regulators concluded that the area was contaminated. They apparently ignored the fact that the background samples exceeded the highest reading taken from within the landfill area for every other constituent measured. In other words, if these were "blind" samples, the same reasoning would have led them to conclude that the background area was contaminated.

Misuse of Statistics. Perhaps the most common way to look for meaningful differences between data sets is to use statistical

tools. Most scientists and engineers had at least one basic course in statistics and can perform simple statistical calculations from memory. In addition, procedures for using more sophisticated or complex techniques are readily available from a number of sources for use on a personal computer.

Entire books have been written about ways in which statistics can be used to mislead or deceive. Fortunately, most environmental issues which may provide an opportunity for the intentional misuse of statistics do not offer sufficient motive to entice most environmental professionals into committing such an act. Consequently, when environmental professionals misuse statistical tools, it is most often out of lack of knowledge.

One of the reasons that statistics are so often misused, is that statistical procedures are so easy to use. Most environmental professionals, engineers in particular, are fairly proficient at mathematical calculations. Since statistics generally require only rudimentary math skills, they pose no great challenge to the environmental professional. Therefore, difficulties most often arise when interpreting the results of these calculations.

One of the most fundamental issues is the concept of significance. For example, we say that differences between two data sets are significant if they exceed some statistical threshold. But, what do we mean by significant? To the statistician, significance is an inherent property of the numbers we use to represent the data. The particular attribute these numbers represent is of little or no consequence. In other words, one set of numbers can be significantly higher than another set of numbers whether they represent color intensity, chemical concentrations, or age. But environmental professionals sometimes try to attribute more meaning to these differences than the statistical method is capable of distinguishing. In other words, they attempt to use statistics as a surrogate for professional judgement.

A few years ago, one of our clients called in desperation. He had hired an engineering firm to oversee the RCRA closure of a hazardous waste storage tank. Consistent with the state regulations, the engineer in charge of the project had used a statistical comparison to background to determine whether releases from the tank had entered the underlying soil. Unfortunately, he had made a small but extremely important error in identifying sampling locations. Rather than collecting background samples from locations that were randomly distributed around the tank area, he chose a "background" area of approximately the same size as the former

tank pad and obtained all of the so-called background samples from within that area.

By itself, this mistake was not sufficient to have created a problem. But it created an opportunity for the engineer to misuse the data. As any soil scientist knows, measurements of almost any soil attribute from samples taken from two different locations are bound to exhibit some degree of statistically significant variation due to the high degree of variability inherent in natural soils. Through the use of statistics, we can identify these differences, but no statistical procedure can tell us the reason for these differences. For that, we need professional judgement.

As expected, the engineer in our example, identified some statistically significant differences between the two data sets. To the practiced professional, these differences were clearly attributable to natural variability. They all involved differences in the concentrations of naturally-occurring chemicals. Some of these chemicals were found at higher concentrations in samples taken from the background area. Others were found at higher concentrations in the samples taken from the tank area. But all of the levels were within the range of concentrations that we would expect to find in natural soils. In addition, none of the chemicals found at statistically higher levels in the tank area were known to have been managed in the tank. Unfortunately, the engineer failed to recognize these important factors and chose instead to base his conclusion on a fundamental misunderstanding of the limits of the statistical method. In short, he concluded that any chemical found at statistically higher levels in the tank area must indicate a release from the tank. He ignored the data showing statistically higher levels of some constituents in the background area.

Unfortunately, the regulator who reviewed the report shared the same misconceptions about the limits of the statistical procedure. She agreed with the engineer's conclusion and required that the facility "clean up the contamination." Following months of negotiations, another regulator finally reversed this decision. But, he based the reversal on the fact that the chemicals in question had not been managed in the tank. He refused to accept the limits of the statistical method as a valid explanation.

Failing to Recognize the Practical Limits of Inductive Reasoning. From grade school through our undergraduate studies we learn to interpret the world in terms of principles, laws, and theories. This approach encourages basic deductive reasoning. In graduate school, scientists begin to focus more on inductive methods. In practical terms,

this means that we are initially taught to solve problems by looking at data in terms of what we know about the world. But the more education we receive, the more we are encouraged to look at data in terms of what it can tell us about the world. Both approaches are effective when used in the proper context and most problems are efficiently solved using a combination of the two.

One of our clients owns industrial rental property. The ground water underlying this property has come to be contaminated with chlorinated organic solvents. To determine which tenant was responsible for the release, our client asked us to calculate the age of the ground-water plume. We approached the problem using classic deductive reasoning. We developed several methods for estimating the age of a plume, each based on sound scientific and/or mathematical principles.

For example, one of our methods was based on the premise that the age of a release can be calculated if: a) the plume is traveling at a constant velocity, and b) we know the distance between the source and the location of the plume on a specific date. Using field data, we were able to demonstrate that the plume at this particular site was traveling at a constant velocity and we knew the location of the plume on several dates. As a result, the argument is inherently valid. The only question then is whether our measurements are accurate (i.e., whether the conclusion is also true or correct).

By combining the date of the release calculated using this method, with dates calculated using several other methods, we arrived at a range of possible dates. We were also able to develop statistical data to identify the most likely date and to assign probabilities to a particular tenancy.

The tenant who was implicated through our efforts, hired a professor from a well-known university to render an opinion. The professor used an inductive approach. He began by examining the data for trends or inconsistencies. He discovered that the velocity of the plume which would have been predicted from aquifer characteristics (e.g., pump test data) was greater than the measured velocity of the plume.

There are several possible explanations for this observance. For example, the constituents of concern may have been traveling through the aquifer more slowly than the water. This is a common phenomenon known as the retardation factor. It is also possible that the predicted velocity of the plume is less accurate since it is based on indirect measurements, while the actual velocity of the plume is based on direct measurements.

However, the professor assumed that both the predicted and measured velocities were accurate representations of the actual velocity. He then concluded that the differences must reflect a gradual change in velocity over time (i.e., the time between the two measurements). He then had no choice but to dismiss as inaccurate the evidence that the plume velocity had actually been constant over time. This reasoning led him to develop a different date for the release that was several months after his client had vacated the property.

The example illustrates the limitations of inductive reasoning; the argument can never be proven to be valid, but can only be shown to be possible. As in the example, the data may suggest two or more possible conclusions or explanations. The academic community responds to this shortcoming by developing new procedures to test the conclusion; the conclusion becomes the hypothesis for another series of experiments. However, outside of the academic community, few of us can afford to pay the cost of this research effort.

Dogmatism. When faced with a problem, most us respond in one of two ways. We either instantly recognize a solution and forge ahead, or we begin to analyze the problem, weighing the alternatives and trying to make an informed decision. Our response to a particular problem depends on a number of factors, including the complexity of the problem and the consequences of an inappropriate decision. But the most significant factor is often our level of comfort or familiarity with the subject matter.

The less knowledge we have about a particular subject, the more thought we are likely to give to a problem involving that subject. Conversely, as we become "expert" in a subject, solutions naturally come easier. This phenomenon is one of the reasons why we employ specialists, or consultants, when faced with an important decision involving a subject which is not our primary area of expertise.

But to what extent should we rely on consultants' advice? The answer is probably obvious. We should rely on their advice to the extent that we are convinced they really are expert in the particular subject matter and to the extent that they can be objective in formulating an opinion. Since most companies that hire outside consultants have procedures to assess their level of expertise, the second requirement, objectivity, provides more opportunities for problems.

Objectivity is influenced by two kinds of forces. For the purposes of this discussion, I will refer to them as "external" and "internal." The external forces exerted on consultants are related to their "ownership" in a particular

problem, as well as pressures from within their own firm to increase the scope of a project. As a result, the most objective consultants are often those who have the smallest investment in a problem, and the least to gain from its resolution. As long as the client recognizes these influences, he or she can assign the proper weight to a particular piece of advice.

Internal forces can be much more complex. The previous example described some of the limitations of inductive reasoning. But the deductive method also has limits. One of the most important of these is that it encourages dogmatism. As we increase our level of knowledge, we also tend to increase our comfort level with a particular subject. Most of us are able to temper this with a healthy amount of self-doubt. But a few people are able to convince themselves that they cannot make mistakes.

This attitude complements the deductive method. The method, or argument, consists of one or more premises and a conclusion. If the conclusion follows necessarily from the premise(s), then the argument is deductive and inherently valid. But a valid argument is not necessarily true. The dogmatist may be inclined to overlook this "minor" point, creating all sorts of valid, but completely inaccurate conclusions.

In the previous example, I described a consulting assignment in which we attempted to establish the age of a ground-water plume. I described how a professor had used the inductive method to derive what I believe is an erroneous conclusion. Ironically, the professor had also used the deductive method earlier in the project and had experienced problems with that method as well.

In a preliminary report, we had hypothesized that the plume was only a few years old. We based this opinion on the relative absence of known degradation products of the contaminant, trichloroethene.

The professor disagreed. Apparently, in his research, he had found no evidence that trichloroethene degrades under aerobic conditions: a conclusion derived from inductive reasoning. He reviewed the available data for this project and concluded that conditions within the aquifer were aerobic. He then transformed his inductive conclusion into one of the premises for a deductive argument that might be restated as follows:

- Trichloroethene does not degrade under aerobic conditions.
- The conditions in this aquifer are aerobic.

- Therefore, trichloroethene could not possibly degrade in this particular aquifer.

His argument was valid because the conclusion follows necessarily from the premises. Unfortunately, his first premise was wrong. Other researchers have been able to demonstrate aerobic degradation of trichloroethene in laboratory experiments. More importantly, three years after the professor gave this opinion, the predominant chemical within the plume is no longer trichloroethene. At some locations, one of its degradation products, dichloroethene, is present at concentrations more than twice as high as the levels of trichloroethene.

SUMMARY -- THE CURE

The solutions to each of the ten common problems described above lead fairly neatly to the following ten-step process to control the cost of environmental investigation and cleanup projects:

1. Begin each project with a clear and accurate statement of objectives.

2. Design the investigation to achieve the objectives using proven and widely accepted methods.

3. When selecting sampling locations, field methods, and analytes, consider site-specific factors.

4. To the extent possible, use existing information to identify sampling locations which are most appropriate to achieve the objectives, then obtain representative samples from those locations.

5. Collect only enough information to achieve the objectives.

6. Use adequate quality control protocols to preserve the integrity of the data.

7. When evaluating the data against the objectives, use an appropriate decision criterion.

8. Recognize the limits of statistical decision tools.

9. Structure your conclusions as deductive arguments, then evaluate their validity as well as their accuracy.

10. Be open-minded to new ideas and unexpected results.

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THE TCP TEST FOR METALS -- SELECTION OF EXTRACTION FLUID

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Resource recovery facilities produce ash which are heterogeneous mixtures of inorganic and biological materials and a variety of chemically inert substances such as glass and ceramics. The decision whether a waste material will be disposed of as a hazardous or nonhazardous waste depends upon the results of tests of several EPA-approved analytical methods. Since the cost for disposal of waste designated as hazardous is many times the cost for disposing of the same amount of nonhazardous material, the economic, the public health and safety realities of decisions about the nature of waste disposal places an enormous burden upon the validity of the test data.

The Toxic Characteristic Leaching Procedure (TCLP, USEPAMethod 1311) for metals is often the determining factor whether a solid waste will be classified as hazardous or nonhazardous. Cd and Pb, with regulatory limits of 1.0 and 5.0 $ug.g.^{-1}$ respectively, are the elements that often determine the waste characterization. The TCLP method for the determination of metals in waste consists of five sequential procedures:

1. Waste characterization (sections 7.1.1 and 7.1.2)
2. Waste homogenization (section 7.1.3)
3. Selection of extraction fluid (section 7.1.4)
4 Sample preparation (sections 7.2.10 to 7.2.12)
5. Analysis (section 7.2.14)

The uncertainty and variability inherent in any physical or chemical test procedure cannot be completely eliminated. For instance, there is always error associated with the sample preparation and instrumental measurement of for any metal. There are established statistical procedures to quantify, report and interpret these types of errors. More difficult to measure and evaluate are the uncertainties associated with selecting an aliquot of the waste material (#1 above) and how differences in the way laboratory personnel interpret and conduct sections of the TCLP protocol (#2 and #3) can affect the final measured analyte concentration.

The New Jersey Departments of Environmental Protection and Transportation, in collaboration with the New York State Energy Research and Development Authority and the Port Authority of New York and New Jersey, is evaluating whether bottom ash from the Warren County, New Jersey resource recovery facility can be beneficially reused by incorporating it into asphalt to be used as road paving material. This much is generally understood by the vast majority of the resource recovery, waste management and laboratory testing communities concerning the application of the TCLP procedure for metals analysis:

- various types of waste streams (ash) from the same waste management facility (bottom, fly or combined) will yield different results
- different mean particle sizes of the same type of ash may yield different results

- application of lime or other treatment technologies can affect TCLP results
- some portions of the TCLP method offer the laboratory analyst discretion in how the method is carried out
- if extraction fluid #1 is selected, bottom ash will likely test nonhazardous for Pb and Cd
- if extraction fluid #2 is selected, bottom ash will likely test hazardous for Pb and Cd

As part of this research and development study, the following questions regarding the application of the TCLP procedure for the determination of metals in ash from the Warren County facility were examined:

- does combined ash behave differently from bottom ash?
- does ash with a mean particle size of <9.5 mm. behave differently than ash with a mean particle size of <1 mm.?
- what are the variables in the extraction fluid selection section of the TCLP procedure?
- do these affect the selection of the extraction fluid?

Archived samples of bottom and combined ash produced at the Warren County (NJ) resource recovery facility in December 1993, and bottom ash obtained from this facility in December 1994 were used in this evaluation study. Samples of various particles sizes, ranging from 0.375 inch mean mass diameter to those prepared in a ball mill (<1 mm. size), were obtained. Multiple aliquots of each ash type were treated according to section 7.1.4 of the TCLP method that determines the selection of the appropriate extraction fluid. The pH was monitored at regular intervals throughout the procedure, various methods and gradients for heating and cooling were employed, and the pH after reaching room temperature recorded over time. Elemental determinations were also made. Tests were preformed on aliquots of the same sample by several analysts and by different laboratories.

Data will be presented on the results of our study and suggestions offered to the USEPA regarding potential modifications to the TCLP method to improve data precision and ultimately the accuracy of waste characterization.

Quality Assurance

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DATA QUALITY -- ASSESSMENT OF DATA USABILITY VERSUS ANALYTICAL METHOD COMPLIANCE

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ABSTRACT

The quality of analytical data used throughout an investigative project is generally determined by assessing the data usability and evaluating the compliance of the data with the analytical protocol. Data usability is typically determined by assessing quantitative and qualitative quality control measures against predetermined criteria, collectively termed the Data Quality Objectives (DQOs), and by determining how well the data can meet the intended use of the analytical measurements. Compliance to the analytical protocol is determined by evaluating the data against contractually mandated reporting and QA/QC criteria.

In many cases, the extent and determination of the usability of the analytical data is a much more important indicator of data quality than the contractual compliance of the analysis performed to generate the data. Assessing the contractual compliance of the analytical data is fairly straightforward, while determining data usability often requires a high degree of professional judgement. Lack of compliance to the analytical method may prevent data usability from being assessed. However, because most environmental data users are non-chemist professionals, far too often contractual noncompliance is unknowingly equated to poor or unusable data. For example, if an organic analysis method blank was not performed as required by the method, but the associated samples contain no positive results and exhibit excellent surrogate recoveries, then the analysis is contractually noncompliant; however, the data usability is not impacted. The authors do not want to imply that noncompliant analytical data is acceptable. Rather, professional judgement must be exercised to determine if the noncompliance impacts data usability.

Conversely, compliant data may not always be usable data. For example, a project DQO might be to determine the presence or absence of methylene chloride at greater than or equal to 10 µg/L in a ground water sample collected from a location downgradient of a source area. Methylene chloride is a common volatile analysis laboratory contaminant due to its use as a semivolatile analysis extraction solvent. The volatile analysis method blank associated with the ground water sample analyzed for this project detected methylene chloride at 50 µg/L, which is contractually compliant and acceptable by Contract Laboratory Program (CLP) analysis protocol. However, the ground water sample volatile analysis detected 20 µg/L of methylene chloride. In this case, the data quality and usability of the analysis have not met the DQO since the method blank analysis suggests that the sample result may have been due to external contamination.

This paper will present a summary of the key issues that must be evaluated to determine when noncompliance to the analytical methods affect data usability.

Planning for Radiochemical Data Validation as Part of the Sample and Analysis Collection Process

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ABSTRACT:

The sample and analysis environmental data collection process requires the coordinated efforts of many individuals. An integral part of this process is validation of the data including the preparation of a validation plan. This plan should integrate the contributions and requirements of all stakeholders and present this information in a clear, concise format. To achieve this goal, the validation plan should be part of initial planning, e.g., DQO(Data Quality Objective) process. Placing validation in the upfront planning process will insure that data reliability and technical defensibility are determined in a cost efficient manner.

Radiochemical validation planning includes developing standard operating procedures and tests for evaluating the data for detection, unusual uncertainty and quality control. The validation tests of detection determine the presence or absence of important analytes while the tests of unusual uncertainty verify that the data are consistent with the statistical confidence limits for error established during the DQO process. The radiochemical tests of quality control serve two purposes. In one application, they establish that the laboratory measurement system was in control during the testing and that the data reporting requirements were met. In a second application, they demonstrate if the sample system is in control (performs within historical limits of similar samples).

The validation plan is an integral part of the QAPP (Quality Assurance Project Plan) and should be included as either a section within the QAPP or as a stand alone document attached as an appendix. The validation plan should be approved by an authorized representative of the project for whom the work is being done, the validation group performing the validation, and any other stakeholder whose agreement is needed (e.g., regulators) for the assessment of the data.

INTRODUCTION

Validation is the process of examining the available laboratory data to determine if an analyte is present or absent in a sample, and if the overall unusual uncertainty is within project limits. Validation is frequently preceded by verification, a related but distinctly different process. Verfication determines if the laboratory carried out all steps required by any contractual requirements governing the analysis and the reporting of the data. After data are validated, they are forwarded to the project staff with the validation report. The project staff integrates the laboratory data, current field information and historical project data to assess overall data quality and use in the decision process by comparing it to the original project Data Quality Objectives (DQOs) (ref.1,2,3). Verification and validation are the performance measures of laboratory data quality. Validation and assessment assure the technical strengths and weaknesses of the overall project data are known, and establish the technical defensibility of the data.

Environmental data operations require the coordinated efforts of many individuals. The validation plan should integrate the contributions and requirements of all stakeholders and present this information in a clear, concise format. To achieve this goal, validation planning should be part of the initial planning process, e.g., DQO process, to assure that the data identified as essential will be validated efficiently to determine their reliability and technical defensibility.

For radiochemical data validation there are three series of validation tests; detection, uncertainity and quality control. The tests of detection determine the presence or absence of the specified analytes, and the tests of unusual uncertainty verify the data are consistent with the statistical confidence limits for error established during the DQO process. The tests of quality control serve two purposes. In one application, they establish if the laboratory measurement system is in control during the analysis, and that the data reporting requirements are met. In a second application, the quality control tests demonstrate that the analytical system (including sample preparation, etc.) is in control. This means that the total process is performed within historical limits indicating a reasonable match among method/matrix/analyte, and that routine expectations of data quality are appropriate.

The verification process, completed before the validation process, compares the laboratory data package to a list of requirements associated with each sample. These requirements are generated by two separate activities. The first activity is the preparation of a contract for analytical services. The second activity is the development of the project sampling and analysis plan with its accompanying quality assurance project plan (QAPP)(ref.4). These two activities determine, *a priori*, the procedures the laboratory should use to produce data of acceptable quality; and in addition, they determine the content of the analytical data package. Verification compares the material delivered by the laboratory against these requirements and produces a report that identifies those requirements which were not met (*called exceptions*). Verification exceptions normally identify:

- required steps not carried out by the laboratory (i.e., correction for yield, proper signatures, etc.)
- analyses not conducted at the required frequency (i.e., blanks, duplicates, spikes, etc.)
- procedures that do not meet pre-set acceptance criteria (i.e., laboratory control sample recovery, etc.)

The radiochemical validation process begins with a review of the verification report and laboratory data package to rapidly screen the areas of strengths and weaknesses of the data set (i.e., tests of quality control). It continues with objective testing of environmental sample data to confirm the presence or absence of an analyte (tests of detection), and to establish the unusual uncertainty of the measurement process for the analyte (tests of unusual uncertainty). Each data point is then assessed as to its integrity and dependability in the context of all available laboratory data.

VALIDATION PLAN

The validation plan is an integral part of the QAPP and should be included as either a section within the QAPP or as a stand alone document attached as an appendix(ref.5). The validation plan should be approved by an authorized representative of the project for whom the work is being done, the validation

group performing the validation, and any other stakeholder whose agreement is needed (e.g., regulator).

Identification of key analytes and samples that drive the project decisions is part of the validation plan. In addition, the plan should define the association of required quality control samples with project environmental samples. For projects with large numbers of samples relying on manual validation of data, the plan may identify a statistically derived sub-set of samples utilized to estimate the reliability of the larger data set. This will result in significant cost savings. As automated systems are developed, this strategy should be dropped in favor of validation of all samples because the cost advantages of smaller validation sets will be eliminated.

During the validation planning process, planners should identify those samples/data sets that have less rigorous standards for data quality and defensibility. The plan should then specify that fewer validation tests be applied to those sets of data or establish relaxed performance criteria. Site-specific data validation guidelines should establish a protocol to prioritize the data validation requirements (i.e., which validation tests are most important). This can eliminate unnecessarily strict requirements that commit scarce resources to the in-depth evaluation of data points with high levels of acceptable unusual uncertainty. For example, results very much above or below an action level may not require rigorous validation. Even relatively large unusual uncertainty would not effect the ultimate decision or action.

The data validation plan should:

- provide sufficient detail about the project technical and quality objectives in terms of sample and analyte lists, limits of detection for the analyses, and level of acceptable unusual uncertainty on a sample/analyte specific basis (where appropriate);
- specify the necessary validation tests (quality control, detection, and unusual uncertainty) and performance criteria deemed appropriate for achieving project objectives; and
- assure that qualified data are properly identified and documented.

The data validation plan should include the following sections:

- title and approval sheet,
- table of contents,
- distribution list,
- quality objectives and criteria for measurement data,
- validation narrative,
- requirements for verification, validation and reconciliation with DQOs,
- reporting,
- training requirements/certification, and
- documentation and records.

A section of the data validation plan should specify the following technical and quality objectives:

- the level of measurement system performance (tests of quality control),
- regulatory decision level and desired analytical measurement level (tests of detection), and
- level of analytical unusual uncertainty at the analytical measurement level (tests of unusual uncertainty).

A section of the data validation plan should address the validation tests, including:

- the quality control samples that apply to the validation effort,
- the specific quantitative validation tests to be used, and
- the statistical confidence intervals and/or fixed limit intervals applied to each of the validation tests.

The reporting and documentation section identifies the priority rating system applied to the set of validation tests used to qualify specific data. This system provides guidance to the validator concerning which of the quality issues (i.e., validation tests) are considered the most important in determining data reliability. At one extreme, this system can be very prescriptive and assign scores and weighting factors for each validation test and a method of summing the results to determine which if any, qualifier should be used. At the other extreme, the validation plan can rely solely on the professional judgment of the validator to determine the qualifier. When deciding which system to use, the planners should attempt to devise the least prescriptive approach that would allow two qualified and independent validators to reach similar conclusions about the data.

The plan should identify documentation and records which should be included in a validation report for the project or task. The reporting format should also be specified. Disposition requirements for records and documents related to the project should be specified.

The validation plan should identify procedures for non-conformance reporting which detail the means by which the laboratory communicates non-conformances against the validation plan. This should include all instances where the *a priori* analytical data requirements and validation requirements established by the DQO process and validation plan, respectively, cannot be met due to sample matrix problems and/or unanticipated laboratory issues (i.e., loss of critical personnel or equipment failure).

CONCLUSION

Data validation is part of the overall data collection process that accompanies most environmental decisions. The primary reason data validation is performed is to provide data that are of known quality and are technically defensible that are integrated with other sources and for a final assessment supporting a decision. Project specific data validation requirements that drive a decision or that are part of a statistically derived set of samples are utilized to estimate the reliability of a larger data set are decided upon during the DQO process. These requirements are documented in the data validation plan. If requirements are too stringent or extensive, the process may commit resources to the evaluation of inconsequential variables. The strategy developed during data validation planning is essential to support acceptable use and integration of field screening and analytical approaches with more expensive and cumbersome laboratory measurements. The acceptance and integration of alternative screening and measurement techniques is a key component of design optimization, e.g. DQO process, and cost-effective environmental program decisions.

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A New Calculation Tool for Estimating Numbers of Samples

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ABSTRACT

Some of the most frequently asked questions involving environmental sampling and analysis are: (1) What kinds of QC samples are needed? (2) How many QC samples are needed? and, (3) How many environmental samples are needed? Answers to the first question are facilitated by using an inexpensive expert system which is part of "***Practical QC***" (a program available from ACS Software). Answers to the other questions are derived by statistical equations and your specific requirements (i.e., Data Quality Objectives). However, although the equations have been known for years, they are not frequently available in a convenient form for use by chemists, project managers, samplers, regulators and others, who would use this information more often if they could understand it and if it was in an easily used form. "***DQO-PRO***" is a series of programs with a user interface like a common calculator and it is accessed using Microsoft® Windows™. ***DQO-PRO*** provides answers for three objectives: (1) determining the rate at which an event occurs, (2) determining an estimate of an average within a tolerable error, and (3) determining the sampling grid necessary to detect "hot spots". ***DQO-PRO*** facilitates understanding the significance of DQOs by showing the relationships between numbers of samples and DQO parameters such as (1) confidence levels versus numbers of false positive or false negative conclusions; (2) tolerable error versus analyte concentration, standard deviation, etc., and (3) confidence levels versus sampling area grid size. The user has only to type in his or her requirements and the calculator instantly provides the answers. For example, if you provide numbers of samples that you have (or plan to take), the calculator estimates various confidence levels or, if you provide confidence levels (as part of your DQOs), the calculator estimates the numbers of samples you'll need to obtain those confidence levels. Switching between numbers of samples and DQO parameters such as confidence levels, standard deviations, tolerable errors, etc. is accomplished by simply leaving blank the parameter to be calculated or by selecting a button on the calculator. Help in the form of definitions and guidance for using the calculator is provided in hypertext windows and also in more detailed help files. When used in conjunction with newly introduced **QC Assessment Kits** that contain blanks and certified matrix spiked material, the program can effectively help project managers and data users make informed decisions and improve the planning process. The key for cost effective use is not to spend more money on more QC samples but rather to use those QC samples already available (or being planned) as part of a statistical population of QC samples. **The program is free.**

Introduction

The purpose of environmental sampling and analysis is to assess a small, but informative, portion of a population and then draw an inference about that population from the data gathered. There are an almost infinite number of samples that could be taken at any given site, so environmental samples must be collected in such a way as to be representative of the environmental area of interest. Typically, environmental samples may be taken from matrices that include water (surface waters, drinking water, ground water, industrial wastewater, etc.), soils, aqueous sediments, vegetation, air, or manufactured products (e.g., paper, waste oils, etc.). Quality control (QC) samples are used to provide an assessment of the kinds and amounts of bias and/or imprecision in the data that is obtained from the environmental samples. Thus, QC samples are used to assess the collection and measurement system in a similar way that environmental samples are used to assess the portion of the environment from which they come. Therefore, representative environmental samples are collected and analyzed to form conclusions about a particular site, and representative QC samples are analyzed to form conclusions about system that measures the environmental samples. This similarity in environmental sample usage and QC sample usage is often not appreciated or even recognized.

There are many different types of QC samples, and each is designed for a specific purpose. Some provide an assessment of bias while others provide an assessment of imprecision. In addition, some are designed to assess laboratory-based variability and others are designed to assess overall variability (both sampling and analysis). An expert system named ***"Practical Environmental QC Samples"*** (1) provides answers for the question of what kinds of QC samples to use for specific purposes but it doesn't calculate how many QC samples are needed to assure specific confidence levels. A new computer program named ***DQO-PRO*** compliments ***Practical Environmental QC Samples*** and calculates the numbers of samples (both QC samples and environmental samples) needed to resolve individual project needs. For example, ***DQO-PRO*** calculates numbers of samples needed to assure, at a selected confidence level, that a localized area of contamination ("hot spot") is not missed. It also calculates numbers of samples needed, at a selected confidence level, to estimate the average concentration of a pollutant in samples and the standard deviation or the relative standard deviation (coefficient of variation) of the method used for its analysis.

The "calculators" in this software tool are provided to assist the sampling design stage of project planning. The calculators were designed to specifically help with the final step (optimize the design for collecting data) of EPA's Data Quality Objectives (DQO) process. The DQO process is a structured way to plan data collection efforts. It was developed by the U.S. EPA Quality Assurance Management Staff (QAMS) to help decision makers define the specific questions that a data collection effort is intended to answer, identify the decisions that will be made using the data, and define the allowable risk of decision errors in specific, and quantitative terms.

The DQO process comprises seven steps:

1. State the problem;
2. Identify the decision;
3. Identify input to the decision;
4. Define the study boundaries;
5. Develop a decision rule;
6. Specify limits on decision errors; and
7. Optimize the design for collecting data.

This results in qualitative and quantitative statements that pinpoint specific study objectives, define the types of data needed, define the statistical populations the data are considered to represent, and specify tolerable risks for false positive and false negative decision errors. The calculators help the user evaluate these statements of need by determining the number of samples needed to meet three different types of study objectives. Used iteratively, the calculators will help optimize the sampling design used to complete a study. The three objectives covered by these calculators are to:

1. Determine when the frequency with which a characteristic that occurs in a population exceeds some frequency of concern (e.g., determine when the frequency of false positive measurements due to laboratory contamination exceeds 5%); [***Success-Calc***]

2. Estimate the average concentration of a target analyte in a specific medium (e.g., the average concentration of a target analyte in water or soils at a site); [***Enviro-Calc***] and

3. Determine if at least one localized area of contamination (a "hot spot") of a given size and shape exists at a site [***HotSpot-Calc***].

Initial DQO Inputs

The initial inputs include a concise statement of the problem which is being addressed, the decision(s) that will be made based on the results of the study, and all of the important parameters that are needed in order to make the decision(s). Parameter inputs may include decisions such as a list of analytes, types of sample containers needed, sample preservation requirements, analytical methods that can be used, types of QC samples needed, etc.

Define the Study Boundaries

The fourth step of the DQO process is to identify the boundaries of the study. This involves not only defining the physical boundaries of the site being investigated, but also the boundaries of the inference space, that is, defining the conceptual population represented by the sample data. Defining the boundaries of the study however, goes beyond defining the physical boundaries of the site. It also includes defining temporal boundaries, i.e., considering and

addressing the potential impacts of seasonality or other time-related considerations and how these will be addressed in the data collection process.

One of the fundamental ideas that must be kept in mind when defining the boundaries of a study is that the decisions made ultimately rest on inference. Although we talk about measuring the concentration at a site and basing our decisions on these, what we actually do is make decisions on the basis of *inferences* that are, in turn, based on *estimates*. When we analyze a sample, the result obtained is only one result out of a theoretically infinite number of possible results for a theoretically infinite number of possible analyses of that sample.

Decision Rule

The decision rule is a summary statement that defines how a decision maker expects to use data to make the decision(s) identified in DQO Step 2. In the same way that multiple decisions, for example, might pertain to multiple areas within a site, there also may be (and often are) multiple decision rules for different areas of the site or for different pollutants. Development of the decision rule involves the following three steps:

1. Specify the parameter that characterizes the population of interest;

2. Specify the action level for the study; and

3. Develop an "if...then" statement that describes the decision rule in terms of alternative actions.

The parameter characterizing the population of interest is a statistical parameter, such as the mean or 90th percentile or upper tolerance limit, for a particular analyte or measurement characteristic. For the calculators programmed in two parts of the software tool (**Success-Calc** and **HotSpot-Calc**) the parameter of interest is the individual measurement results for each sample or grid point. For the other calculator (**Enviro-Calc**) the parameter of interest is the average concentration (e.g. the average concentration of a target analyte over the entire sampling site).

Specify Limits on Decision Errors

As noted in the above discussion on defining study boundaries, decisions about a site ultimately rest on estimates of parameters of statistical populations. The true average concentration at a site is not known and is not knowable because it is the mean of an infinite population. Therefore, decisions based on the average site concentration must be made using estimates of the true site average, developed on the basis of limited sampling data for an infinite population. This introduces sampling error into the estimate that is used as the basis for decision making.

These estimates, which are based on measurement data, also have an inherent uncertainty associated with them because of random and systematic errors in the measurement process. These elements of uncertainty reflect measurement error. Because the decisions are based on estimates that contain inherent uncertainty, there is always some risk of error in the final decision.

For any binary decision, that is, a decision for which there are two possible outcomes, there are two ways to make a correct decision and two ways to make an incorrect decision. The comparison of an average site concentration with an action level is one example of a binary decision. The two possible decisions are that the site exceeds the action level or that it does not. If the true (but unknowable) site concentration does not exceed the action level, and if our estimate leads us to the decision that the site concentration does not exceed the action level, then we have made a correct decision. Likewise, if the true (but unknowable) site concentration exceeds the action level, and our estimate of the site concentration leads us to conclude that the site concentration exceeds the action level, then we have made the other possible correct decision. Thus, there is one possible correct decision for each of the two possible states of nature.

There is also one possible incorrect decision for each of the two possible states of nature. If the true (but unknowable) site concentration does not exceed the action level, but our estimate leads us to the decision that the site concentration *does* exceed the action level, then we have made an incorrect decision. Likewise, if the true (but still unknowable) site concentration exceeds the action level, and our estimate of the site concentration leads us to conclude that the site *does not* exceed the action level, then we have made the other possible incorrect decision.

These two types of decision errors are commonly referred to as false positive errors and false negative errors. To reduce the risks of false positive and false negative errors, the study design must include sufficient data collected in a statistically sound manner to adequately estimate the population parameter used as a basis for decision-making. Uncertainty due to sampling error can be reduced by collecting large numbers of samples. Uncertainty due to measurement error can be reduced by using more precise and accurate analytical methods and by performing multiple analyses of each sample and averaging the results. However, reducing uncertainty and the associated risks of decision errors increases the costs of collecting data. Therefore, one of the most important steps of the DQO process is the sixth step, in which the acceptable risks of the two types of decision errors are established.

Optimize the Design

The seventh and final stage of the DQO process is to develop and optimize the sampling design. This involves integrating the output of the previous six steps into the most cost-effective data collection design that satisfies the DQOs. At this step the final sampling design is developed and the number of samples to be collected is defined. For this step the ***DQO-PRO*** calculator tool is most helpful.

Three sampling models are addressed in ***DQO-PRO.***

1. When using ***Success-Calc*** to determine if the frequency of some characteristic in a population (such as a false positive or negative rate or the percent of a site which is contaminated) exceeds a limit or a frequency of concern, the number of samples required is driven by the confidence that the user desires to correctly conclude that the true frequency of the population exceeds the limit. Also, the number of samples is driven by the decision rule used to claim that the true frequency exceeds the limit. The minimum number of samples needed is always associated with a decision rule that does not allow any samples to contain the characteristic of concern (e.g., the analytical results for method blank samples cannot report a hit for any target analyte in order to be able to conclude that the true frequency of laboratory contamination is less than X% for that analyte). As the decision rule allows for more samples to contain the characteristic of concern (for example, 1 or more false positives) in the process, the number of samples needed to make a decision with the specified confidence increases. Given these general design considerations, the sampling design needed to meet DQOs can be developed and optimized.

2. When estimating the average concentration of a target analyte with ***Enviro-Calc*** the number of samples is driven by the magnitude of error that can be tolerated in the estimate of the average. Also, the number of samples needed is driven by the amount of confidence the user desires in the estimate of the average within the tolerable error.

3. In ***HotSpot-Calc*** the number of samples will be driven by the size of the hot spot that it is desirable to detect and the allowable error in ***missing*** the hot spot. Optimization of the sampling design for this model involves balancing total sampling and analysis costs (number of samples) against the size specified for a hot spot, the shape of the hot spot, and the acceptable risk of a false negative error.

Sampling Design

The objective of sampling is always to gather information that will allow us to answer some question or questions about a particular statistical population. In many cases, sampling objectives can be defined in terms of one of three basic conceptual sampling models:

1. Sampling to determine if the frequency of some characteristic exceeds a limit (e.g., the percent of a site contaminated or the percent of measurements that are false-positives because of laboratory contamination).

2. Sampling to estimate the average concentration of some target analyte; and

3. Sampling to estimate the minimum size of a "hot spot" that is acceptable to be missed.

The first question that must be answered when developing a conceptual model for a particular sampling application is whether the pollutant or pollutants of interest are expected to be distributed over the entire site or localized in "hot spots." Hot spots are most often associated with spills, leaks, or other similar point sources of relatively nonmobile contaminants. Hot spot sampling is used when the objective is to find these localized areas of contamination. In this model, the site is viewed as an area that consists of some number of discrete units, where each unit is either contaminated (above some level considered "hot") or not contaminated. If "hot spots" are found, they may be cleaned up, and the rest of the site is typically left alone. An analogous sampling problem would be sampling to determine if there are any black beans in a bowl full of red beans.

In contrast to the "hot spot" model, the other two conceptual models are applicable to situations where it is more likely that the pollutants of interest are distributed over the entire site. In these models the objective is to determine the average concentration for the site as a whole or to determine the percent of a site that is contaminated. Because the resulting characterization is of the site as a whole, the remediation strategies for these two cases also apply to the whole site: either the whole site is cleaned up or it is not. These sampling models are analogous to sampling in order to estimate the average weight of the beans in a bowl.

The choice of an appropriate sampling model depends on characteristics of the site in question and upon the contaminants of interest at that site. In many cases, and particularly when little information is available about the distribution of pollutant concentrations at a site during the sampling design stage, the most cost-effective sampling strategy will be to use a phased approach. A phased approach typically involves an initial screening phase, followed by one or more definitive sampling phases. The design of the screening phase will vary, depending on the specific objectives and the specific information needed to optimize the definitive designs. Often, the screening phase is conducted using "screening methods" for sampling and analysis. Screening methods are usually amenable to on-site analysis, thus providing quick feed-back and low cost compared with off-site analyses. The trade-off for screening methods is typically lower qualitative specificity, and poorer precision and accuracy. Because screening samples are relatively cheap, one common use for them is to collect samples from a grid over the whole site, and then use the data to stratify the site for subsequent sampling. Data from a screening phase are particularly useful for developing the variability estimates used to determine the number of samples required for definitive sampling.

Success-Calc

One of the most basic QC data assessments is to determine the presence of false positive and false negative measurements in environmental analytical data. An analyte that is incorrectly concluded to be present in a sample is a false positive; these can cause regulatory and financial consequences for a laboratory's clients. One cause of false positives is misinterpretation of the identity of interfering analytes for the target analytes. When interferents are present in a sample, the method must be modified to eliminate them, but when they are present in the materials used

to prepare or analyze samples (e.g., bottles, solvents, reagents, filters, columns, detectors, etc.), their sources must be determined and the interferent removed if possible. Various kinds of QC samples (e.g., as determined from the ***Practical QC*** (1) program) can be used to determine where, in the chain of events, the interferents are contributed but the first step is to recognize their presence. Method blanks, which consist of a blank matrix similar to the samples, but without the target analytes, are used to determine overall if false positives are present in the materials and/or the process used to prepare and analyze samples (but they don't identify the source of error).

A false negative occurs when an analyte is concluded to be absent in a sample while, in reality, it is present at detectable levels. False negatives commonly occur from poor recovery of target analytes from a matrix, or from interferences that mask the target analytes. They are especially troublesome to government and regulatory personnel and also to scientists who work with risk assessments because they result in pollutants being concluded to be absent when, in fact, they are present.

Most environmental analyses are conducted in "batch" modes to facilitate cost effective analyses. In doing so, one method blank (also called a lab blank) and one or two method spikes (or matrix spikes) are typically analyzed along with about 10 to 20 environmental samples. The resulting data for all of the environmental samples in that batch are accepted or rejected on the basis of those QC samples.

When used this way, the QC data of a batch does not provide a statistically sufficient amount of information for the environmental samples. One or two QC samples, which is how these QC samples are grouped, does not provide enough information to predict the reliability of the other environmental samples that are grouped with them. An implicit assumption that the environmental samples analyzed in conjunction with a method blank and one or two spiked method blanks (or matrix spikes) do not contain false positives or false negatives because the accompanying one or two QC samples did not contain them is not necessarily correct. *Thus, the present way of assessing QC data contains a basic flaw that is not usually recognized.*

How can method blanks and method spikes (i.e., spiked method blanks) be used as representatives for the environmental sample population? The answer is to use a statistically valid number of QC samples. That number depends on the Data Quality Objectives (DQOs) of a particular sampling and analysis project. As an example, the number of QC samples needed can vary from 6 (for an 80% probability that the associated environmental samples will not contain more than 25% false positives or false negatives) to 458 (for a 99% probability that associated environmental samples will not contain more than 1% false positives or false negatives).

Success-Calc is designed to determine the number of samples needed to detect a specified frequency of some characteristic occurring in the population (e.g., the % defectives or % contamination). In an environmental program it can be used for a number of different

purposes. It can be used to design a QA program (i.e., the number of blanks and spikes needed to test for a percentage of problems in the sampling or analytical process) or it can be used to design an investigation program (i.e., the number of environmental samples needed to determine if some percentage of a site is contaminated.). This calculator does **NOT** calculate the number of samples needed to estimate the frequency at which a characteristic occurs, rather, it calculates the number of samples required to decide when the true frequency of occurrence exceeds some predefined frequency using a specified decision rule.

An important point to note is that many of the QC or environmental samples needed for a statistical population are available (or can easily be made available); they are just not presently used in this way. Thus, increased costs associated with large numbers of samples may not be necessary - they may, in fact, be minimal or even reduced with proper planning. For example, consider that a method blank is typically analyzed for each batch of samples; this results in a large number of blank samples that may be useable for a statistical population of a method and matrix when gathered over the period of several weeks or months. The key to obtaining a statistically useable population of sample data is that all significant parameters that can affect analytical method performance must remain constant. *Significant parameters include the instrumentation and method, the analyst, and the matrix.*

Approach

The approach used resolves an objective to determine if the frequency at which some characteristic (e.g., false-positive measurements or contamination at a site) occurs is greater than a desired frequency. For example, this calculator will determine the number of samples needed to determine if the true rate of false positive measurements due to laboratory contamination is greater than 5% with 95% confidence. Three pieces of information are needed:

1. The frequency of concern;
2. The confidence desired in concluding that the true rate exceeds the frequency of concern; and
3. The decision rule that will be used to conclude if the true frequency exceeds the frequency of concern.

If the frequency of concern is less than 10%, the calculator uses an equation based on an exponential-approximation to the binomial distribution that provides an approximate determination of the number of samples required (N). If the frequency of concern is greater than 10%, an iterative approach is used that calculates the confidence achieved for some specified number of samples. In this case, the equation used takes the number (N) a user enters and calculates the confidence (for a specified decision rule) with which one can correctly conclude that the samples could come from a population that has a higher frequency of occurrence than desired. This approach was used instead of an exact calculation to show the user the tradeoffs of modifying the numbers of samples, the decision rule, and the desired

confidence. It thus allows the user to evaluate if the cost of these additional samples is worth the improved decision-making confidence.

This approach also allows the user to change decision rules while manipulating N and the frequency of concern. The decision rule is the statement of how many samples must exhibit the characteristic of concern (e.g., target analyte detections in blanks or environmental samples from a site) before the user will conclude that the true frequency of this characteristic in the population exceeds the frequency of concern. The easiest, and least expensive, decision rule is:

> If zero of the samples collected exhibit the characteristic, then the true frequency is less than the frequency of concern. If one or more samples collected exhibits the characteristic, then the true frequency is greater than the frequency of concern.

Decision rules that allow samples to have the undesirable characteristic, but allow the user to conclude that the true frequency is less than that of concern, allow for "errors" due to a variety of sources but they also require more samples be collected. For example, using the above decision rule of zero "hits" in blanks to determine if the true frequency of false positives from blank contamination is greater than 5%, with 95% confidence, approximately 60 method blanks are required. Changing the decision rule to allow one "hit" in a blank, and still conclude that the true rate is greater than 5% if two or more blanks have hits, requires approximately 90 samples. The equations used for this approach are presented below.

Equations

If the frequency which is desirable to detect is less than 10% the following equation is used:

$$n = nL(alpha)/nL(1-Y)$$

where: alpha = 1 - the desired confidence;
Y = the frequency to detect (this must be less than 10%).

The 10% limit is based on comments by W.G. Cochran (2). The equation itself is based on the exponential distribution and assumes that the characteristic to be detected occurs very infrequently, as opposed to the binomial, which can tolerate any frequency from 0 to 100%. The reference for this approach is information available from EPA on "Xmax and the Exponential Distribution Model in the Development of Tolerance Intervals". This information is used in conjunction with guidance on evaluating gas pipelines for PCB contamination, but is currently not published.

If the frequency which is desirable to detect is more than 10%, we must use the binomial equation and iteratively solve for an appropriate n. In this case:

$$Pr = n!/r!(n-r)!*q^{(n-r)}*p^{r}$$

where n = the number of samples in a sample collection;

r = the number of samples with the characteristic to be detected;

p = the true percentage of the population with the characteristic to be detected; and,

q = the true percentage of the population without the characteristic to be detected and q = 1-p.

Solve for Pr, which is the probability that a sample of size n can be collected from the population where there are truly p% items with the characteristic and have only r samples have the characteristic (e.g., false-positives or contamination). Then, calculate 1-pr and that is equivalent to the confidence in concluding that the true rate is less than p.

The best decision rule for the user is usually that which requires the fewest samples, i.e., the zero/one rule described earlier. However, if a different decision rule is used, Pr is calculated for each "r" allowed and the resulting Pr(s) summed. For example, if the user picks a decision rule of 1 or fewer "characteristic" results passes, then we must calculate the Pr for 1 and add it to the Pr for 0. If the user picks r = 2, we must add the Pr for 2 to the Pr for 1 to the Pr for 0 for a total Pr. Then take 1 minus this total Pr to get the confidence.

The final confidence, n, r, and p define the sampling design that will meet the users objectives (3). When the user implements the sampling design from this exercise, the decision based on the results of the sampling exercise will be that either the true frequency exceeds the frequency of concern or it does not. If it does (i.e., more samples reflected the characteristic than allowed) the user may desire to estimate the range of true frequencies possible, given the observed results. Or, if the number of samples with the observed characteristic was small, the user may desire to determine what decreased confidence they have that the true rate is less than the frequency of concern.

The last portion of the ***Success-Calc*** determines the minimum and maximum percentage of the population with the chosen characteristic given that some number of samples collected indicated the presence of this characteristic. The user enters the number of samples collected, the number of samples with the chosen characteristic, and the confidence level that the user desires when estimating the minimum and maximum frequency with which the characteristic could occur. This calculation is analogous to setting an upper and lower confidence level for a mean (4).

The equations for calculating the lower confidence level (LCL) and upper confidence level (UCL) for the binomial distribution are:

LCL = {1+((n-r+1)*F(1-alpha/2;2n-2r+2,2r)/r)}^-1

UCL = {1+((n-r)/(r+1)*F(1-alpha/2;2r+2,2n-2r))}^-1

where F = the F statistic with the above specified degrees of freedom;
n = the number of samples collected;
r = the number of samples with some characteristic (r in the earlier equations); and,
^-1 = exponeniate the result to the negative 1.

Enviro-Calc

Enviro-Calc is designed to determine the number of samples needed to estimate an average analyte concentration in site-specific media within a specified absolute or relative error with a specified confidence. This calculator assumes that measurements of analyte concentration will be normally distributed and that a random sampling plan will be used to collect samples. While simple, random sampling plans are often used in environmental investigations, the assumption of measurements following a normal distribution is less certain. Therefore, unless the user has previous information indicating that the assumption of normality is reasonable, the number of samples estimated by this calculator should be considered to be sufficient only to gather preliminary information about an investigative media. Additional sampling may be required in a second or third phase after initial data have been analyzed and the underlying assumptions tested.

Hot-Spot Calc

HotSpot-Calc is design to determine the grid spacing needed to detect the presence of a single hot spot of a specified size and shape with a specified probability of missing the hot spot. This calculator is based on the following key assumptions:

- the hot spot is circular or elliptical;
- sample measurements are collected on square, rectangular, or a triangular grid;
- that the definition of a "hot spot" is clear and agreed to by all decision makers; and,
- that there are no misclassification errors (i.e., that there are no false-positive or false-negative measurement errors).

This last assumption is the most often over looked assumption and requires careful consideration of the QA program and its design to prevent misclassification errors.

The objectives of hot spot sampling are fundamentally different than the objectives of the other two sampling models. Whereas the other two models focus on estimating the site-wide average concentration or the percentage of an area contaminated, the primary objective of hot spot sampling is to pinpoint localized areas of contamination. A single site might have multiple hot spots of different origin.

Basically, hot spot sampling involves performing a systematic search of a site for "hot spots" of a certain specified shape and area. The search is conducted by sampling every point on a two-dimensional grid. The probability of finding a hot spot is determined as a function of the specified size and shape of the hot spot, the pattern of the grid, and the relationship between the size of the hot spots and the grid spacing. For example, if one uses a square grid to search for circular hot spots of radius r, the probability of locating a hot spot, if one exists, is 100% when the distance between grid points is r. Obviously, this probability decreases as the grid spacing increases relative to hot spot size.

Assumptions

The methods discussed in this section are based on those described by Gilbert (5). They are based on the following assumptions:

- A hot spot may be a surface area, or a volume at any depth below the surface (i.e., at a particular soil horizon), but the surface projection of the hot spot is assumed to be circular or elliptical in shape;
- Samples are collected on a two-dimensional grid of a specified pattern;
- The distance between grid points is large relative to the projected surface area of the sample that is actually removed for analysis;
- The criteria for defining a hot spot are unambiguous with respect to the measurement method and the concentration considered "hot," and there are no classification errors in applying these criteria.

Although triangular grids have been shown to give more information than square or rectangular grids and are therefore recommended as the preferred approach, all three grid designs are addressed.

QC Assessment Kits

When ***DQO-PRO*** is used to optimize a study design so that statistical confidence levels planned with sampling and analysis projects can be achieved, all significant analytical parameters must be maintained without change during the period of time that the QC samples are being accumulated. Significant parameters that can affect analytical method performance include the instrumentation, the analyst, and the matrix.

- Changing or modifying instruments can affect instrument detection levels and many other measurement parameters.

- Analysts with varying degrees of experience and different analytical techniques can also affect results of the measurement system.

- Different matrices may have different artifacts, interferences, and also affect the recovery of target analytes differently.

Laboratories can readily document the consistent use of instrumentation and an analyst for a given period of time or a specific project. Environmental matrices, however, are more difficult and inconvenient to maintain consistency with over a period of time; this is especially true with soils. Thus, a consistent source of representative matrices is also important for an assessment of false positive and false negative conclusions from the analytical measurement system. We are providing ***DQO-PRO*** at no cost to people who wish to use it. In addition, we have packaged representative soils in convenient QC Assessment Kits. Using these kits provides ongoing control of the third major parameter (the matrix) needed to maintain consistency among a statistically relevant population of QC samples over time or for a project.

The QC Assessment Kits contain 10 units of conveniently packaged soil for method blanks using any desired method for PCBs, PCDDs, PCDFs or any other target analytes. Some QC Assessment Kits also contain soils from the identical lot of homogenized soil that are pre-spiked with PCBs, PCDDs and PCDFs and thoroughly homogenized. Alternatively, two QC Assessment Kits with blank soils can be purchased and one of them spiked with custom prepared target analytes at any desired concentrations. The soils used in these kits were selected from pristine areas in North Carolina and California so they represent both East Coast and West Coast regions. Both soils are sandy loam; this type of soil was selected because it commonly occurs throughout the world and also because most organic pollutants spiked onto this type of soil typically give average recoveries (not high as with sand and not low as with clays).

The more kits that are used over any given time period, where all significant parameters remain constant, the higher the statistical probability becomes that low rates of false positives or false negatives can be identified in the associated environmental samples. **Since similar QC samples would be analyzed anyway, analyzing a group or batch of samples from a QC Assessment Kit will not significantly increase costs, but it will significantly improve the assumption of measurement process consistency because it removes the variability associated with unknown matrices and poorly homogenized samples.** Time limitations of 3 to 6 months are recommended as reasonable lengths of time over which to accumulate statistical populations of QC data from these kits. Documented method parameters should be consistent in laboratories that frequently use a given method for several weeks to several months. Table 1 provides an example of potential benefits, in terms of increasing statistical confidence to detect a low error rate, that can be gained by using QC Assessment Kits over a controlled period of time.

Table 1 Numbers of QC Samples Versus Confidence Levels (Probability) of Not Exceeding Selected Average Error Rates

Number of Kits	Number of QC Samples	Confidence Level With 20 % Error Rate	Confidence Level With 10% Error Rate	Confidence Level With 5% Error Rate	Confidence Level With 1% Error Rate
1	10	89%	65%	40%	10%
2	20	99%	88%	64%	18%
5	50	100%	99%	92%	39%
10	100	100%	100%	99%	63%
15	150	100%	100%	100%	78%
20	200	100%	100%	100%	87%
30	300	100%	100%	100%	95%
50	500	100%	100%	100%	99%
100	1000	100%	100%	100%	100%

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USE OF STANDARD REFERENCE MATERIALS AS INDICATORS OF ANALYTICAL DATA QUALITY

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ABSTRACT

A large program of studies was performed as part of a natural resource damage assessment conducted in the Southern California bight. These studies included biochemical and physiological work on birds, fish, and sediments. As part of these studies, samples of sediments and tissues were analyzed for the presence and quantification of dichlorodiphenyltrichloroethane and its metabolites (DDTs) and polychlorinated biphenyl congeners (PCBs). The analyses were performed by two different laboratories, one analyzing tissue samples, and the other analyzing tissue and sediment samples, over a period of approximately 14 months. The quality assurance program for these analyses specified the analyses of appropriate Standard Reference materials (SRMs) for indication of the quality of the analytical measurements. The SRMs were extracted and analyzed as part of the sample string at a rate of one for every ten samples; analyses were by dual column GC/ECD. Fifty sediment SRMs (SRM 1941 and 1941a) and 92 tissue SRMs (SRM 1974 and 1974a) were analyzed for this project. Data from the analyses of these materials were monitored on a near real-time basis to determine if the data met the required quality control criteria of plus or minus 30% of the National Institute of Standards and Technology values. If results for an SRM did not meet the criteria, corrective action for that batch of samples (n = 10) was performed. The use of SRMs and the near real-time assessment of the data from the repetitive analysis of these materials were the critical components in developing a data set that met the data quality objectives for this project.

INTRODUCTION

Beginning in 1990, a large program of studies was performed as part of a natural resource damage assessment conducted in the Southern California bight. These studies included biochemical and physiological work on birds, fish, and sediments. As part of these studies, samples of sediments and tissues were analyzed for the presence and quantification of dichlorodiphenyl-trichloroethane and its metabolites (DDTs) and polychlorinated biphenyl congeners (PCBs). Because it was possible that the results from these analyses would be used in a court of law, it was necessary to be able to define and demonstrate the accuracy, precision, and comparability of the analytical data.

No particular analytical method was specified to the laboratories for extracting and analyzing samples for this project. Instead, the *Analytical Chemistry Quality Assurance Plan* (ACQAP) (Manen, 1993) for this work specified a "common foundation". This "common foundation" included: 1) the analytes to be identified and quantified, 2) the minimum sensitivity of the analytical methods, and 3) the use of calibration materials from the National Institute of Standards and Technology (NIST). In addition, prior to the analysis of samples, each laboratory was required to demonstrate proficiency through the analysis of a blind, accuracy-based material; provide written protocols for the analytical methods to be used; calculate method detection limits for each analyte in each matrix of interest and establish an initial calibration curve in the appropriate concentration range for each analyte. Each laboratory was audited once before samples were analyzed, and once during the project to document that the laboratory was in compliance with the ACQAP specifications.

The laboratories were also required to demonstrate continued analytical proficiency by the analysis of surrogates, method blanks, calibration checks, matrix spikes, and replicates. The critical on-going quality control check was the analysis of a standard reference material (SRM). The use of SRMs is considered to be one of the best available approaches for decisions on the accuracy of measurement data (Becker, *et al.*, 1992). By

analyzing an SRM with every batch of ten samples, the SRM results provided information regarding the successful completion of all steps in the analytical sequence for that batch. The near real-time monitoring of these data re-emphasized the importance of these data to the project and allowed for cost-effective corrective actions. Comparing the SRM data over the period of the project demonstrated the overall accuracy and precision of the developed data. Lastly, use of the SRMs provided a traceability to a national standard for the data.

METHODS

Two different laboratories performed the analyses over a period of 14 months. One laboratory analyzed both tissue and sediment samples; the other analyzed tissue samples only. Both laboratories used similar methods of extraction and analysis. Sample extraction was performed using methylene chloride, followed by extract clean-up and fractionation using alumina and high pressure liquid chromatography (HPLC). Instrumental analysis was performed using dual column gas chromatography-electron capture detection (GC-ECD). Ten percent of the sample analyses were confirmed by gas chromatography-mass spectrometry (GC-MS).

The GC columns used were 30-m long by .25-mm I.D. fused silica capillary columns with DB-17 and DB-5 or RTX-5 bonded phase. The samples were analyzed for a suite of seven DDT isomers and metabolites and 42 PCB congeners. The data from the two columns were reduced to one results, *i.e.*, the data reported herein are "merged". All results are also reported corrected for recovery of an internal standard added to the samples prior to extraction.

Each batch of ten samples was accompanied through the analytical process, extraction, cleanup and quantification by an SRM. For the sediment samples, this was either SRM 1941 or 1941a, *Organics in Marine Sediments*. For the tissue samples, bird eggs and fish livers, the best reference material match was SRM 1974 or 1974a, *Organics in Mussel Tissue (Mytilus edulis)*. Only SRM 1941a provided certified values for organochlorine compounds. The other three SRMs provided non-certified or informational values for the analytes listed in Tables 1 through 4. These values were

obtained by NIST using solvent extraction and GC-ECD analysis (Schantz, *et al.*, 1990; Wise, *et al.*, 1991).

Analytical results with supporting instrument read-outs were reported to an independent data validator on a batch basis, *i.e.*, ten samples with accompanying quality control data; calibration, surrogate recovery, SRM, blanks, matrix spikes, and replicates. Data were examined by the data validator shortly after being reported. The ACQAP required that the laboratory obtain SRM results within plus or minus 30% of NIST value on average for all analytes and that no more than 30% of the individual analytes exceed plus or minus 35% of the NIST values. If these criteria were not met, corrective actions, ranging from re-injection to re-extraction and re-analysis for the entire batch of samples, were performed.

RESULTS

Results for 50 sediment SRMs (SRM 1941 and 1941a) are summarized in Tables 1 and 2. A concentration for PCB 66 was provided for SRM 1941, but the NIST data summary listed PCB 95 coeluting with PCB 66. Thus, the results were not comparable to the analytical results obtained for this project. SRM results were less than 10 times the method detection limit for 4,4'-DDT in SRM 1941, and for PCB 95, PCB 128, and 2,4'-DDE in SRM 1941a. Thus, these results are not provided in the data summary. Results for 92 tissue SRMs (SRM 1974 and 1974a) are summarized in Tables 2 and 3. Tissue SRM results for PCB 28 were reported by NIST. PCB 28 coeluted with PCB 31 for most project tissue sample results. Thus PCB 28 data were not comparable to the NIST SRM results. SRM results were less than ten times the method detection limit for PCB 44 in SRM 1974a and for 2,4-DDE, 2,4'-DDT, 4,4'-DDT in both SRMs.

The same logic for merging the two-column results was used for the SRMs as for the samples. The overall selection logic was to report the result from the column that gave the lowest reliable value. Selection of the lowest value is the same logic as used in the EPA Contract Laboratory Program Pesticide/PCB Statement of Work (U.S. EPA, 1991). An exception to the merge logic was made for PCB congeners 138 and 187. Results from column DB-17 for

these two PCB congeners showed consistently poor comparability with NIST results. Thus, only RTX or DB-5 data were used for the two congeners (for both the samples and the SRMs).

The minimum and maximum results for each analyte listed in Tables 1 through 4 indicate that the percent difference from the NIST confidence interval was greater than 35% for any one analyte in any one SRM. The range of minimum and maximum values was less for the tissue SRM with fewer results exceeding 35% difference from NIST. The quality control criteria allowed that up to 30% of the analytes could vary by more than 35% from NIST, if the overall average percent difference was less than 30%. However, if an analyte in the SRM did vary more than 35%, the sample results for that analyte in the associated batch (n = 10) were qualified as estimated (J). DDD and DDE concentrations in the samples were significantly greater in the samples than in the SRMs. This resulted at times in SRM results that were several ng/g higher than the NIST value. The associated sample DDD/DDE concentrations were at least an order of magnitude greater than SRM and method blank results, thus the apparent carryover was judged not to affect the sample results.

DISCUSSION

The probability that these analytical data would be presented in a court of law required a means of demonstrating the overall precision and accuracy of the dataset. The relatively unusual sample matrices, bird eggs and fish livers, and the problems associated with the analysis of these matrices, as well as a range of contaminant concentrations from parts per thousand to parts per billion, complicated the problem. The QA program developed and implemented for this project relied heavily upon the analysis of SRMs and the near real-time monitoring of the resultant data. This approach is based on statistical techniques which consider the results from the repetitive analyses of a reference material to be part of an infinite population of measurements. The data from the analysis of the reference materials can then be considered as random samplings of the output and can be used for evaluation of the measurement process (Taylor, 1983).

The repetitive analysis of SRMs and the near real-time monitoring of the data from these analyses were not the only mechanisms used to develop and demonstrate the quality of the dataset, but they were a critical component. They provided a mechanism to verify the precision and accuracy of analytical methods employed by the laboratories, demonstrated the comparability of the results from the two laboratories, and assured consistent results over time.

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Table 1
NIST 1941. Organics in Marine Sediment.

Standard Reference Material			ACQAP Limits (3) ng/g		Laboratory SRM Results						
Analyte	Value (1) ng/g	Uncertainty (2)	LCL	UCL	Merged Result (4)	Average Result ng/g	Minimum Result ng/g	Maximum Result ng/g	Standard Deviation	Number of Analyses	Percent Difference
18	9.9	0.25	6.19	13.6	18	7.18	0.98	13.3	3.25	32	27
28	16.1	0.4	10	22.1	28	13.79	10.2	38	5.54	26	14
					31/28	37.18	9.26	88.4	31.01	6	131
52	10.4	0.4	6.36	14.4	52	12.33	8.26	15.6	1.60	32	19
101	22	0.7	13.6	30.4	101	22.52	16.4	51.2	6.08	32	2
105	5.76	0.23	3.51	8.01	105	5.70	3.94	7.07	0.76	32	1
118	15.2	0.7	9.18	21.2	118	16.33	12.7	20	1.95	22	7
					118/2,4'-DDD	14.89	12.9	16.9	1.32	10	2
138	24.9	1.8	14.4	35.4	138	23.13	16.2	30.3	3.82	32	7
153	22	1.4	12.9	31.1	153	22.00	16	28.5	3.31	32	0
180	14.3	0.3	9	19.6	180	14.75	11	17.7	2.10	32	3
170	7.29	0.26	4.48	10.1	170	7.23	6.93	7.52	0.42	2	1
					196/170	7.01	3.41	11.9	1.38	30	4
187	12.5	0.6	7.53	17.5	187	12.98	8.95	18	2.62	32	4
195	1.51	0.1	0.88	2.14	195	1.67	1.15	3.01	0.43	32	11
206	4.81	0.15	2.98	6.64	206	5.46	3.88	6.4	0.72	32	14
209	8.35	0.21	5.22	11.5	209	8.93	6.23	12	1.17	32	7
4,4'-DDD	10.3	0.1	6.6	14	4,4'-DDD	9.64	9.64	9.64	0.00	1	6
					4,4'-DDD/114	7.81	4.93	10.4	1.28	31	24
4,4'-DDE	9.71	0.17	6.14	13.3	4,4'-DDE	11.61	5.83	30.6	5.89	32	20
											Mean = 15

Notes: All values are in dry weight.
SRM: Standard Reference Material.
LCL: Lower Control Limit.
UCL: Upper Control Limit.

1. Noncertified concentration.
2. NIST confidence interval which is one standard deviation of a single measurement (triplicate injection).
3. Acceptance limit for the Southern California Damage Assessment Analytical Chemistry Quality Assurance Plan (ACQAP), Manen, 1993.
4. The single analyte results are chromatograhically resolved. Analyte results separated by a "/" are chromatographic co-elution results.

Table 2
NIST SRM 1941a. Organics In Marine Sediment.

Standard Reference Material			ACQAP Limits (3) ng/g		Laboratory SRM Results						
Analyte	Value (1) ng/g	Uncertainty (2)	LCL	UCL	Merged Result (4)	Average Result ng/g	Minimum Result ng/g	Maximum Result ng/g	Standard Deviation	Number of Analyses	Percent Difference
44	4.8	0.62	2.5	7.1	44	4.39	1.21	4.91	1.28	18	9
49	9.5	2.1	4.08	14.9	49	5.52	1.37	9.73	2.69	18	42
52	6.89	0.56	3.92	9.86	52	6.85	2.4	8.2	1.77	18	1
66	6.8	1.4	3.02	10.6	66	6.07	1.96	7.18	1.90	18	11
87	6.7	0.37	3.99	9.42	87	6.16	2.19	8.17	1.70	18	8
99	4.17	0.51	2.2	6.41	99	3.97	1.48	4.64	1.15	18	5
101	11	1.6	5.55	16.5	101	11.17	3.99	12.2	2.96	18	2
105	3.65	0.27	2.1	5.2	105	2.85	1.05	3.45	0.94	18	22
110	9.47	0.85	5.31	13.6	110	9.82	3.69	12.1	2.45	18	4
118	10	1.1	5.4	14.6	118	7.71	2.69	9.18	2.48	17	23
					118/2,4'-DDD	7.79	7.79	7.79	0.00	1	22
138	13.38	0.97	7.73	19	138	13.23	5.13	15.5	3.43	18	1
153	17.6	1.9	9.54	25.7	153	13.64	4.83	15.4	4.62	18	23
180	5.83	0.58	3.21	8.45	180	7.09	2.09	8.28	1.52	18	22
170	3	0.46	1.49	4.51	196/170	3.23	1.09	3.97	0.81	18	8
206	3.67	0.87	1.52	5.82	206	4.06	0.591	5.61	1.05	18	11
209	8.34	0.49	4.93	11.8	209	8.58	3.36	9.52	2.12	18	3
4,4'-DDD	5.06	0.58	2.71	7.41	4,4'-DDD	4.77	4.42	5.11	0.30	4	6
					4,4'-DDD/114	6.08	2.38	21.8	0.00	14	20
4,4'-DDE	6.59	0.56	3.72	9.46	4,4'-DDE	12.47	3.17	84.8	1.70	18	89
											Mean = 16

Notes: All values are in dry weight.
SRM: Standard Reference Material.
LCL: Lower Control Limit.
UCL: Upper Control Limit.

1. Certified concentration.
2. NIST confidence interval which is one standard deviation of a single measurement (triplicate injection).
3. Acceptance limit for the Southern California Damage Assessment Analytical Chemistry Quality Assurance Plan (ACQAP), Manen, 1993.
4. The single analyte results are chromatograhically resolved. Analyte results separated by a "/" are chromatographic co-elution results.

Table 3
NIST SRM 1974. Organics in Mussel Tissue (Mytilus edulis).

Standard Reference Material			ACQAP Limits (3) ng/g		Laboratory SRM Results						
Analyte	Value (1) ng/g	Uncertainty (2)	LCL	UCL	Merged Result (4)	Average Result ng/g	Minimum Result ng/g	Maximum Result ng/g	Standard Deviation	Number of Analyses	Percent Difference
18	3	1	0.95	5.05	18	2.50	0.402	5.07	0.85	26	17
44	8	3	2.20	13.80	44	7.69	5.15	9.51	0.94	26	4
52	12	5	2.80	21.20	52	11.82	9.35	13.92	1.13	26	2
66	13.6	0.06	8.24	18.96	66	11.82	7.1	14.52	1.79	26	13
101	13	1	7.45	18.55	101	14.49	11.544	19.08	1.64	26	11
105	5.6	0.4	3.24	7.96	105	5.57	4.188	6.58	0.60	26	1
118	13.6	0.6	8.24	18.96	118	15.91	13.13	20.71	1.92	22	17
					2,4'-DDD/118	19.51	17.24	21.56	1.77	4	43
128	1.9	0.3	0.94	2.87	128	1.91	1.26	2.41	0.33	26	1
138	14	1	8.10	19.90	138	16.17	12.36	19.81	1.92	26	15
153	18	1	10.70	25.30	153/114	13.76	10.52	15.95	1.32	18	24
					153	13.79	11.976	15.653	1.35	8	23
180	1.7	0.2	0.91	2.50	180	1.76	1.284	2.31	0.28	18	3
					157/180	1.91	1.55	2.43	0.35	8	12
187	3.7	0.1	2.31	5.10	187	3.45	2.18	4.46	0.51	26	7
2,4'-DDD	2.5	0.9	0.73	4.28	2,4'-DDD	2.20	1.2	3.3	0.51	26	12
4,4'-DDD	8.4	0.4	5.06	11.74	4,4'-DDD	6.95	5.03	9.88	1.94	6	17
					4,4'-DDD/114	5.50	3.8	9.53	1.37	20	35
4,4'-DDE	5.9	0.2	3.64	8.17	4,4'-DDE	6.91	3.59	16.81	3.21	26	17
											Mean = 14

Notes: All values are in wet weight.
SRM: Standard Reference Material.
LCL: Lower Control Limit.
UCL: Upper Control Limit.
1. Noncertified concentration.
2. NIST confidence interval which is one standard deviation of a single measurement (triplicate injection).
3. Acceptance limit for the Southern California Damage Assessment Analytical Chemistry Quality Assurance Plan (ACQAP), Manen, 1993.
4. The single analyte results are chromatograhically resolved. Analyte results separated by a "/" are chromatographic co-elution results.

Table 4
NIST SRM 1974a. Organics in Mussel Tissue (Mytilus edulis).

Standard Reference Material			ACQAP Limits (3) ng/g		Laboratory SRM Results						
Analyte	Value (1) ng/g	Uncertainty (2)	LCL	UCL	Merged Result (4)	Average Result ng/g	Minimum Result ng/g	Maximum Result ng/g	Standard Deviation	Number of Analyses	Percent Difference
18	3.98	NA	2.59	5.37	18	3.17	2.5	4.76	0.52	66	20
52	13.5	NA	8.78	18.2	52	12.52	10.54	15.62	0.91	66	7
66	10.54	NA	6.85	14.2	66	11.42	8.73	14.3	1.05	66	8
101	14.51	NA	9.43	19.6	101	15.09	11.11	17.09	1.06	66	4
105	7.23	NA	4.7	9.76	105	5.58	4.03	7.34	0.71	66	23
118	18.34	NA	11.9	24.8	118	15.70	10.38	19.79	1.64	57	14
					2,4'-DDD/118	16.39	14.77	18.35	1.28	9	11
128	2.66	NA	1.73	3.59	128	2.11	1.01	2.99	0.31	66	21
138	19.91	NA	12.9	26.9	138	16.54	14.52	20.94	1.33	66	17
153	19.86	NA	12.9	26.8	153	13.76	12.53	18.26	1.47	14	31
					153/114	14.33	11.16	18.06	1.68	52	28
180	1.84	NA	1.2	2.48	180	2.40	1.54	4.07	0.87	12	30
					157/180	2.19	1.4	3.27	0.48	54	19
187	4.00	NA	2.6	5.4	187	3.74	3.16	4.68	0.35	66	6
2,4'-DDD	1.86	NA	1.21	2.51	2,4'-DDD	1.60	0.71	3.39	0.41	66	14
4,4'-DDD	4.06	NA	2.64	5.48	4,4'-DDD	4.61	3.51	6	0.66	13	14
					4,4'-DDD/114	3.77	3.12	5.44	0.49	53	7
4,4'-DDE	6.49	NA	4.22	8.76	4,4'-DDE	6.78	2.47	18.34	2.93	65	4
					4,4'-DDE/87	12.13	12.13	12.13	0.00	1	87
											Mean = 19

Notes: All values are in wet weight.
SRM: Standard Reference Material.
LCL: Lower Control Limit.
UCL: Upper Control Limit.
1. Noncertified concentration.
2. NIST uncertainty and confidence interval not provided for SRM 1974a.
3. Acceptance limit for the Southern California Damage Assessment Analytical Chemistry Quality Assurance Plan (ACQAP), Manen, 1993.
4. The single analyte results are chromatograhically resolved. Analyte results separated by a "/" are chromatographic co-elution results.

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THE GENERATION OF CALIBRATION CURVES FOR MULTI-POINT STANDARDIZATIONS DISPLAYING HIGH RELATIVE STANDARD DEVIATIONS

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ABSTRACT

Many analytical methods, especially the GC methods, state that a calibration curve should be used if the percent relative standard deviation (RSD) precision criterion for the initial calibration standards is exceeded. However, no guidance is usually given in the methods on how the calibration curve is generated from the initial calibration data points or what determines an acceptable calibration curve. This lack of guidance has led to inconsistencies within and among laboratories. For example, in its analysis of organochlorine pesticides by dual-column GC (SW846 Method 8080), one laboratory used linear calibration graphs for certain compounds because these compounds were "historically" linear up to the highest calibration standard concentration, despite the fact that the data showed distinct tapering at the high end of the calibration curves. The same laboratory used quadratic curve-fit for other compounds when the data showed a very good straight-line fit for the data (low %RSD). This paper discusses the lack of guidance for quantitating positive results from non-linear calibration curves and suggests a possible solution to the problem. The paper provides an easy method for generating calibration curves using available software and includes quality control and corrective actions. The adoption of such a procedure as detailed in this paper would help to make comparisons of positive results from different laboratories more reliable since the laboratories will be using similar calibration and quantitation techniques.

INTRODUCTION

Many analytical methods, especially the gas chromatography (GC) methods, state that a calibration curve should be used if the percent relative standard deviation (RSD) precision criterion for the initial calibration standards is exceeded. However, no guidance is usually given in the methods on how the calibration curve should be generated from the initial calibration data points or what should determine an acceptable calibration curve. For example, SW846 Method 8000, which is the parent method of many of the GC methods in SW846, states that if the percent RSD for the calibration factors for a given compound obtained in the standardization of the instrument is less than 20%, then the laboratory can assume that the calibration exhibits linearity and the average of the calibration factors can be used for quantitating positive all results for that compound across the range of the calibration standards. If the %RSD is greater than 20%, the method indicates that a calibration curve should be generated. However, no guidelines

are specified for the generation of this calibration curve. Consequently, laboratories vary with regard to the way in which they generate calibration curves for these analyses. Some laboratories simply plot the data points on a graph and generate a best-fit line through the points using available linear regression software. This seems inappropriate, since the method implies that high %RSDs demonstrate that the instrument response is *not* linear across the calibration range being examined. Other laboratories use a point-to-point method of calibration, in which a straight line is drawn between the origin and the data point for the first (low concentration) standard, another straight line is drawn between the data points for the first and the second standards, and so forth. This is a more accurate method of quantitation, but it suffers from the drawback of being very difficult to verify. One five-point calibration curve for an instrument standardization would require five separate equations to calculate the positive results for a single compound. Another laboratory based the quantitation of compounds on past performance in calibration curves. For example, in its analysis of organochlorine pesticides by dual-column GC (SW846 Method 8080), this laboratory used linear calibration graphs for certain compounds because these compounds were "historically" linear up to the highest calibration standard concentration, despite the fact that the data showed distinct tapering at the high end of the calibration curves. Inter-laboratory comparability with regard to instrument calibration is of increasing importance because of the rising cost of performing site investigations. Companies involved with the clean-up of contaminated sites are realizing the value of performing laboratory audits and evaluating laboratory performance through performance evaluation (PE) sample studies. Yet how can one judge the results for the analysis of a PE sample performed by several laboratories if each is generating its positive results in different ways? As will be seen later, a large discrepancy between results can occur depending on the method of quantitation the laboratory uses. In order to make comparisons between the results for a given analysis from different laboratories more meaningful, the laboratories should be using the same method of quantitation to calculate the positive results.

SUMMARY OF METHOD

First, the laboratory should analyze five standards (per SW846 Method 8000) of increasing concentration on an instrument that has been set up according to the manufacturer's specification. The low concentration standard should be at a concentration equal to the reporting limit for the analyte. The concentrations of the other standards should be selected to represent the range of interest for the analyte, based on the expected levels of the analyte in the samples and the expected linear range of the analyte. The calibration factor (CF) for each analyte in the standards should be calculated using the following equation:

$$CF = \frac{Instrument\ Response}{Amount\ Injected}$$

The average CF and %RSD for the calibration factors for an analyte are then calculated using the following equations:

$$\overline{CF} = \frac{\sum_{i=1}^{5} CF_i}{5}$$

$$\%RSD = \sqrt{\frac{\sum_{i=1}^{5} (CF_i - \overline{CF})^2}{4}} \times \frac{100}{\overline{CF}}$$

If the %RSD is less than or equal to 20.0% (or the quality control criterion stated in the method used), then the laboratory should use the average calibration factor for the calculation of the positive results for the analyte in the samples and calibration check standards. If the %RSD is calculated to be greater than 20.0%, the laboratory should generate a quadratic curve for the calculation of the positive results. The equation should be of the form $y = ax^2 + bx$. Next, the upper limit of the calibration curve should be determined using the following procedure: find the slope (m) of the calibration curve at the low concentration standard (x'). This is done using the equation $m = 2ax' + b$. This equation represents the first derivative of the quadratic equation. Divide this slope by five and find the concentration (x) which corresponds to this reduced slope (m') by using the equation $x = (m'-b)/2a$. (This equation comes from rearranging the equation of the slope to give the concentration in terms of the slope.) This concentration represents the point at which the calibration curve has degraded to only 20% of the slope of the curve at the low concentration standard.

If this concentration is less than the fourth calibration standard, then the laboratory should adjust the operating conditions of the instrument and recalibrate the instrument. If the upper limit is determined to be between the fourth and fifth (high concentration) calibration standard, then the laboratory can analyze samples and quantitate positive results up to the concentration determined to be the upper limit of the curve; if a sample displays a result higher than the upper limit, the laboratory should dilute the sample and

reanalyze accordingly. If the upper limit is determined to be greater than the high concentration standard, then the concentration of that standard should be considered the upper limit.

In addition, after the instrument has been calibrated but before samples are analyzed, the laboratory should analyze a standard at a concentration in the middle of the calibration range. If this calibration check standard fails the criterion specified in the method a new calibration curve should be generated. If the calibration check standard passes the specified criterion, then the laboratory can proceed to analyze samples.

In the following section, the use of this procedure using laboratory-generated data will be examined.

PRACTICAL USE OF PROCEDURE

In the analysis of project samples for endosulfan II by SW846 Method 8080, one large environmental production laboratory provided the following data:

TABLE 1 Raw Data and Calibration Factors for Endosulfan II

x (conc., μg/L)	y (area counts)	Calibration Factor
0.125	160,000	1,280,000
0.250	320,000	1,280,000
0.50	645,000	1,290,000
1.0	1,080,000	1,080,000
2.0	1,410,000	705,000

Due to past analytical performance for this compound, the laboratory used a linear regression program to create a straight-line calibration curve of the form $y = mx + b$. However, the %RSD was calculated to be 22.3%. In such a case, it would be more appropriate to use a quadratic equation to generate a calibration curve. The software used was FIT, Version 1.0 by Matthias Kretschmer, available from WindowChem Software. The two equations derived from the raw data were as follows:

Laboratory-derived equation: $y = (654,140)x + 216, 042$

FIT-derived equation: $y = (-372,252)x^2 + (1,450,011)x$

A plot of the raw data and the calibration curves is presented below. As can be observed, the results from the two curves can generate large discrepancies for a given sample response. In the region of responses of 1,000,000 area counts, the difference

between the concentrations from the linear curve and the quadratic curve can be as much as 0.30 μg/L or more. Table 2 summarizes the predicted concentrations from both calibration curves for given area counts and the differences between the predicted values. As expected, the differences are minimal only near the regions where the two curves intersect. Even so, the differences are notable, especially at the low end of the curve (near 200,000 area counts) and in the middle of the curve (around 1,000,000 area counts).

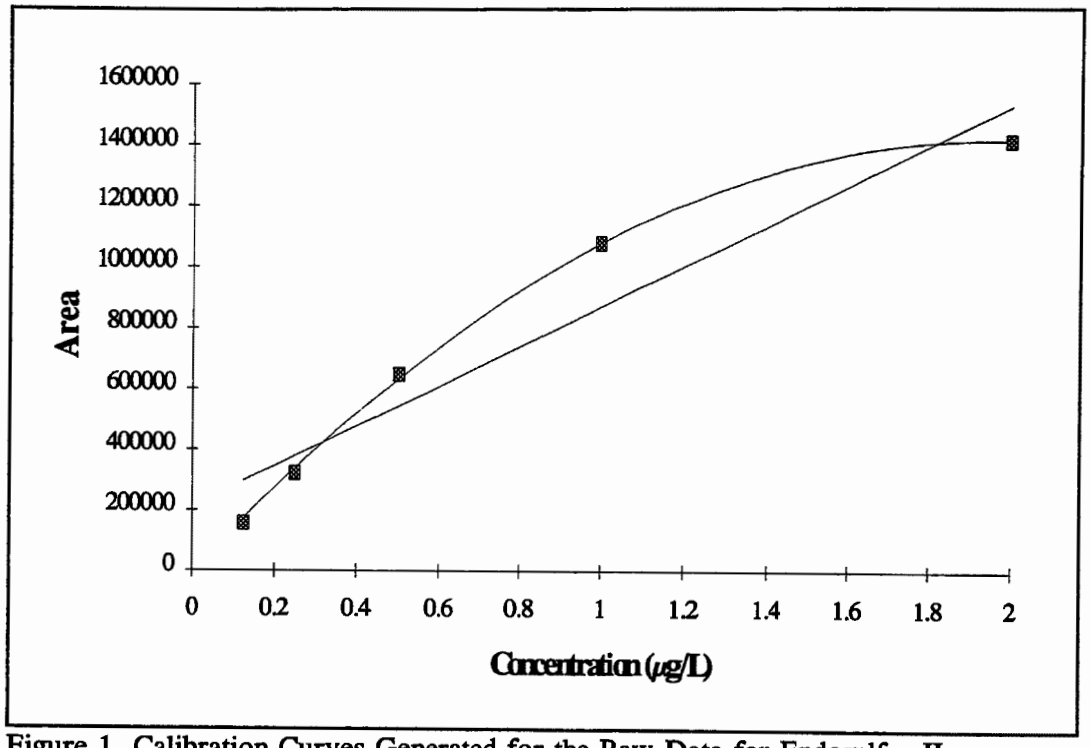

Figure 1 Calibration Curves Generated for the Raw Data for Endosulfan II

TABLE 2 Predicted Concentrations from the Calibration Curves for a Given Area Count and the Differences Between the Predicted Concentrations

Given Area	Concentration (μg/L) from Quadratic Calibration Curve	Concentration (μg/L) from Linear Calibration Curve	Difference (μg/L)
150,000	0.106	-0.101	-0.207
200,000	0.143	-0.025	-0.168
250,000	0.181	0.052	-0.129
300,000	0.219	0.128	-0.091
350,000	0.259	0.205	-0.054
400,000	0.299	0.281	-0.018
450,000	0.340	0.358	0.018
500,000	0.382	0.434	0.052
550,000	0.426	0.511	0.085
600,000	0.471	0.587	0.116
650,000	0.517	0.663	0.147
700,000	0.565	0.740	0.175
750,000	0.614	0.816	0.202
800,000	0.665	0.893	0.227
850,000	0.719	0.969	0.250
900,000	0.775	1.046	0.271
950,000	0.834	1.122	0.288
1,000,000	0.896	1.198	0.303
1,050,000	0.961	1.275	0.313
1,100,000	1.032	1.351	0.319
1,150,000	1.109	1.428	0.319
1,200,000	1.193	1.504	0.311
1,250,000	1.288	1.581	0.293
1,300,000	1.399	1.657	0.258
1,350,000	1.539	1.734	0.194
1,360,000	1.574	1.749	0.175
1,370,000	1.612	1.764	0.153
1,380,000	1.654	1.779	0.125
1,390,000	1.704	1.795	0.090
1,400,000	1.768	1.810	0.042

Given Area	Concentration (μg/L) from Quadratic Calibration Curve	Concentration (μg/L) from Linear Calibration Curve	Difference (μg/L)
1,405,000	1.810	1.818	0.007
1,410,000	2.022	1.825	-0.196

An examination of the slope of the quadratic calibration curve shows that the calibration range for the data points for endosulfan II should not be extended to 2.0 μg/L. However, using the linear calibration curve, the laboratory assumed that the data points were valid throughout the range of calibration standards up to and including the high calibration standard concentration of 2.0 μg/L. Instead, the data shows that an upper limit of approximately 1.6 μg/L would be more appropriate.

TABLE 3 Slope of Quadratic Calibration Curve at Given Concentrations

Concentration (μg/L)	Slope of Quadratic Curve
0.125	1,356,948
0.200	1,301,110
0.300	1,226,660
0.400	1,152,209
0.500	1,077,759
0.600	1,003,309
0.700	928,858
0.800	854,408
0.900	779,957
1.000	705,507
1.100	631,057
1.200	556,606
1.300	482,156
1.400	407,705
1.500	333,255
1.600	258,805
1.700	184,354
1.800	109,904
1.900	35,453
2.000	-38,997

As can be seen, the slope of the curve of the quadratic curve is negative at the high end; therefore, the data points should be considered unreliable at the upper end of the calibration curve since one area count response can produce two concentration values. This fact is obscured by using the linear calibration curve. But what constitutes an acceptable upper limit to a quadratic calibration curve? A good rule of thumb is a 20% guideline. The upper limit to the calibration curve should be the point where the slope of the curve has decreased to only 20% of the slope at the low standard concentration. In this example, the slope of the graph at 0.125 μg/L is 1,356,948. One-fifth of this value is 271,390, which corresponds to a concentration of 1.583 μg/L. Therefore, the upper limit of the calibration curve should be approximately 1.600 μg/L. Since this value falls between the two highest initial calibration standard concentrations, the laboratory can use the calibration curve but should dilute and reanalyze any sample displaying an on-column concentration of endosulfan II greater than 1.600 μg/L. If the calculated upper limit were less than 1.0 μg/L (the concentration of the fourth calibration standard), the laboratory would have to restandardize the GC. If the calculated upper limit were greater than 2.0 μg/L (the concentration of the fifth calibration standard), then the upper limit would be 2.0 μg/L since the laboratory should not report values at concentrations greater than the highest standard used for instrument calibration.

Another issue with the calibration curves concerns minimum area counts - what is the minimum area count necessary to achieve the reporting limit for the analyte? Using the previous equations, the minimum area required to report a positive result of 0.125 μg/L for endosulfan II in a sample is 175,435 for the quadratic calibration curve. The minimum area required to report a positive result for endosulfan II in a sample 297,809 for the linear calibration curve, which is almost 70% higher than the area count required to produce the same result from the quadratic calibration curve. This is due to the fact that the linear calibration curve crosses the y-axis at an area count of 216,042. This value is almost 60,000 area counts higher than the area count obtained from the low concentration standard. Indeed, the minimum area count required to obtain a sample concentration of 0.125 μg/L using the linear calibration curve of the previous sample is almost *twice* the area count obtained in the analysis of the low calibration standard. This demonstrates the utility of forcing the calibration curve through the origin. Forcing the calibration curve through the origin helps to minimize the amount of error between the true and calculated concentrations at the low end of the calibration curve. It eliminates the possibilities of a positive y-intercept (which serves to increase the minimum area required to report a positive result at the low standard concentration) and of a negative y-intercept (which serves to decrease the minimum area required to report a positive result at the low standard concentration so that any detection could be calculated to be greater than the reporting limit).

SUMMARY

A method for generating a quadratic calibration curve which is forced through the origin has been described. The quadratic equation obtained from the initial calibration data is easy to use and its results are equally easy to interpret without a detailed knowledge of statistics. Many types of software are currently available which can perform these calculations; analytical chemists can learn how to set up and run the software within a day. Having a consistent approach to the generation of calibration curves would permit a more accurate assessment of the results of a performance sample study. The method for generating calibration curves as presented in this paper is easy to follow and can be adopted by a laboratory with a minimum of effort.

Data Acquisition and Computer Networking : A Key to Improved Laboratory Productivity

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It is no surprise to anyone connected with the environmental laboratory community that the days of strip chart recorders with red ink pens are long gone. Many of today's analysts likely have never used such a device, since that was in one sense the first era of data acquisition. There are those who argue that a second era began in the 1970's with the advent of the computer data acquisition device. Spurred initially in a typical environmental laboratory by the need to analyze and reduce vast quantities of data from gas chromatography-mass spectrometry (GC/MS) instruments, the first data acquisition systems were based on minicomputers, large floor model computers by today's standards. These systems generally involved one minicomputer that operated sequentially as a data acquisition, data reduction and data storage device. There was a productivity penalty paid which some labs circumvented by buying a second minicomputer. In the intervening 20 years, this basic model still holds, though the computer data handling capabilities have gotten larger and the price much cheaper.

Came the 1980s and environmental GC/MS analyses took on a whole new series of quality assurance and data reporting functions. But by and large, it was still done on computer systems tied one-on-one to a GC/MS instrument. QA/QC and data reporting were often done on a separate computer systems with the use of spreadsheets and stand alone EPA reporting software packages.

Now we are approaching the third wave in environmental data handling with a need to integrate all computer and reporting functions into one system. This need arises from the enormous pressure on a laboratory to improve the efficiency of their information collection and data reduction in order to minimize analyst time and to maximize the quality of their environmental data.

Instrument and Environmental Protection Agency History

Since the formation of EPA in December 1970, over 20 major pieces of environmental legislation have been enacted. Over the same time period, there have been major improvements in analytical instrumentation that mirrored these legislative acts.

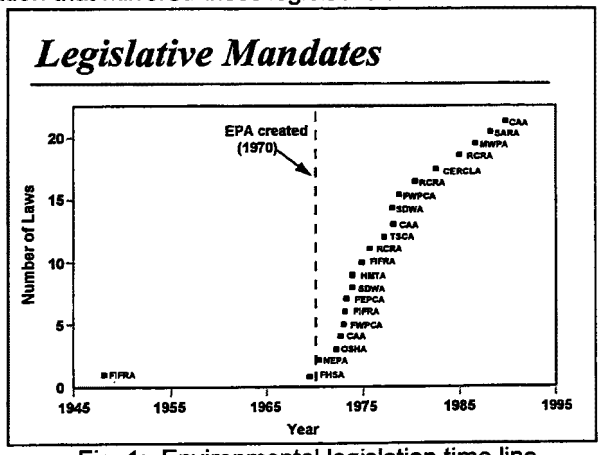

Fig. 1: Environmental legislation time line

In the 1960s, GC/MS required packed columns with a complex interface between the chromatography and spectroscopy instrument sections. Instruments cost $100,000 or more, and

were collections of relatively exotic vacuum and electronic technology. Individual mass chromatograms were collected manually by watching a Faraday cup collector of ions. When the meter indicated that the total number of ions was increasing (i.e., a peak was eluting from the GC column into the MS ion source), an operator initiated a magnetic scan across a typical 20 to 600 amu mass range. Photographic oscillographic paper was used to collected the spectrum. An experienced mass spectroscopist would then count across the amu mass range, identifying the m/e value of each of the major ion fragments. The identity of the unknown compound would then be constructed based on knowledge of ion fragment identities, isotope ratio values and operator experience. Ph.D.s typically operated these instruments and identified unknown compounds. The process took a great deal of time and experience.

From an environmental viewpoint, there was little incentive to improve the productivity of this process, since none of the then existing environmental statutes required individual chemical analysis. Most environmental monitoring requirements based on gross parameters such as Total Suspended Solids (TSS) and Biological Oxygen Demand (BOD).

Then began the wave of environmental legislation shown in Figure 1 above. The growth of this legislation was congruent with the new era of computerized GC/MS operations. In the early 1970s, relatively large and certainly expensive mini-computers were used to collect GC/MS data. But these were "big iron" single tasking computers operating on each manufacturer's proprietary computer operating system. Instruments collected data and then had to process the data. And the processing phase could only be considered by today's standard to be semi-automated. Individual chromatographic peaks had to be manually identified by an operator, key mass spectra identified and background subtracted, and then matched against standard libraries of GC/MS data using a forward search algorithm. Instruments could not be collecting data while processing and searching. Finnigan made the first break through in offering a multi-tasking GC/MS acquisition and data processing Incos system in 1977. Other manufacturers soon followed. While such systems were more productive than previous ones (and certainly more productive than an operator manually collecting strip chart spectra and counting up m/e values), the system is nonetheless based on expensive minicomputers and a lot of operator experience and interaction.

EPA Approach to Environmental Monitoring

Besides computerizing what had been a manual instrumental system, EPA changed the world in the 1970s as well. With the development of chemical-specific waste water monitoring methods, EPA established a fixed list of analytes for which monitoring would be performed. Now industries would no longer just look for all the possible chemicals which might be in an industrial effluent, but rather for a list of volatile, base, neutral and acid compounds that would act as indicators. These were known as "priority pollutants". The theory was that if EPA could establish upper limits for these indicator compounds which a plant's waste treatment process must not exceed, any chemical pollutant not on the priority pollutant list would likely be effectively treated as well. In addition to limiting monitoring to specific chemicals, the priority pollutant list also led to the development of specific environmental analytical methods. This monitoring model - fixed lists of analytes and fixed analytical methods - began in the mid 1970s and has held for the last two decades. What has grown is the analytical quality assurance and EPA reporting requirements.

In the mid-1980s came the era of the personal computer. As much as to reduce the cost of the mini-computer as well as to take advantage of spreadsheet and database software, GC/MS instruments moved to PCs, but still each with its own. In addition, the reporting requirements have increased. It is not sufficient to report just data. Now legal regulations are imposed requiring all quality assurance and quality control be reported along with the analytical data. It is not uncommon for GC/MS reports to take five times longer to generate that to acquire the raw chromatographic data. Environmental labs were faced with a situation where data from GC/MS

and GC data acquisition systems had to be individually evaluated for compliance with QA limits and manually combined to generate EPA-compliant reports.

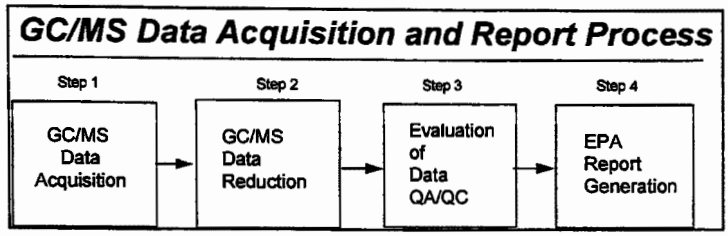

Fig. 2

The four steps in modern GC/MS operations are illustrated in Figure 2. Labs need to perform all these steps in order to have their data judged acceptable.

The other trend of the 1980s was competition. Environmental labs had to lower their costs because the amount of money received for each sample analysis had declined to the point where not only Ph.D.s couldn't be afforded, neither could M.S. or even B.S. chemists. Many labs operated with B.A. level staff who were only trained to perform EPA fixed analyte-fixed method analyses. These trends are illustrated in Figures 3 and 4.

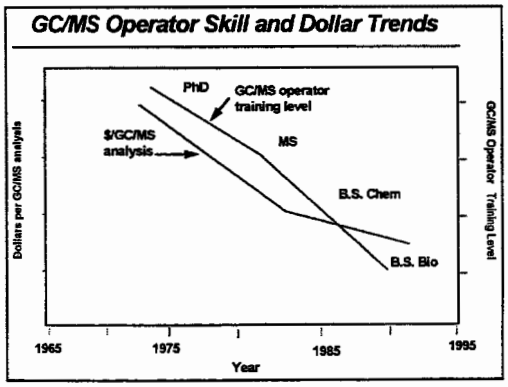

Fig. 3

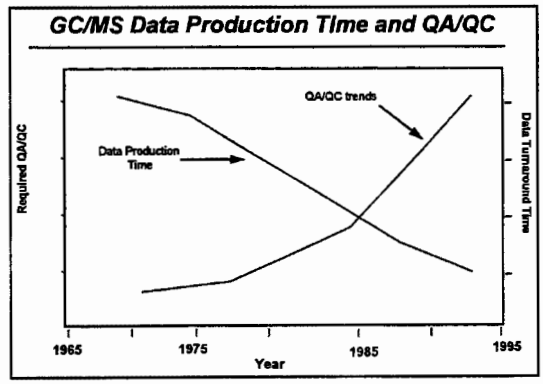

Fig. 4

Productivity in the Environmental Analytical Laboratory

So here we are in the 1990s. Environmental protection still fundamentally depends on good analytical chemistry performed with high levels of quality assurance. But environmental labs are faced with the need to optimize resources and minimize costs. We've moved well beyond the red pen and strip chart recorder. But we also have resources that were unavailable even just 5 years ago. Most of us have office work places where PCs are networked for e-mail and shared files.

So the infrastructure is already there. Networks exist, and these days software exists to integrate all four GC/MS functions from data acquisition to report generation in a single system. In a modern system, one PC on a network can be acquiring data, another performing quality assurance evaluations, while yet a third generates EPA compliant reports. And given the nature of environmental analytical chemistry, i.e., soil, water and air samples being examined for a fixed series of analytes using fixed analytical methods, the four steps of a GC/MS determination can be performed by analyst without Ph.Ds.

Network systems with distributed processing can process data on any one of the PCs connected to a network. One can produce calibration and quantitation data with enhanced data review without need to revert to the minicomputers of old. Given the distributed nature of the GC/MS data production task, PCs may not always be engaged in data acquisition, reduction, QC evaluation and reporting functions. In a network environment, a PC which is found idle from its primary task can be passed a processing task required by some other computer in a network. The object of the overall GC/MS undertaking is to make the chromatography in step one of Figure 2 the rate determining function.

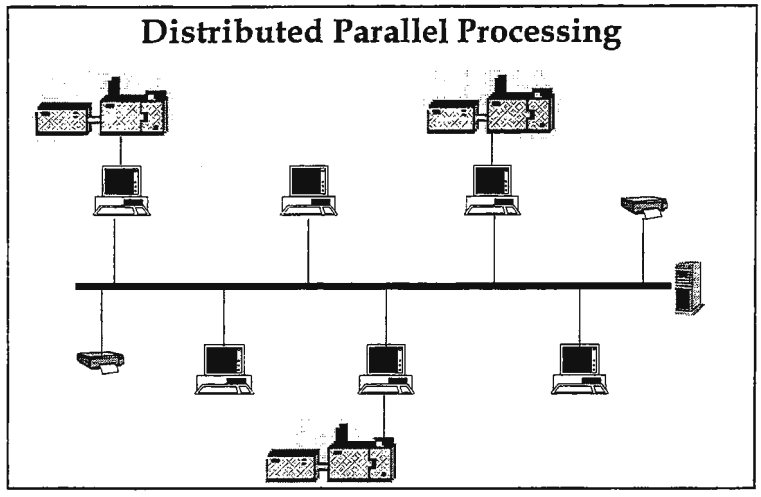

Fig. 5: Distributed parallel processing links multiple instruments as a network of personal computers with the capability to assign pending tasks to any available PC

In short, in a distributed processing system, multiple tasks can be performed as efficiently as possible, since tasks can be sent to any PC on a network. The modern lab, set up to produce EPA reports as a routine measure, can take data from a group of 10 samples, evaluate the data, and generate the required reports all in the same day. In practice, CLP-like data packages can be prepared in only 2 hours more than the 8 hours needed for chromatography with a distributed processing package of software and a laboratory computer network with 3 personal computers on it. Laboratory productivity, as measured by sample data packages completed per unit of time or by number of labor hours needed to complete a data package, has been improved by thousands of percent compared to the original manual GC/MS work.

ISSUES REGARDING VALIDATION OF ENVIRONMENTAL DATA

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ABSTRACT

The collection and analysis of environmental data is subject to a number of conditions that often have an effect on the technical usability of the data. These conditions are frequently related to matrix, and the manner in which varying sample collection, sample preparation and analysis create bias of the final analytical results. End users of such data need to be made aware of these potential biases. Data Validation can give users a level of confidence in the reported values, and can also identify reporting/calculation errors (through data verification). The US EPA has required data validation for Superfund-related sample analyses since the early 1980's, and several DOE sites require data validation as well. However, there are varying opinions regarding the extent of validation, and the effects of several variables. These differences of opinion are most noticeable when dealing with radiochemistry data, for which no standard protocols exist for either analysis or data validation.

Data validation should be concerned with all aspects of the sample, from sampling through data generation and reporting. Data validation should evaluate such items as sample holding times, sample preservation, instrument performance (calibration, method blanks, etc...), QC sample results, and, if necessary, raw data inspection (TIC evaluations, for example). These items allow the validators to determine precision, accuracy, completeness, and contract compliance of the data; the end users can evaluate representativeness once these other parameters are evaluated.

There is definitive guidance for the validation of CLP inorganic and organic data, as presented in the National Functional Guidelines. This has resulted in a fairly uniform validation effort for much of the chemical environmental data generated by the CLP Statements of Work for Organic and Inorganic analyses. There are those who say that these methods are restrictive, but some level of consistency is achieved by their use. Radiochemical data generation and validation is another story- several Agencies are grappling with the attempt at standardizing methods, and subsequent data validation. The Fernald Environmental Management Project (FEMP) is among several DOE sites attempting to create standard data verification/validation procedures. We have taken the lead on the development of such procedures, many of which rely on software data evaluation. The DOE is working toward the development of electronic data verification/validation software that can be used across the entire DOE complex. The creation of such software will reduce the effort required to perform these tasks, and will result in consistency across the DOE

complex.

It is the author's contention that all data used for making any environmental decisions, especially data generated to satisfy regulatory requirements, must be verified and validated. The FEMP has invested much time and resources to standardize these procedures, and believes that these procedures can serve as a model, or at least a good starting point for other environmental firms. It is our objective to share some of our "lessons learned", and inform the environmental community of our progress.

INTRODUCTION

One of the most powerful and indispensable tools available to the environmental decision-maker is validated data. Validated data are used to define nature and extent of contamination, evaluate resulting effects on human health (risk assessment), and the extent to which a remediation effort was successful (were contaminants of concern adequately reduced or removed?) Data generated under SUPERFUND is subjected to verification and validation as a matter of course; EPA has defined guidance for the validation of organic and inorganic data, especially data generated via the CLP Program. This effort is often manual, however, software exists to expedite the process and remove some of the subjectivity inherent with manual validation efforts. The verification/validation of radiochemical data, however enjoys no such standardized guidance- it is an area under much development, especially within the DOE complex. The DOE is attempting to standardize verification/validation procedures for radiochemical data.

One cross-cutting issue centers around differentiating between validation and verification. There is a difference between the two processes which is not often recognized, much less addressed. The DOE has been attempting to define these terms, and identify specific functions that are performed for each of these processes. At the DOE Fernald site, we have been tackling these differences, and attempting to build the data evaluation process around a more technically defensible view of verification and validation.

Another issue deals with applying conventional validation wisdom to samples representing unconventional matrices. At many DOE sites, samples are often radioactive, which poses unique problems to the analyses of these samples. Even in cases where samples are not "hot", the laboratories are forced to attempt digestion/ extraction of matrices best described as semi-refractory. Traditional QC performed on such samples often indicates problems, or, in some cases, fails to indicate analytical problems because of the analytical methods requiring sample spiking just prior to extraction, which is not a good indicator of extraction/ digestion efficiency of the target compounds from these difficult matrices. There are no easy answers to these types of problems, but a

recognition that they exist is a first step at addressing them.

Much effort has been expended in an attempt to streamline costs associated with verification and validation. On several DOE sites, these processes account for as much as one-half the total costs associated with a particular sampling event. (Associated costs include sampling, lab analysis, data package generation, verification, validation, database activities, and final evaluation/data use.) There are numerous software programs in existence today that purport to reduce the time necessary for verification/validation (V&V) by factors of two, three or more. This author has not evaluated these programs, but some indeed have merit. As computer software and algorithms become more advanced and user-specific, the ability to perform automated V&V will increase in acceptance by users and regulators as well.

DISCUSSION

Historically, the validation process included the entire sequence of events from receiving and logging in data packages, through verifying completeness and contractual compliance through the determination of actual data usability, often even including database entry and approval. In reality, and now more often in practice, these steps are referred to individually, and not lumped together under the general misnomer of "validation". The DOE has defined two basic steps in the overall process- **data verification**, and **data validation**. The current definitions are presented below.

> ***Analytical Data verification***: A process of evaluation for completeness, correctness, consistency, and compliance of a set of facts against a standard or contract. Data verification is defined as a systematic process, performed by either the data generator, or an entity external to the data generator.[1]
>
> ***Analytical Data Validation***: A technically based analyte and sample specific process that extends the qualification process beyond method or contractual compliance and provides a level of confidence that an analyte is present or absent; if present- the associated variability. Data validation is a systematic process, performed external to the data generator, which applies a defined set of performance-based criteria to a body of data that may result in qualification of the data. Data validation occurs prior to drawing a conclusion from the body of data.[1]

These definitions may appear to be a bit "dry"- to explain: data verification can be thought of as contractual compliance (is everything there that was asked for by the contract governing the analyses), data completeness is all the necessary information present that is needed to

validate the data), data consistency (when the same information is found in the data package in multiple locations, was the same information transcribed/ downloaded at each location) and data correctness (are the results calculated correctly). These criteria are sometimes known as the four C's. These criteria are also applicable to electronic data deliverables (EDD)

Data validation is concerned with technical usability of the data. The validator, in an ideal world, is handed a data package (paper or electronic) that has been verified to the four C's criteria, and assesses the data on the basis of associated QC, sampling information, analytical performance, and other relevant information. The validator assesses the impacts of these factors, and assigns data qualifiers to individual data points, analyte groups, or results for entire samples, depending on the nature and severity of the affecting factor(s). Qualification can range from suggesting that a data point is imprecise (biased), to the rejection of a result, or group of results.

The question naturally comes, "What is the VALUE of verified and validated data?" The answer to this question is manifold. First, it must be understood that all data potentially contains error. Very few results are "pure"- that is, absolutely correct. Just the process of collecting a sample, attempting to achieve some degree of homogeneity (representativeness) introduces some uncertainty, and the uncertainties associated with sample preservation, shipment, and analysis all add to (i.e. "propagate") the uncertainty, or imprecision, of the final analytical results for the sample. It is the aim of the verification/ validation process (V&V) to identify these uncertainties, and give the data user a good feeling for the confidence of their data. It is generally accepted, that if samples were collected, preserved, shipped, and analyzed within the bounds of accepted protocols, then barring any unusual occurrences, the resultant data will not be qualified. These data represent results of the highest level of confidence within the scope of the protocols followed. So, in summary, data verification and validation serve to increase the user's level of confidence in a particular data set- the data are "of known and accepted quality", except where indicated. The intended uses(s) of the data are specified in Project Specific Plans (PSPs), and in the Data Quality Objectives (DQOs) for the project. V&V identifies data that are usable for the intended purpose(s) as outlined in these documents.

Another factor in why data should undergo V&V is wrapped up in the term "defensibility". Analytical data are often used in litigation, and if the result(s) in question have not been thoroughly assessed, then the usability of the data is questioned seriously. Data that are found to be non-defensible prove to make or break a case. It is crucial that all data used to make legal (or potentially legal) decisions are carefully evaluated in light of all factors that can affect the result- and this is

the V&V process.

The V&V process as envisioned by EPA is to assure that reported concentrations of a particular analyte are indeed indigenous to the sample, and not attributable to laboratory or method contamination. Inadvertent contamination can also occur during the sample collection, shipping and preservation.

Another factor to consider is the proper calibration of laboratory instrumentation prior to sample analysis. Improper/ incomplete calibration will result in incorrect identification and quantitation of analytes. The analysis of Laboratory Control Samples (LCSs) helps to assure calibration accuracy.

Verification can be accomplished manually or via verification software that is commercially available. Either way, verification is performed in a similar manner- assuring that the four C's are evaluated. Many organizations have standardized checklists to streamline manual verification, ensuring consistency between data sets. Validation is performed similarly- standardized protocol exists for assessing the impact of the various factors discussed above on data. The EPA's "National Functional Guidelines" furnish data validators with a widely accepted protocol for evaluating inorganic and organic data. This assures a high degree of uniformity in the application of validation criteria regardless of the entity performing the process.

In recent years, it has become necessary to perform the V&V process on radiochemical data, especially within the DOE complex. Validators at the Fernald site began initiating communication with other DOE sites in an effort to share information regarding various approaches that were being taken with regard to radiochemical validation. As DOE sites began exchanging information, it rapidly became clear that many sites had very little guidance with respect to this area- for several reasons. First, no standardized procedures exist for radiochemical analysis; so how can data be validated by a defined set of guidelines when a variety of methods is being utilized? Second, laboratories performing radiochemical analyses report their data in a variety of formats; up until recently, the concept of a "data package" was rather foreign to many laboratories, through no fault of their own. Customers had never requested a standardized set of data deliverables for the purpose of V&V, so the laboratories did not have to provide one. At the FEMP, as the RI/FS process gained momentum in the early 1990's, it became clear that validation of radiochemical data was necessary. Over the past four years, the validation group at the FEMP has expended a great deal of effort in an attempt to identify verification criteria, and then validation criteria. Often these criteria were nuclide or method-specific (alpha, gamma, proportional counting, LSC, etc...), due to significant differences in sample preparation, and counting between these methods. In 1993, the DOE formed a complex-wide work group to begin the arduous process of attempting to define standardized V&V guidance that

could e used across the entire DOE complex, and even be applied to EPA data as well. This work group has made progress, and a draft guidance document is in the process of completion. Many of the lessons learned at the FEMP are being incorporated into this document.

Third, there is no consensus regarding the effects of various QC indicators on the associated data. Various validation entities view these effects differently, and weight their importance differently as well. In organic and inorganic validation, the EPA has defined the relative importance and associated effects of QC information on the data. No such national standardization of the impacts of QC data exist for radiochemical validation.

Consequently, significant areas of discussion have centered around the evaluation of calibration, analytical/result uncertainty (TPU), batch-specific QC, utilization of numerous detectors, and other factors. Several working conferences have been convened, and sub-groups formed to address the various issues. It is not the intent of this paper to identify the resolutions of these issues, due, in part, to the fact that resolution has not yet been finalized on several of the issues. It is the author's hope that the awareness level has been raised regarding some of the issues, and that knowledgeable professionals, experienced in the assessment of data, will be encouraged to participate in the attempts at standardizing radiochemical data assessment.

The National Functional Guidelines for Organic and Inorganic Validation deal with the validation of aqueous and soil matrices, for the most part.[2] The behavior of holding times, spikes, surrogates, internal standards, etc.. have been well-studied in these more common matrices. The acceptance ranges of the QC parameters are based on studies of the QC behavior in hundreds of samples, and the acceptance limits used by the CLP SOWs are based on a statistical evaluation of the QC results. However, when dealing with more complex matrices, such as concrete, paint scrapings, fly ash, and other unique, more refractory matrices frequently encountered at DOE sites, the QC results do not reflect the expected behavior of soils that are found at most EPA sites. Data Validation professionals at the FEMP have recognized that unique matrices do not behave in the same way as routine soil or water samples, and we have made some "adjustments" to some of the EPA guidelines, especially with regard to spike and lab duplicate performance. This study is still underway, but it can be said that a somewhat looser set of criteria has been employed, via matrix-specific variances. Concrete has proved to require these variances most of all, probably due to the high concentrations (percentage levels) of mineral elements, as well as the non-homogeneous nature of samples. QC behavior with respect to radiochemical analyses has proved to be the most challenging problem. Because of the nuclide separation/isolation methods, 100% actual recovery of spiked analyte is nearly impossible to achieve. The use of tracers helps in the evaluation of method efficiency, but there is still no standardized protocol for

evaluating QC data from radiochemical analyses. Again, it is the author's hope that knowledgeable professionals will be of assistance by providing input to the eventual solutions to these challenges.

SUMMARY/ CONCLUSIONS

Data Verification and Validation are a necessary part of the sample collection, analysis, and data evaluation process. This issue of legal defensibility makes the careful assessment of data most important. Any data that is generated could conceivably be called into question; without V&V, no level of confidence can be associated with the data.

There are accepted guidelines for the V&V of inorganic, organic, and conventional data resulting from the analyses of the more common matrices of soils and aqueous media. These processes can be performed manually, or via software systems. V&V for non-routine matrices, and of radiochemical data in general, enjoys no such standardization; differences in the scope and content of radiochemical data review do not allow for a consistent evaluation of the level of confidence for radiochemical data, which is necessary to achieve the goals of various projects, especially those related to environmental cleanup and remediation. Making the environmental community aware of these issues is a first, but important step in coming to grips with these issues, and it is sincerely hoped that careful thought will be given to the issues raised in this paper, and helpful dialogue will follow.

REFERENCES

[1] Draft Document: *Radiochemistry Data Verification and Validation*, January 6, 1995

[2] *National Functional Guidelines for the Validation of Organic Data; National Functional Guidelines for the Validation of Inorganic Data*, 1994

DEFINITIONS

1. **Data Verification**

VERIFICATION: A process of evaluation for Completeness, Correctness, Consistency, and Compliance (the 4 C's) of a set of facts against a standard or a contract. DATA VERIFICATION is defined as a systematic process (performed by either the data generator, or an entity external to the data generator) of determining the 4 C's of a data deliverable.

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2. **Data Validation**

A technically based analyte and sample specific process that extends beyond method or contractual compliance (verification) and provides a level of confidence that an analyte is present or absent; if present- the associated variability. Data validation is a systematic process, performed external to the data generator, which applies a defined set of [contractual or] performance-based criteria to a body of data. Data Validation occurs prior to drawing a conclusion from a body of data.

The 4 C's

1. **Completeness**: The presence of all the necessary technical information that is needed to verify and validate the data.

2. **Consistency**: When the same information located in multiple sections of a data package is transcribed/ downloaded correctly at each of the locations.

3. **Correctness**: The assurance that results are calculated correctly.

4. **Compliance**: The assurance that all the information required by the governing analytical SOWs and client contracts is present in the data deliverable.

A Snapshot of items Validation evaluates in determining Data Usability

- Sample Collection Process (physical sampling, preservation...)
- Holding times: from sampling to analysis, and from lab receipt to analysis
- Analytical Quality Control Analyses
  - Blanks
  - Matrix Spikes
  - Laboratory Duplicates
  - Organic Surrogate Spikes
  - Lab Control Samples (LCSs)
  - Interference checks
  - Calibration Stability
  - Sample-specific issues (dilutions, re-analyses...)
  - Radiochemical tracer yields
  - Radiochemical Uncertainties (TPU, Counting errors)

Issues that Complicate Validation

1. Effects of difficult matrices (high organic content materials, high mineral content samples, samples with significant radioactivity [especially Th]

2. Consistent Application of radiochemical QC parameters

    * Confusion regarding the Meaning of QC parameters
    * Confusion regarding when QC are non-compliant
    * Confusion regarding how to apply non-compliant QC (extent of bias; is data estimated or unusable?)

3. Where verification leaves off, and validation begins.

Suggested Path Forward

1. Recognize that all data requires verification and validation at some level.

2. Adopt a consistent approach to verification and validation, such as the EPA National Functional Guidelines for Inorganic and Organic data.

3. Recognize that there are complicating issues with validation of environmental data, and that resolution is needed.

4. Participate in discussions regarding the verification and validation of radiochemical data. (Worgroup is headed by Jeff Paar, of Martin Marietta, Oak Ridge, TN)

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QUALITY ASSURANCE/QUALITY CONTROL AT A POTW

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ABSTRACT

An essential component of any large field investigation is a working quality assurance/quality control (QA/QC) program. A group of citizens living in the community surrounding a Publicly Owned Treatment Works (POTW) facility were concerned that the operation of the POTW facility potentially contributed to the adverse health effects they experienced. Since their primary concern was the air emissions from the various plant operations, they requested that their county department of public works conduct an air sampling study of the POTW facility. Upon the citizens' request, the county funded a $1.5 million study to develop a technically sound and legally defensible investigative program to determine whether the operation of the POTW facility had the potential to contribute to the adverse health effects of the local residents.

Many aspects of the laboratory and field quality assurance/quality control activities conducted for this investigation have been custom designed. An ambient air monitoring network was designed to allow for the simultaneous collection of air samples from ambient air monitoring stations strategically located in the neighborhoods surrounding the POTW facility. Samples were collected on a routine basis as well as during periods in which there were high incidences of odor complaints. The target compound list for this project was based on compounds known to cause odors at a POTW facility and compounds that were on the Clean Air Act list of volatile organic compounds. Samples were analyzed for volatile organic compounds by U. S. Environmental Protection Agency (EPA) Method TO-14, for sulfur compounds by a modified U.S. EPA Method 16, for chlorine by NIOSH Method 6011, and for ammonia by NIOSH Method S347. Because these methods do not require extensive laboratory QA/QC, these methods were modified for this investigation to include additional laboratory QA/QC samples such as laboratory duplicate samples, laboratory control samples, and matrix spike/matrix spike duplicate samples. In addition, since many laboratories do not routinely offer complete and comprehensive data package deliverables, specific data package deliverables were developed to substantiate the reported analytical results and additional QA/QC. As one of the additional QA/QC measures developed for this study, split samples were collected and analyzed by both the project laboratories and other laboratories. In addition, blind performance evaluation samples were submitted to the project laboratories. This paper will discuss the details of the design of the field study, the modified analytical methods, the data package deliverables, and the results from the split samples and performance evaluation samples. In revealing the details of the QA/QC measures employed in this investigation, this paper will demonstrate the effectiveness and utility of a well-designed QA/QC program.

CONDUCTING A PERFORMANCE EVALUATION STUDY - IT'S NOT JUST ANALYTICAL RESULTS

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Abstract

Conducting an effective Performance Evaluation (PE) study can provide more than an indication of the laboratory's analytical expertise. Typically, a PE study is used to determine the laboratory's accuracy in identifying and quantifying the compounds contained in the PE sample as compared to known identities and concentrations. An effective PE study can also include evaluating the client, technical and administrative services, sample login and receipt, data packaging, method compliance, and quality assurance.

This presentation will focus on an initial Performance Evaluation study which involved thirteen laboratories. A review of the initial setup procedures with the Performance Evaluation sample supplier, contacting the laboratories, answering questions from laboratories, and the non-analytical and analytical results obtained from the study will be presented.

Introduction

The PE study involved 13 laboratories selected for participation in a single-blind PE study using whole-volume samples. Since all laboratories were informed of the study date, no laboratory was placed at an advantage or disadvantage based on sample workload conditions or potential of subcontracting the PE samples to another laboratory facility.

The parameters chosen for analysis, the required analytical methods, the volume and bottle types received, and the preservation of the samples are summarized below.

Parameters	Method	Volume/Bottle	Preservation
Volatiles	Method 8240A/8260A	3 × 40 mL/VOA vial	HCl pH <2
Semivolatiles	Method 8270A	2 × 1 L/Amber glass	Cool to 4°C
PCBs	Method 8080	2 × 1 L/Amber glass	Cool to 4°C
Trace Metals	Method 6010A/7470/7060/ 7421/7740/7841	1 L/HPDE	HNO_3 pH <2
Cyanide	Method 9010	1 L/HPDE	NaOH pH >12

Once the final group of parameters was identified, the individual analytes and required concentrations were determined with input from several PE sample manufacturers. The following questions were answered prior to the final design of the PE study.

- Should off-the-shelf standards or custom standards be used in the PE study?
- What analyte concentrations are required?
- Should ampuled-PE samples or whole volume samples be used?

In this study, our goal was to include a wide range of analytes from each group of parameters, therefore, off-the-shelf standard lots (except for a PCB PE sample) were used. The volatile organics included chlorinated alkanes, alkenes, and aromatics. The semivolatile PE sample contained substituted phenols, base/neutrals, phthalates, PAHs, and several pesticides which were included in the PE sample lot, but are not typically analyzed by the method chosen for semivolatile analysis. The PCB sample was custom-made to include both Aroclor 1016 as well as Aroclor 1254. The inorganic PE samples contained typical Target Analyte List parameters. Performance evaluation sample lots containing concentrations at low-to-midrange of typical instrument calibration ranges were requested for the organic parameters. The PE samples were prepared as whole volume samples, which eliminated differences in PE sample dilution techniques between laboratories by a reputable vendor. The PE samples for all laboratories were prepared from the same lot number to further reduce variance and permit result comparison between laboratories. The PE samples were preserved and shipped on ice under Chain-of Custody procedures for delivery to 11 laboratories in October of 1994. A second set of freshly prepared PE samples was sent in November of 1994, to two laboratories which were added to the PE study.

Initial Contact with the Participating Laboratories

Initial contact with the laboratories is an important first step in conducting an effective PE study and evaluation of the customer service provided by the laboratory. The information that is relayed to the laboratories must be clear, concise, and consistent. One individual should make all contacts to the laboratories, through a letter, which introduces and explains the PE study. The following questions should be answered:

- What parameters will be analyzed?
- What method will be used?
- What list of compounds?
- Will the PE samples be ampuled or whole-volume?
- If the samples are whole-volume, when does the holding time commence?
- What preservation requirements will the samples be arriving under?
- When will the samples arrive and from which supplier?
- When is the due date for results?
- What types of data deliverables are required?
- Who will be the single-contact for questions and submission of data?

In our initial contact letter, we decided ***not*** to provide answers to several of the questions posed above. In this way we could evaluate a laboratory's customer service response to missing or incomplete information with regard to a regular sample submission. The facilitator of the PE study must keep an accurate phone log of the questions asked and the answers provided for later use in final evaluation. In our letter we did ***not*** provide information on the list of compounds to be reported or holding times. This omission resulted in many, but not all, of the laboratories calling to ask the list of compounds to be analyzed. Since whole volume PE samples were used in this study in an attempt to mimic actual field samples, holding times began on the date of PE sample preparation. Holding times listed in each analytical method were used for evaluation purposes. Again several labs did not inquire about holding times; however, most correctly assumed that method holding times were to be followed. Additional questions or problems incurred by the laboratories also provide an indication of the communications systems and corrective actions employed by the laboratories on a daily basis.

Review of Non-Analytical Factors

As stated above, the phone log provided the PE study facilitator with a wide range of good information on each of the laboratories participating in the study. Below are some examples of the information collected during the PE study.

- Many laboratories called to ask which list of compounds was requested. However, upon final review of the reported data, several labs had not analyzed the method lists or provided additional compounds such as pesticides, when only PCBs for Method 8080 had been requested.

- Several laboratories called to indicate that a specified method was not performed, however, a slightly different method or modification to the method was used by the laboratory. These types of communications indicate good review and communication by customer service as well as the analytical departments. Several laboratories provided different methods than those requested, without approval. For example, Method 524.2 data with a 25 mL purge was used instead of the specified Method 8240/8260, which indicates a 5 mL purge volume. This resulted in much lower reporting limits for the analyte list. The lower reporting limits may result in additional problems for the project staff.

- Several laboratories called to inform the facilitator that the extraction holding times for the semivolatiles and/or PCBs had been exceeded and requested information as to the recommended course of action. This again indicates very good communication when problems are encountered and corrective action is necessary. In this example, the analysts had assumed that the PE samples were contained in ampules, which do not have specified holding times. However, the initial letter submitted to the laboratory indicated that the samples would arrive as whole volumes and not as ampules (for which holding times are typically started when the ampules are opened).

The final results reported can also provide information beyond the compound results printed on the pages. Depending on the type of data deliverables requested, a review of data deliverables from "results only" to full CLP-style deliverables can be completed. Full data validation by highly trained chemists, knowledgeable in the analytical method requirements and data deliverables, can provide an indication of the total quality of the data. The data can be reviewed for compliance to method requirements, sample custodies, holding times, blank contamination, surrogate recoveries, matrix spike/matrix spike duplicate recoveries, laboratory control sample recoveries, initial and continuing calibrations, quantitation of results, proper corrective actions, and reporting errors. Even "results only" packages can provide an indication of the type of deliverables provided in this package. Data packages that contain excess information not necessary for the client's needs, can be reduced, saving money for the client. Conversely, data packages can be supplemented if found deficient to meet project requirements prior to project initiation. "Results only" packages can also provide an indication of the laboratory's quantitation limits, whether the lab reports values below the quantitation limit, and if the package is "user-friendly". Chain-of-Custody Records and laboratory sample log-in and receipt forms can provide an indication of the quality and accuracy of sample receipt procedures. Examples of these procedures include whether or not temperatures of sample coolers are taken and recorded, the pH measurement of preserved samples are reported, signatures and date and time of sample receipt are completed on the Chain-of-Custody Records, if the laboratory uses internal Chain-of-Custody documentation and documents any warranted corrective action procedures. Several items are presented as examples of "non-analytical" factors found during this study .

- One laboratory received the PE samples at 11° C and did not report the problem to the PE facilitator.

- One laboratory provided full CLP-style data packages instead of the "results-only" package requested.

- One laboratory provided multiple copies of the same data delivered on different days, which could cause additional confusion when data is reviewed by the data user.

Methodology and Scoring

The laboratory results were compared to the certified performance evaluation sample results and then evaluated against the 95 percent confidence limits provided by the PE sample supplier. A Microsoft Excel spreadsheet was prepared to determine the percent recovery of each analyte, compliance with the 95 percent confidence limits, individual analyte scores, and a final laboratory score. The percent recovery is determined by dividing the laboratory-reported result by the true value reported by the PE sample supplier, multiplied by 100, and a percent reported on the spreadsheet. Confidence limits were determined by comparison of the laboratory-reported results to the lower and upper confidence limits. In addition, average percent recoveries were computed for the following subset parameters, volatiles, acid extractables, base/neutral extractables, polychlorinated biphenyls (PCBs), metals, and cyanide for each laboratory and charted for comparison purposes. Four analytes (heptachlor, *gamma*-BHC, boron and molybdenum) were not scored since these compounds/elements are not typically included as normal parameters analyzed by the analytical methods requested.

The laboratory results were scored on an individual analyte basis using the following scoring criteria:

Recovery Criteria	Points Awarded
90-110 percent	10 points/analyte
80-120 percent	8 points/analyte
70-130 percent	6 points/analyte
60-140 percent	4 points/analyte
50-150 percent	2 points/analyte
<50 or >150 percent	0 points/analyte

In addition, the following negative and/or positive scores were also assessed, as necessary, at the reviewer's discretion. Major laboratory deficiencies, such as incorrect identification or missed holding times, were assessed a negative 10 point score for each infraction which was deducted from the final analytical score. Minor laboratory deficiencies, such as late or multiple submission of results, were assessed a negative 5 point score for each infraction. Positive scores for "user-friendly" data, verification of sample receipt, and data receipt by the laboratory were also scored as additional points

- Incorrect identification of Aroclor 1016
- Missed semivolatile holding time
- Late deliverables/incomplete deliverables
- Wrong deliverables format/multiple submissions of results
- Missing analyte or additional analyte not present in mix detected at levels above quantitation limit
- Temperature excursion not reported to Environmental Standards, Inc.
- Identification and/or quantitation of pesticides as Tentatively Identified Compounds in Base/Neutral Extract
- Verification of sample receipt
- Verification of data receipt after submission to facilitator

Analytical Results

The laboratories, in general, scored well for the volatile organic compounds, with average recoveries ranging from 66 to 139 percent. The compound acetone was routinely detected, but was not reported by the PE sample supplier at a certified amount. The presence of acetone is probably due to laboratory contamination or as a standard solvent from the PE sample. Several laboratories identified the dichlorobenzene isomers contained in the volatile PE sample as Tentatively Identified Compounds. One laboratory did not identify the dichlorobenzenes. One laboratory did not identify 1,2-dichloroethane in their PE sample.

The acid extractable compounds exhibited average recoveries of 34 to 72 percent. It is difficult to obtain good recoveries for these compounds as exhibited by the 95 percent confidence limits reported by the supplier. In addition, acid surrogates typically used for semivolatile analysis also exhibit wide recovery acceptance limits. Several laboratories did not identify 2-nitrophenol, or 2,4-dimethylphenol in their PE samples although the concentrations of these compounds contained in the PE samples were above the laboratories' reporting limits. One laboratory also reported the presence of 4-methylphenol which was not present in the PE sample, according to the supplier.

The base/neutral extractable compounds exhibited average recoveries of 35 to 71 percent, which are similar to the average recoveries for the acid extractables. The compound, hexachlorobutadiene, and the phthalate ester compounds seemed to exhibit low recoveries for many of the participating laboratories. In addition, several laboratories reported low recoveries for the polynuclear aromatic compounds. One laboratory reported a positive result for anthracene which was not present in the PE sample according to the supplier.

The polychlorinated biphenyl PE samples contained both Aroclor 1016 and Aroclor 1254. The decision to use two Aroclors in a custom PE standard was made to determine the laboratories' ability to accurately identify and quantitate multiple Aroclors. The decision to use these two Aroclors was based on non-overlap of the Aroclor peaks. If the sample had contained Aroclors that had many common peaks (e.g., Aroclors 1248 and 1254), the results may have caused problems during the evaluation process. All laboratories correctly identified Aroclor 1254, with recoveries ranging from 33 to 82 percent. However, only five of the thirteen laboratories correctly identified Aroclor 1016. The remaining laboratories incorrectly identified the multi-peak pattern as Aroclor 1242, which is similar to the Aroclor 1016 pattern.

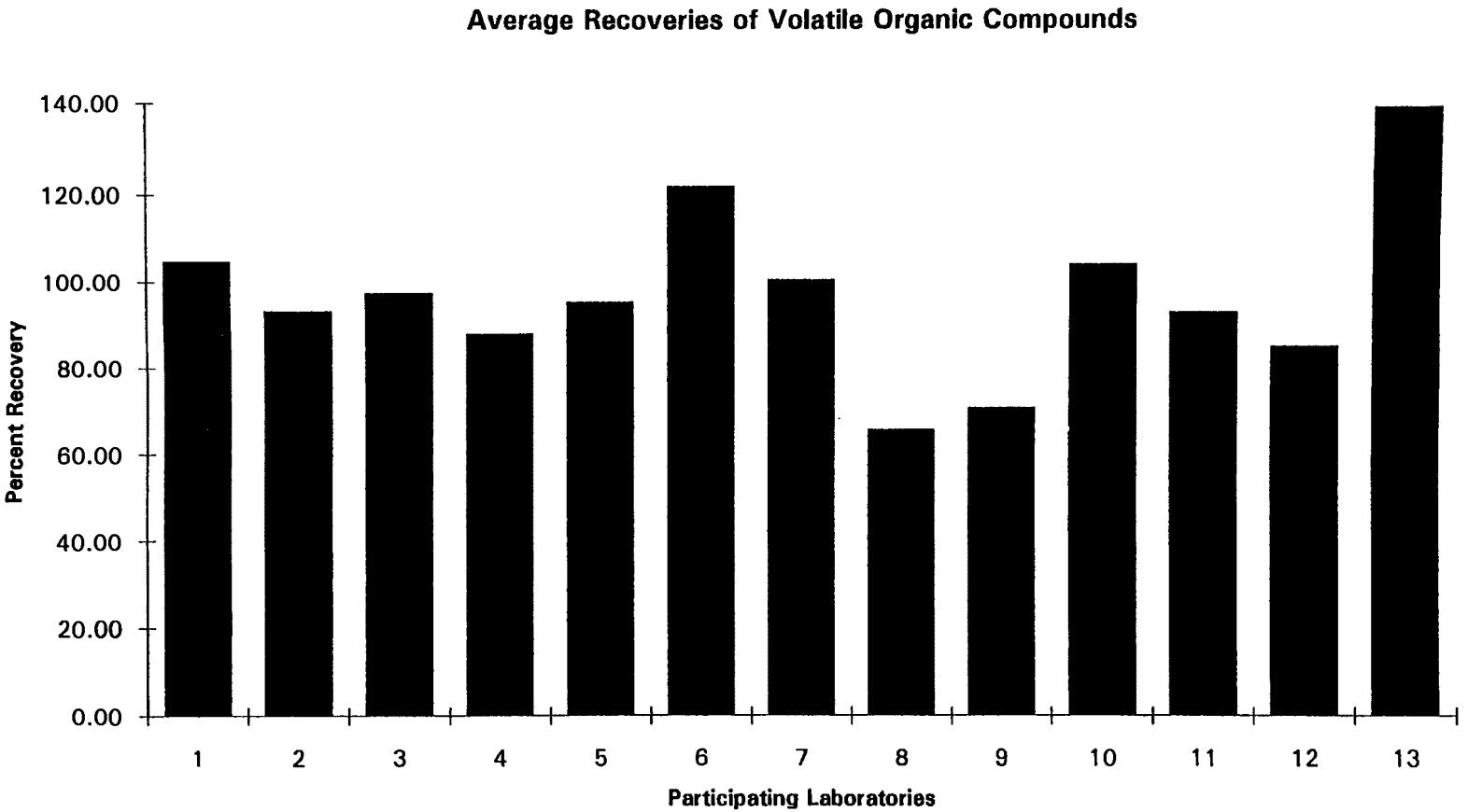
The laboratories scored very well for the metals, with average recoveries ranging from 84 to 162 percent. Cyanide also exhibited good recoveries, ranging from 81 to 100 percent. Several laboratories had low recoveries for aluminum, iron, and mercury. One laboratory did not report results for copper.

The laboratory-reported results were outside the 95 percent confidence limits for five to 15 compounds for the total of 50 compounds tested. The average was approximately eight compounds, with the majority of laboratories incorrectly identifying Aroclor 1016 in the PCB PE sample. Many of the laboratories also reported low recoveries for the acid extractables, base neutrals, and mercury.

Graphs showing the average recovery by fraction for each laboratory are presented in Attachment 1.

Conclusion

The additional work necessary to conduct an effective Performance Evaluation study can provide a wide range of analytical, as well as non-analytical, data for evaluation of the laboratories in our study. Information obtained from evaluating client services, sample log-in and receipt, and data packaging departments can help to determine the level of quality, responsiveness, and completeness that may be expected from the laboratory on an actual project. However, it should be realized that this "snap-shot" in time may not fully demonstrate the laboratories' capabilities on an actual project. The information obtained from the Performance Evaluation study is best used in conjunction with information obtained through laboratory audits, which also provide insight into the analytical and equally important, non-analytical procedures practiced at the laboratory.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140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Percent Recovery
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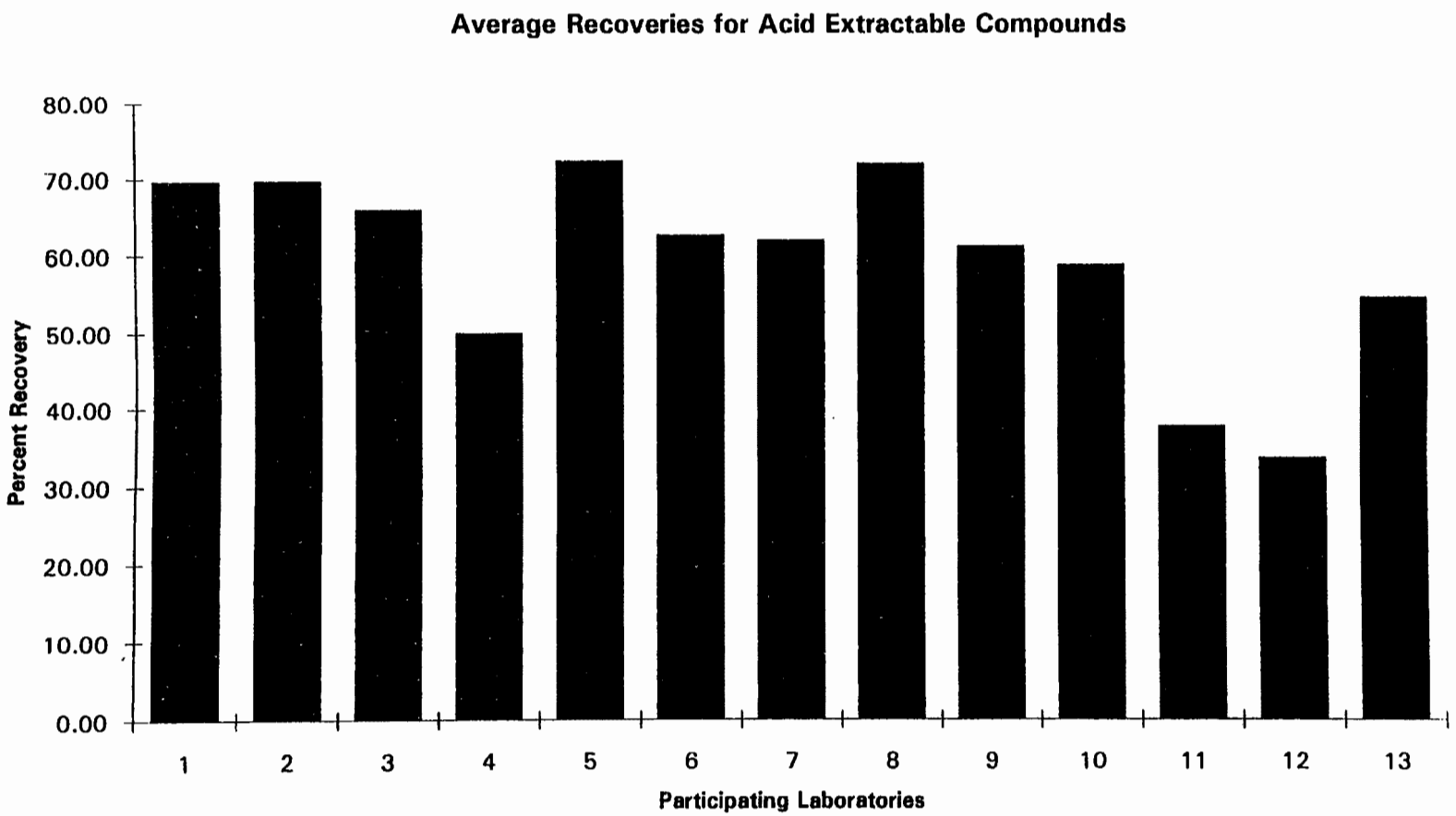
2
3
4
5
6
7
8
9
10
11
12
13
Participating Laboratories


Average Recoveries for Acid Extractable Compounds
80.00
70.00
60.00
50.00
40.00
30.00
20.00
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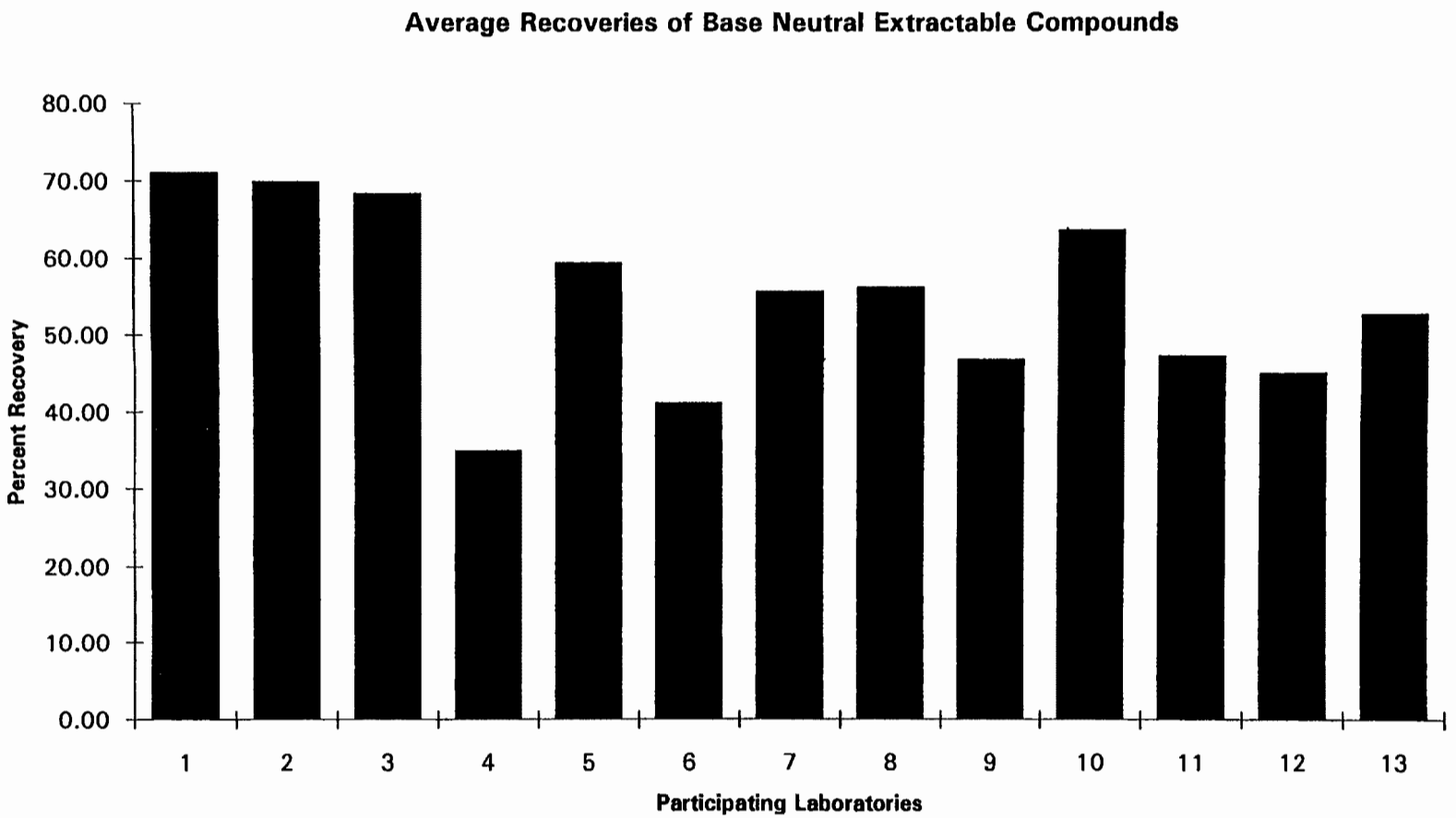
6
7
8
9
10
11
12
13
Participating Laboratories


Average Recoveries of Base Neutral Extractable Compounds
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Recovery
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2
3
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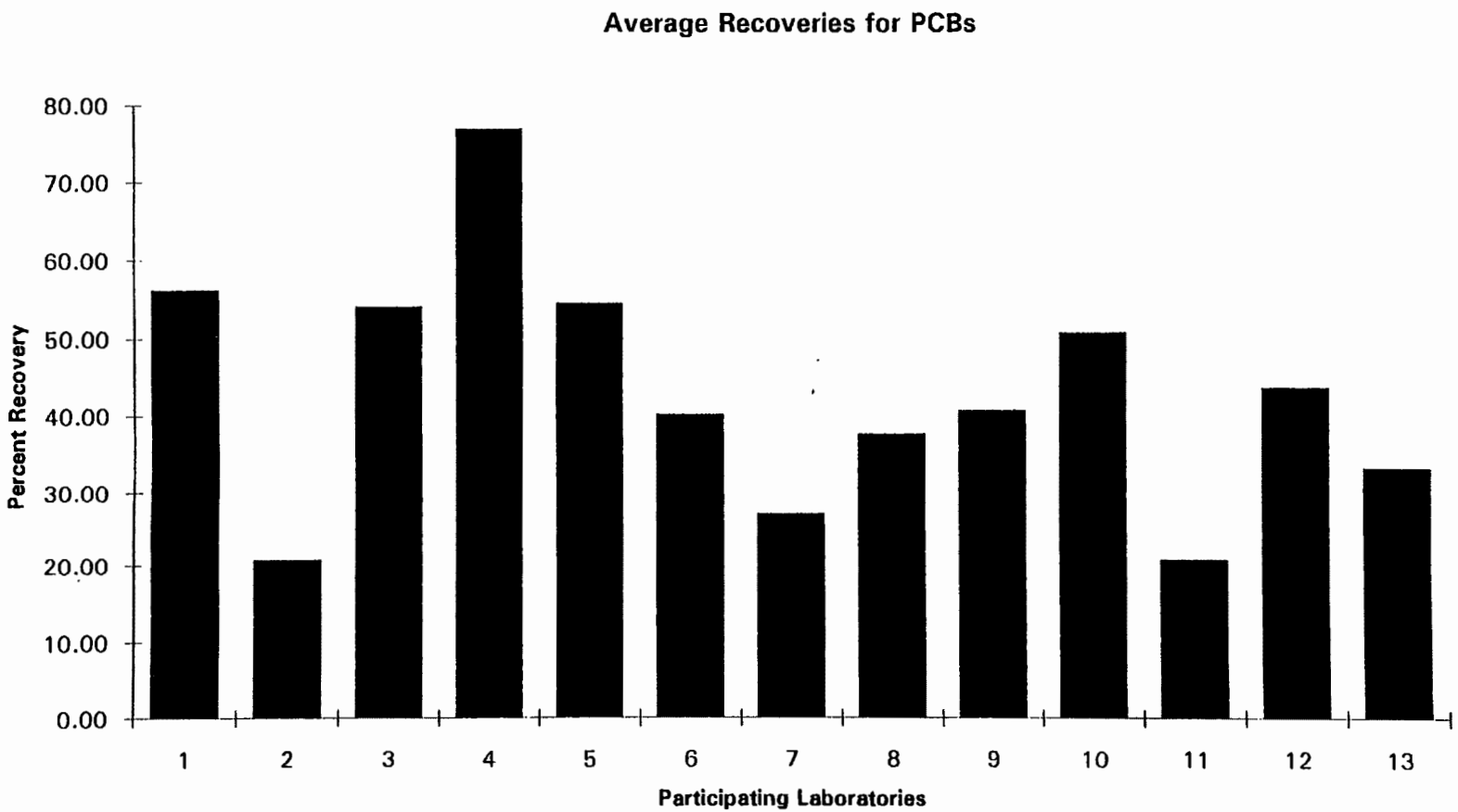
5
6
7
8
9
10
11
12
13
Participating Laboratories


Average Recoveries for PCBs
Percent Recovery
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
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6
7
8
9
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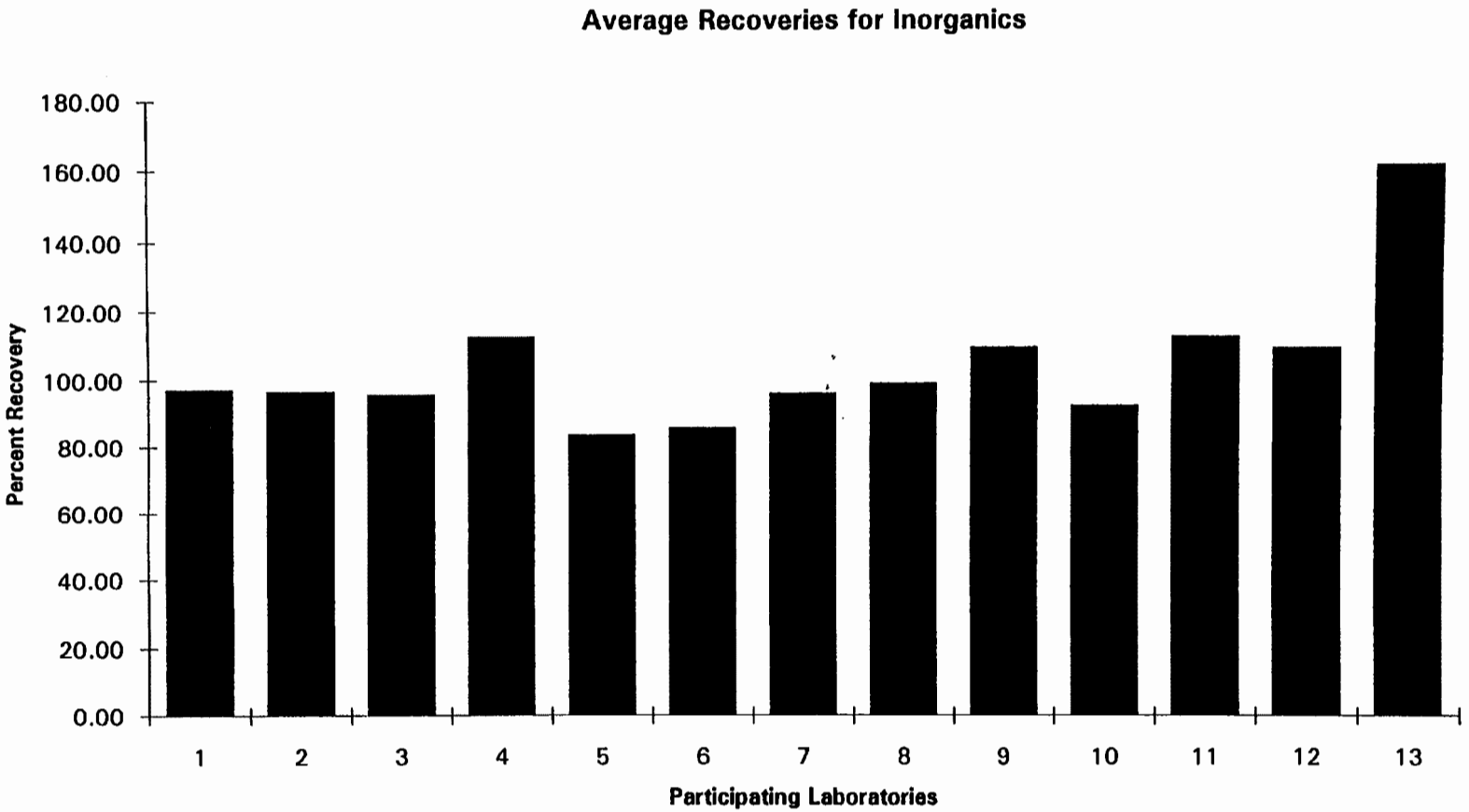
11
12
13
Participating Laboratories


Average Recoveries for Inorganics
Percent Recovery
180.00
160.00
140.00
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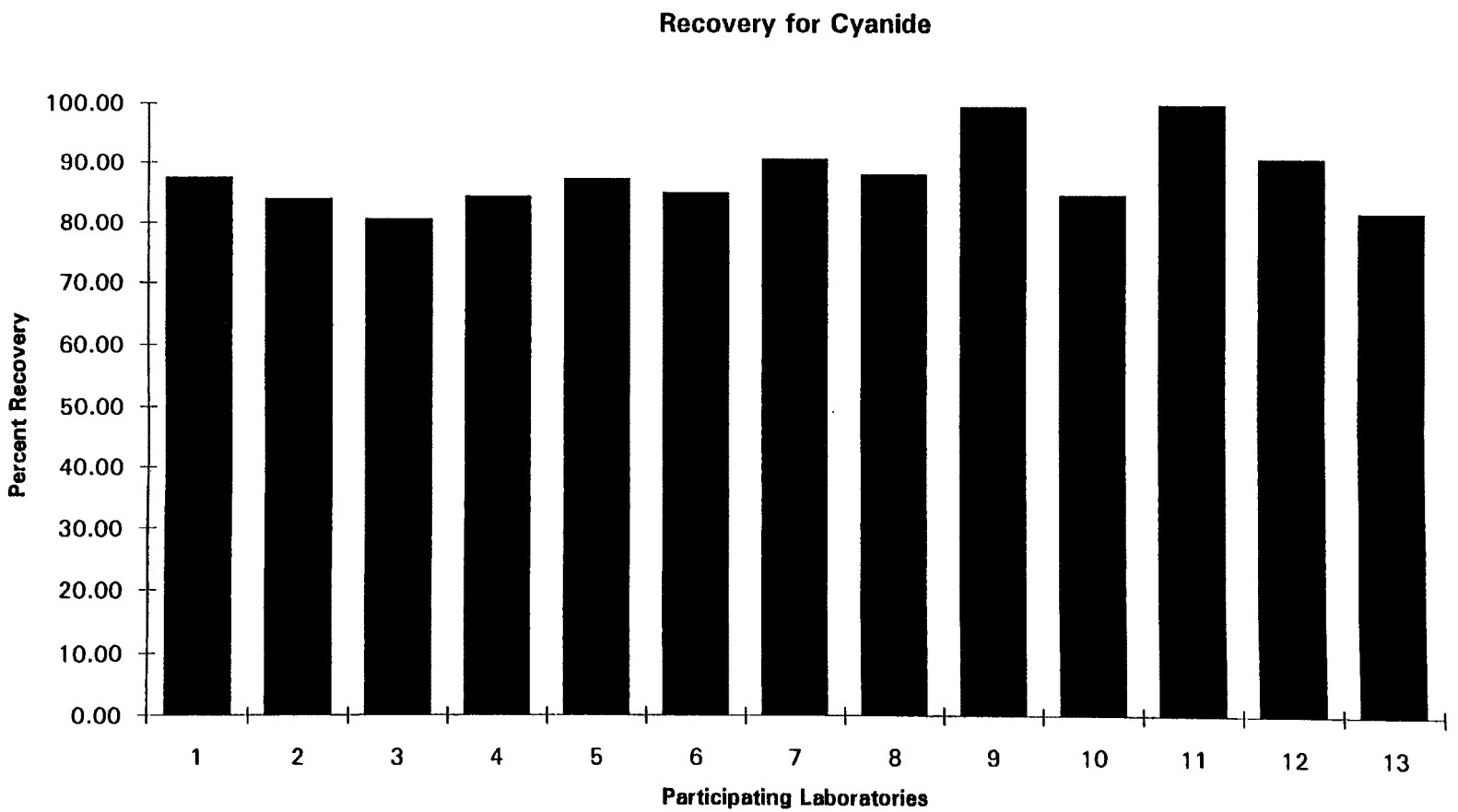
Participating Laboratories


Recovery for Cyanide
Percent Recovery
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Participating Laboratories

FATE OR EFFECT OF DATA PRESENTED WITH QUALIFIER AND LABORATORY ESTABLISHED QC LIMITS

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ABSTRACT

Data presented with qualifiers such as "B" in organic and inorganics, "J" in organics and "E" in both organics and inorganics often leads to the non acceptance of data as estimates. Estimated data do not always serve the project's needs. Data reported below background, due to so called matrix effect and qualified as "J", meaning found below the practical quantitation limits but detected above the instrument or method detection limit, ultimately cause the data to be used as estimates. Non-detect data sometimes are used as a tool for data censoring. Some data are presented with the qualifiers "M" or "EMPC" which means data reported with imperfect spectral match or estimated maximum possible concentration, respectively. Data flagged with these symbols often lead to false positive data reporting. These type of data are often found in low level detection limit studies such as groundwater , drinking water or dioxin/furan analyses. False positive reporting of data is also encountered with "B" flagged data. Some of these data are also reported as estimates based on data reviewer's opinion. False positive and false negative data reporting is expensive, delays and adversely hampers the project. There should be controls on these types of data reporting. The term "data rejection" should be employed, but is not, due largely to loosely regulated methods and the lack of clearly defined QC limits. EPA SW-846 methods, used under the RCRA program, use laboratory established QC limits and no guidance has been given for "cut off" levels. Due to these deficiencies, data precision, accuracy and sensitivities subsequently suffers. In general, data assessments are affected due, inpart, to the ambiguous use of qualifiers and poorly defined or regulated laboratory established QC limits.

INTRODUCTION

Data generated in hazardous toxic radiological waste (HTRW) studies are viewed differently by each of the three main technical staffs involved with data production and review: 1) analytical chemist (the principle data generator), 2) data evaluator/validator, and 3) data user (often the regulatory authorities such as the EPA). Data generated by the laboratory must meet method required internal quality control (QC) criteria, including the EPA contract laboratory program (CLP) and SW-846 laboratory established (LE) QC limits (1, 2). The laboratory normally uses qualifiers (flags) when certain internal QC results are outside of the criteria. Data evaluators/validators add another functionality to the review process, namely "data quality objective" (DQO) requirements during quality assurance report (QAR) preparation. At this stage of review, the data may be labeled with additional qualifiers. During QAR preparation, data with out qualifiers are segregated for use. Data with qualifiers are treated with caution with the concurrence of

the regulator authority, whenever possible. This paper exposes some of the common problems in reporting data with qualifiers and the implications of this in site evaluation. It would be difficult and cumbersome to discuss all of the EPA functional guideline qualifiers (1, 2), therefore examples of some common qualifiers such as "B", "E" and "J" are discussed. These qualifiers are added to the data because of questionable precision, accuracy, and sensitivity and to indicate false positive and false negative reporting.

DATA COLLECTION AND EVALUATION

Data from various commercial laboratories were compiled and evaluated. The data presented here are for samples that were split or collected sequentially and analyzed by two independent laboratories. This was done to demonstrate inter- and intra-laboratory data comparability, data reproducibility and to further illustrate the implications of qualified data on data usability. Split samples were analyzed for volatile organics by EPA methods 8260 or EPA 8020, semi-volatile organics by EPA method 8270, dioxin/furans by EPA methods 8290/1613, and radiological parameters by EPA methods 9310/9320. Some of the data are presented with laboratory method blank contaminants, elevated detection limits, surrogate, matrix spike, relative percent difference (RPD) failures or holding times expiration. Gasoline range organics (GRO) and diesel range organics (DRO) data, determined EPA modified 8015 (3) and EPA modified 8100 (4), respectively, were chosen to demonstrate the limits of performance based methods where the internal QC criteria are inadequately defined.

RESULTS AND DISCUSSION

Positive results presented in Tables 1 and 2 are qualified with either the "B" or "J" flag except for the QA laboratory's data of phenanthrene and pyrene. The "B" and "J" flags attached to the data indicates the respective analytes were detected in the associated method blank and detected below the quantitation limit, respectively. The common laboratory contaminants, such as water soluble volatiles or phthalates as reported in Tables 1 and 2, are not considered significant if the sample concentrations are less than 10 times the concentration in the associated method blank. It is noted that the project acetone datum is greater than 10 times the blank concentration (Table 1), and is reported with a "B" qualifier. The presence of this analyte was supported by the other laboratory where the datum was qualified with "J" and laboratory blank contamination was not encountered. In both instances, data would be considered estimates. Most likely, the detected acetone results of both laboratories were due either to laboratory cross-contamination or some sort of laboratory artifact.

The project laboratory reported all semi-volatile organics (BNA) data in Table 2 as either not detected (ND) or with a "J" flag. The BNA project data are considered low estimates based on two out of six surrogates, and six (acidic) out of 22 matrix spike recoveries below EPA/LE QC limits. Instead of accepting the project data as low estimates, the data should be rejected. The QA laboratory reported four of six positive BNA data with a "J" flag. The QA laboratory's internal QC was acceptable and it was noted to have been performed using the sample. The dilemma is that all the qualified

data presented in Table 2 has been considered estimated while in reality the evidence supports the rejection of the project data. There should be some mechanism to reject data in lieu of accepting data with qualifiers as estimates.

The QA data in Table 3 are reported as estimates due to holding time expiration, and benzene was found at a higher level as compared to the sequential blind duplicate data. In general, the clean-up level for benzene in soil is 50 ppb and the QA data (68 ppb) would trigger clean-up while the project blind duplicate data indicate no action needs to be taken. It was noted that the internal QC of both the laboratories were within EPA or LE QC limits.

Data of radiological analyses in Table 4 are questionable and are not suitable for decision making. Gross alpha found in project groundwater sample -09WA was detected close to the action level of 5 pCi/L, but was not detected in the blind duplicate sample and was detected at a lower level in the QA (external laboratory) sample. Low levels of gross alpha and radium 226/228 reported by the laboratories are probably due either to background noise or some sort of laboratory artifacts. In all probability, these data should be attributed to false positive reporting. It was noted that the internal QC data of both laboratories was acceptable per method requirements.

The majority of dioxin/furans data in Table 5 are reported with the qualifier "estimated maximum possible concentration" (EMPC). Low levels (parts per quadrillion) of dioxin/furans are reported as positive hits, but in reality are false positive data. A few analytes are reported with two qualifiers, B and EMPC, indicating that the respective analytes were also detected in the associated method blanks. Project blind duplicate and QA data could not be compared, as the QA laboratory accidentally spiked the sample with targeted analytes. Despite this, about one half of the results for the QA sample are flagged with the qualifiers EMPC or EMPC and B due to an imperfect spectral match and/or to laboratory cross contamination. Dioxin/furan analysis which utilizes high performance GC/MS methodologies are very expensive, often as high as $3000/per sample. And after paying the high cost of analysis, the data reported, in some cases, are not useable due either to laboratory cross contamination or artifacts. Data are reported per SW-846 under the RCRA program guidelines due, inpart, to laboratory established QC requirements where the QC limits are not very well defined. In projects involving risk assessment it is normal for false positive dioxin/furan data to be used with qualifications, in lieu of rejection, for site evaluation because of DQO requirements.

The data presented in Tables 6a and 6b are State of Alaska Department of Environmental Conservation (ADEC) methods for GRO and DRO analyzed by modified EPA methods 8015 and 8100, respectively. Internal QC requirements and limits of data acceptability are not well defined except for surrogate, laboratory control (LC) recoveries and RPD results. GRO data reported by the project and QA laboratories do not agree due, inpart, to the fuel quantification approach used by the laboratories and non-identical samples submitted. Some of the early eluting hydrocarbons of DRO eluted in the GRO range and were quantitated as GRO. As the clean-up action level for GRO in Alaska is 50 ppm and falsely elevated GRO results reported by the QA laboratory (49 ppm), is on the borderline and puts the issue of clean-up into question. If the presence of GRO in the soil is confirmed, additional analyses such aromatic volatile organics (AVO) and haloginated volatile organics (HVO) may be required to verify the need for clean-up. In

general, the false positive reporting of GRO results by the laboratories are due to the use of loosely defined performance based methods. In this particular case, false positive GRO reporting hampered the progress of the project. Costs associated with this anomaly could be as high as hundreds of thousands dollars, if decisions are based solely on these data.

CONCLUSIONS

There is a need for a mechanism to reject data instead of using qualified, but questionable, data. Internal QC requirements of EPA SW-846, where LE QC limits and /or method required QC limits are used to evaluate the data, are not well defined. The National Functional Guidelines (2) used in the EPA CLP offer some limited data rejection guidelines, but data eventually can be used with qualifications. The project BNA data in Table 2 should have been rejected due to internal QC failure, but data were reported as estimates. Often not detected (false negative) data are reported as estimates, due to internal QC failure, as seen in one of the blind duplicate data of Table 2. Possible false positive data, such as presented in Tables 4 and 5, are expensive and hamper the progress of the project. Data could not be rejected due, inpart, to loosely defined precision, accuracy and sensitivity QC criteria. Data evaluators hired to validate data are often as expensive as the cost of analyses. Frequently, after evaluation the data are reported with qualifiers. Data rejected based on EPA functional guidelines are most of the time reported as estimates and are finally used in decision making as qualified data.

False positive GRO data reported in Table 6 may have hampered the progress of the project due to loosely regulated methods. Based on the DRO data, further clean-up may have been required, but the additional analyses required to substantiate the levels of GRO found would not be required. Use of the modified performance based EPA methods, with loosely defined internal QC requirements, should be discouraged. It is further recommended here that a total petroleum hydrocarbon methods for fuel (GRO and DRO), using gas chromatography with stringent internal QC requirements should be developed to avoid unexpected additional costs during the progress of the project.

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4. AK102 (modified EPA 8100), Diesel Range Organics, Alaska Department of Environmental Conservation, Alaska, 1992.

TABLE 1

COMPARISON OF VOLATILE ORGANICS (EPA 8260) DATA

Analytes Detected	Project Lab 213SL	Detection Limits	QA Lab 201SL	Detection Limits
Acetone	130 **B**	14	24 **J**	130
2-Butanone	13 **J**	14	ND	130
Methylene Chloride	18 **B**	6.8	ND	6
Percent Solids	73.2		78.0	

Units = µg/Kg (ppb)
J = Estimated concentration
B = Found in method blank [acetone at 10 ppb, 2-butanone at 2 ppb and methylene chloride at 8 ppb]
ND = Not detected

SUMMARY: The project and QA data agree within a factor of five to each other or their detection limits for all targeted volatiles and are comparable except of the project data of acetone due to laboratory cross-contamination. All three detected analytes are common laboratory contaminants and were detected within a factor of ten to the levels found in the associated method blank, except for acetone. Acetone datum was reported with a qualifier as if it was considered due to method blank contamination. The presence of acetone is also supported by the QA laboratory's data, where no method blank contamination was encountered.

TABLE 2

COMPARISON OF SEMI-VOLATILE ORGANICS (EPA 8270) DATA

Analytes Detected	Project Lab H001SL	Project Lab H007SL	Detection Limits	QA Lab H008SL	Detection Limits
Phenanthrene	ND	49 **J**	430/450	700	600
Anthracene	ND	ND	430/450	200 **J**	600
Fluoranthene	ND	88 **J**	430/450	600 **J**	700
Pyrene	ND	92 **J**	430/450	1300	600
Benzo(a)anthracene	ND	ND	430/450	300 **J**	500
Chrysene	ND	64 **J**	430/450	400 **J**	700
Di-n-butylphthalate	80 **J,B**	ND	430/450	ND	900
bis(2-Ethylhexyl)phthalate	100 **J**	80 **J**	430/450	ND	1000
Percent Solids	76	74		79	

Units = µg/Kg (ppb)
J = Estimated concentration
B = Found in method blank [di-n-butylphthalate at 40 ppb]

SUMMARY: The project blind duplicate and QA data agree within a factor of four to each other or their detection limits for all targeted analytes and are comparable. Data comparisons at or below detection limits are not considered significant at these levels of detection.

TABLE 3

COMPARISON OF AROMATIC VOLATILE ORGANICS (EPA 8020) DATA

Analytes Detected	Project Lab 030SL	Project Lab 031SL	Detection Limits	QA Lab 031SL*	Detection Limits
Benzene	ND	ND	7/72	68	37
Toluene	13	ND	7/72	ND	37
Ethylbenzene	ND	ND	7/72	ND	37
Total Xylenes	74	440	7/72	110	37
Percent Solids	68.5	69.9		67.3	

Units = µg/Kg (ppb)
ND = Not detected
* = Expired holding time

SUMMARY: The project blind duplicate and QA data agree within a factor of five with each other or their detection limits except for the project blind duplicate data of total xylenes and the QA data of benzene. Since both laboratories had acceptable internal QC data, the discrepancies could not be analytically resolved except for the fact that the QA sample was analyzed past the recommended maximum holding time of 14 days.

TABLE 4

COMPARISON OF RADIOLOGICAL PARAMETERS (EPA 9310/9320) DATA

Analytes Detected	Project Lab 09WA	Project Lab 11WA	Detection Limits	QA Lab 10WA	Detection Limits
Gross Alpha	4 ± 2	ND	2	0.90 ± 0.58	0.05
Radium-226	1.9 ± 0.6	ND	0.6	1.94 ± 0.39	0.48
Radium-228	ND	ND	1	0.59 ± 0.41	0.54

Units = pCi/L
ND = Not detected

SUMMARY: The project blind duplicate and QA data agree within a factor of three and are comparable.

TABLE 5

COMPARISON OF POLYCHLORINATED DIOXINS AND FURANS (EPA 8290) DATA

Analytes Detected	Project Lab 01-WA	Project Lab 03-WA	Detection Limits	QA Lab 02-WA	Detection Limits
2,3,7,8-TCDD	ND	ND	3.2/3.1	ND	5.3
1,2,3,7,8-PeCDD	ND	ND	4.4/9.9	16.6	--
1,2,3,4,7,8-HxCDD	ND	ND	3.7/3.8	13.9 **EMPC**	--
1,2,3,6,7,8-HxCDD	ND	ND	2.3/2.3	23.7 **EMPC**	--
1,2,3,7,8,9-HxCDD	ND	ND	3.7/4.6	15.8 **EMPC**	--
1,2,3,4,6,7,8-HpCDD	ND	ND	1.0/1.4	21.3 **EMPC**	--
OCDD	11.6 **EMPC**	12.0 **B**	4.9/3.5	91.2 **EMPC,B**	--
2,3,7,8-TCDF	ND	ND	2.8/2.6	ND	4.4
1,2,3,7,8-PeCDF	5.6	ND	2.8/2.6	9.2 **EMPC**	--
2,3,4,7,8-PeCDF	ND	ND	2.7/2.5	17.0 **EMPC**	--
1,2,3,4,7,8-HxCDF	ND	ND	2.4/1.7	14.8	--
1,2,3,6,7,8-HxCDF	5.25	4.7	1.5/1.1	17.5	--
2,3,4,6,7,8-HxCDF	ND	ND	2.0/1.5	17.8	--
1,2,3,7,8,9-HxCDF	ND	ND	2.0/1.5	17.1	--
1,2,3,4,6,7,8-HpCDF	7.5 **EMPC**	7.3 **EMPC**	2.3/1.3	18.0	--
1,2,3,4,7,8,9-HpCDF	ND	ND	2.6/1.6	19.8	--
OCDF	8.3 **B**	6.4 **EMPC**	2.0/1.6	40.7	--
Total TCDD	3.9	ND	3.2/3.1	ND	5.3
Total PeCDD	ND	ND	4.4/9.9	16.6	--
Total HxCDD	ND	ND	2.6/2.7	40.8 **EMPC**	--
Total HpCDD	ND	ND	3.7/4.6	21.3 **EMPC,B**	--
Total TCDF	ND	ND	0.0/0.0	ND	4.4
Total PeCDF	ND	ND	2.7/2.5	26.2 **EMPC**	--
Total HxCDF	ND	4.723	1.9/1.4	67.3	--
Total HpCDF	ND	ND	2.5/1.4	37.7	--

Units = pg/L (ppq)
B = Found in method blank
EMPC = Estimated maximum possible concentration

SUMMARY: Project blind duplicate data agree for all targeted analytes. Project blind duplicate and QA data do not agree for over one half of the targeted analytes, due to QA laboratory error in which the QA sample was accidentally spiked with dioxin/furan analytes.

TABLE 6a

COMPARISON OF GASOLINE RANGE ORGANICS (ADEC 8015 MOD.) DATA

Analytes Detected	Project Lab E023SL	Project Lab E053SL	Detection Limits	QA Lab E054SL	Detection Limits
GRO	18	9.0	5.0	49	5
Percent Solids	100	100		72.2	

Units = mg/Kg (ppm)

SUMMARY: The project blind duplicate data agree within a factor of two to each other. The QA data agree within a factor of five to one project sample (E023SL) but does not agree with the blind duplicate (E053SL). It was noted, that the percent solids of the QA and project samples are not the same, which indicates non-identical sample aliquots submitted for analysis.

TABLE 6b

COMPARISON OF DIESEL RANGE ORGANICS (ADEC 8100 MOD.) DATA

Analytes Detected	Project Lab E023SL	Project Lab E053SL	Detection Limits	QA Lab E054SL	Detection Limits
DRO	2100	2500	500/240	2030	10
Percent Solids	80	83		72.2	

Units = mg/Kg (ppm)

SUMMARY: The project blind duplicate and QA data agree within a factor of two to each other and are comparable.

ISO GUIDE 25 VERSUS ISO 9000 FOR LABORATORIES

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Abstract

Before laboratories jump on the ISO 9000 bandwagon, they should understand whether this type of third-party recognition is really appropriate for the needs of their customers. From the point of view of the user of test data, the quality management systems approach to granting recognition to laboratories is deficient in that it does not provide any assessment of the technical competence of personnel engaged in what can only be described as a very technical activity, nor does it address the specific requirements of particular products or measurements. The better method of achieving these two objectives is through laboratory accreditation bodies, operating themselves to best international practice, requiring laboratories to adopt best practices and by engaging assessors who are expert in the specific tests in which the customer is interested.

Summary

Users of test data should be concerned with both the potential for performing a quality job (quality system) and technical competence (ability to achieve a technical result). The best available method of achieving these two objectives is through laboratory accreditation bodies, operating themselves to best international practice, requiring laboratories to adopt best practices
and by engaging assessors who are expert in the specific tests in which the customer is interested. Acceptance of test data, nationally or internationally, should therefore be based on the application of Guide 25 to assure the necessary confidence in the data's validity.

Introduction

Internationally, as well as here in the United States, there is considerable debate and confusion about the similarities, differences and relationships between laboratory accreditation (usually performed using ISO/IEC Guide 25, General requirements for the competence of calibration and testing laboratories") and quality system certification (or registration) to one of the three ISO 9000 series of quality system models, usually 9001, 9002 or 9003. For a laboratory, quality system certification is normally performed using ISO 9002.

Quality system certification has become a popular method of providing assurance of product quality. But does it? The large number of organizations offering certification to ISO 9000 series has created, perhaps accidentally and certainly deliberately in some cases, the scenario that certification to ISO 9000 assures product quality, and for laboratories, validity of specific test (and calibration) results. To the well informed, this is misleading.

There are several significant differences between laboratory accreditation using Guide 25 and quality system certification, but the key difference can be summarized by the fact that the essence of Guide 25 is to ensure the validity of test data, while technical credibility is not addressed in ISO 9002.

Why is there so much confusion?

First, there is a significant problem of semantics. Second, the purposes of each standard are different and thus examination against them gives different levels of assurance. The ISO 9000 series of standards provide a generic system for quality management of an organization, irrespective of the product or service it provides.

Guide 25 is a document developed specifically to provide minimum requirements to laboratories on both quality management in a laboratory environment and technical requirements for the proper operation of a laboratory. To the extent that both documents address quality management, Guide 25 can be considered as a complementary document to ISO 9002 written in terms most understandable by laboratory managers.

There is, however, a view being expressed that the application of ISO 9002 is sufficient for the effective operation of a laboratory, and thus ensuring validity of test data. This opinion has caused some confusion in the laboratory community itself and also, more broadly, among users of laboratory services. The problem is compounded when accreditation of the laboratory by a third party is required.

The Semantics Problem

Terminology used in this area of conformity assessment is in a state of flux, and is confusing or even misleading. The three "tion" words -- "accreditation," "certification" and "registration" -- are often used interchangeably. For example, the US EPA talks about accredited asbestos workers and certified drinking water laboratories when others in the same agency talk of certifying laboratory personnel and accrediting laboratories.

The problem is compounded by some very specialized bodies using the words in a different context altogether. For example, U.S. building code groups refer to accredited products rather than certified products and Underwriters Laboratories (or UL) uses the term "listed" instead of "certified" partly because the word "certified" carries with it the connotation of a guarantee,

which according to UL representatives is misleading and goes beyond what UL product safety certification actually is.

The ISO Council Committee on Conformity Assessment (CASCO) has attempted to resolve the semantics problem by standardizing the following definitions:

accreditation: procedure by which an authoritative body gives formal recognition that a body or person is competent to carry out specific tasks.

certification: procedure by which a third party gives written assurance (certificate of conformity) that a product, process or service conforms to specified requirements.

registration: procedure by which a body indicates relevant characteristics of a product, process or service, or particulars of a body or person, in an appropriate publicly available list.

Internationally, certification has become the dominant term. However, their common use in the United States is not always in harmony with this international guidance, nor particularly with European practice. The European approach is to label both quality system registrars and product certifiers as certification bodies. There is very little if any use of the term registration in Europe. So we have certification bodies performing either or both product certification and quality system registration.

There seems to be some agreement in the U.S. that "accreditation" is a formal recognition that a body is competent to carry out specific tasks; while "certification" is either self declaration by a supplier (also known as self-certification -- CASCO discourages, preferring the term "supplier declaration") or a formal evaluation by a third-party that a product conforms to a standard.

"Registration" is the common term in the United States when referring to certification of quality systems. So we have laboratory accreditation defined as a formal recognition that a laboratory is competent to carry out specific tests or specific types of tests; and quality system registration being defined as a formal attestation that a supplier's quality system is in conformance with an appropriate quality system model (i.e., either ISO 9001, 9002 or 9003). Thus, the ASQC's Registrar Accreditation Board (RAB) accredits quality system certification bodies.

Traditionally, certification in the U.S. has related to products, processes or services, but because of the European influence we are hearing more references to the certification of quality systems, or the very misleading short-hand, "ISO certified" seen in many advertisements. ISO is vigorously discouraging this type of reference as inappropriate, inaccurate and possibly an infringement on the ISO trademark. Unfortunately, this type of advertising is largely to blame for perpetuating the confusion and hyping quality system registration beyond that which it can honestly deliver.

Differing Purposes of the Standards

ISO 9000 Series

The primary aim of the ISO 9000 standards is defined in the "Scope" section of ISO 9001:

> ". . . specifies quality-system requirements for use where a supplier's capability to design and supply conforming product needs to be demonstrated."

The standards' primary purpose is, therefore, to provide a management model suitable for the supply of a conforming product or service between two parties -- a supplier and his customer. However, the focus on the use of the ISO 9000 standards as two-party models has shifted greatly as more and more use is made of them for third-party certification purposes. In today's complex world, there are limited opportunities for all customers to have direct relationships with their suppliers, so third-party certification bodies are, in effect, taking on the roles of representatives of multiple second parties (all the customers which rely on independent certification for their reassurance about a supplier). It is important, therefore, that users of third-party certification understand what form of reassurance is provided when an organization is certified against a quality system standard.

Since the ISO 9000 standards are generic, it is often a significant challenge to interpret their use in different industry sectors, or in organizations of different sizes or technical complexities. Quality system certification does not, however, certify the quality of a particular product or service for compliance with specific technical specifications, but only the management system's compliance with a defined model (ISO 9001, 9002, or 9003).

The "Introduction" to the ISO 9001 standard makes this distinction between systems and product conformance, where it states: "It is emphasized that the quality-system requirements specified in this International Standard, ISO 9001, are complementary (not alternative) to the technical (product) specified requirements." Essentially, the ISO 9000 standards are reminding customers that they need to consider whether assurance is required not only on the compliance of a supplier's management system, but also on the technical compliance of the products provided by the supplier. This product assurance may be provided through a range of mechanisms such as product certification, product or process audits by the purchaser and vendor-supplied test data.

ISO/IEC Guide 25-1990

Unlike the ISO 9000 series, ISO/IEC Guide 25 was not established primarily as a contractual model for use between suppliers and their customers. Its aims are to:

- Provide a basis for use by accreditation bodies in assessing competence of laboratories;

- Establish general requirements for demonstrating laboratory compliance to carry out specific calibrations or tests; and

- Assist in the development and implementation of a laboratory's quality system.

Historically, Guide 25 was developed within the framework of third-party accreditation bodies. Its early drafting was largely the work of participants in the International Laboratory Accreditation Conference (ILAC) and the latest edition was prepared in response to a request from ILAC in 1988.

To understand the significance and purpose of Guide 25 and its relationship to ISO 9002, it is essential that it be viewed in light of its development history -- it was initially to assist the harmonization of criteria for laboratory accreditation. Guide 25 is now being used by laboratory accrediting bodies throughout the world and is the basis for mutual recognition agreements among accrediting bodies.

Laboratory accreditation is defined in ISO/IEC Guide 2 as "formal recognition that a testing laboratory is competent to carry out specific tests or specific types of tests." The key words in this definition are "competent" and "specific tests." Each accreditation recognizes a laboratory's technical capability (or competence) defined in terms of specific tests, measurements, or calibrations. In that sense, it should be recognized as a stand-alone form of quite specialized technical certification -- as distinct from a purely quality management system certification -- as provided through the ISO 9000 framework.

Laboratory accreditation may also be viewed as a form of technical underpinning for a quality system in much the same way that product certification could be considered as another form of complementary underpinning for a certified quality management system.

Similarities and Differences

Both the ISO 9000 series and ISO/IEC Guide 25 are used as criteria by third-party certification bodies, and both contain quality systems elements. The systems elements of ISO 9000 are generic; those of ISO/IEC Guide are also generic but more specific to laboratory functions. The textual differences between ISO 9002 and Guide 25 are obvious, but, when interpreted in a laboratory context, it is generally accepted that the systems elements of the two documents are closely compatible. This is acknowledged in the introduction of Guide 25 which states: "Laboratories meeting the requirements of this Guide comply, for calibration and testing activities, with the relevant requirements of the ISO 9000 series of standards, including those of the model described in ISO 9002, when they are acting as suppliers producing calibration and test results."

It is not true, however, that laboratories meeting the requirements of ISO 9002 will thus meet the requirements or the intent of Guide 25. In addition to its system requirements (which are compatible with ISO 9002), Guide 25

emphasizes technical competence of personnel for their assigned functions, addresses ethical behavior of laboratory staff, requires use of well-defined test and calibration procedures and participation in relevant proficiency testing programs. Guide 25 also provides more relevant equipment management and calibration requirements, including traceability to national and international standards for laboratory functions; identifies the role of reference materials in laboratory work; and provides specific guidance relevant to the output of laboratories -- the content of test reports and certificates -- together with the records requiring management within the laboratory.

Although Guide 25 contains a combination of systems requirements and those related to technical competence, for laboratory accreditation purposes, the Guide is normally used only as a starting point. Guide 25 recognizes in its "Introduction" that ". . . for laboratories engaged in specific fields of testing such as the chemical field . . . the requirements of this Guide will need amplification and interpretation . . . ."

In A2LA's system of laboratory accreditation, these additional technology-specific criteria are contained in special program requirements documents such as the "Environmental Program Requirements."

However, there is another level of technical criteria which must be met for the accreditation of laboratories. That is the technically-specific requirements of the individual test methods for which the laboratories' competence is publicly recognized. So the hierarchy of criteria which must be met for laboratory accreditation purposes:

- ISO/IEC Guide 25;
- Any field-specific criteria; and
- Technical requirements of specific test methods and procedures.

Apart from comparisons on the similarities and differences between the purposes of ISO 9000 and Guide 25 and their use for third-party conformity assessment purposes, it is important to examine the differences in skills and emphasis of assessors involved in quality system certification and laboratory accreditation assessments.

For quality system certification, emphasis is traditionally placed on the qualifications of the assessor to perform assessment against the systems standard. The systems assessor (often referred to as the Lead Assessor) is expected to have a thorough knowledge of the requirements of that standard. In current practice internationally, a quality system assessment team may or may not include personnel who have specific technical backgrounds or process familiarity relevant to the organizations being assessed.

For laboratory accreditation, the assessment team always involves a combination of personnel who have expert technical knowledge of the test or measurement methodology being evaluated for recognition in a specific laboratory, together with personnel who have specific knowledge of the policies and practices of the accreditation body and the general systems applicable to all accredited laboratories. Thus, the laboratory

accreditation assessment includes a technical peer-review component plus a systems compliance component.

There are some other elements of difference in the respective assessment processes. For example, laboratory accreditation involves appraisal of the competence of personnel as well as systems. Part of the evaluation of a laboratory includes evaluation of supervisory personnel, in many cases leading to a recognition of individuals as part of the laboratory accreditation.
The technical competence and performance of laboratory operators may also be witnessed as part of the assessment process. The loss of key personnel may affect the continuing accreditation of the laboratory by the accrediting body. For example, A2LA recognizes key staff whose absence would reduce the laboratory's technical competence and may prompt a reassessment before it would be normally scheduled.

The final product of a laboratory is test data. In many cases, laboratory accreditation assessments also include some practical testing of the laboratory through various forms of proficiency testing (interlaboratory comparisons or reference materials testing).

Quality system certification is not normally linked to nominated key personnel. The technical competence of managers and process operators is not a defined activity for quality system assessment teams. It is through the documented policies, job descriptions, procedures, work instructions, training requirements of organizations and objective evidence of their implementation, that quality system certifiers appraise the people component of a system. Staff turnover is not an issue in maintaining certification.

Complementary Functions

Recognizing that there are differences in the purpose, criteria and emphasis of ISO 9000 and Guide 25 and their use for conformity assessment purposes, it is worthwhile to consider how the roles of quality system certification and laboratory accreditation can best interact.

Quality system certification for a laboratory should be viewed as a measure of a laboratory's capability to meet the quality expectations of its customers in terms of delivery of laboratory services within a management system model as defined in ISO 9002 or 9001 -- a "quality" job. Secondly. laboratory accreditation should be viewed by customers as an independent reassurance that a laboratory is technically and managerially capable to perform specific tests, measurements or calibrations -- a "technically competent" job.

If satisfaction is needed on both these characteristics, then a combination of quality system certification and laboratory accreditation may be appropriate.
If a laboratory's function is purely for internal quality control purposes within an organization and not requiring any formal output in terms of certificates or reports to either external customers (or internal customers within a larger organization requiring formal test reports), it may be

appropriate for the laboratory to operate within the overall ISO 9002 framework of the parent company. Nevertheless, such laboratories and their senior management may also benefit from the external, independent appraisal provided by the technical assessors used in laboratory accreditation. However, if a laboratory issues certificates or reports certifying that products, materials, environmental conditions, or calibrations conform to specific requirements, they may need to demonstrate to their clients or the general community that they are technically competent to conduct such tasks. Laboratory accreditation provides the independent measure of that competence.

Scope of Accreditation/Certification

Organizations may be certified to a quality system standard within very broad industry or product categories. Naturally, organizations with a very narrow product range are certified in these terms.

Laboratories, on the other hand, are accredited for quite specific tests or measurements, usually within specified ranges of measurement with associated information on uncertainty of measurement, and for particular products and test specifications.

Accreditation bodies encourage laboratories to endorse test reports in the name of the accreditation body to make a public statement that the particular test data presented has been produced by a laboratory which has demonstrated to a third party that it is competent to perform such tests.

The ISO 9000 series of standards are not intended to be used in this way. They address the quality system, not specific technical capability. The use of a quality system certification body's logo should not be used as a certification mark or endorsement as to the conformity of a particular product with its specified requirements. Similarly, it should not be used to endorse the competent performance of tests, calibrations or measurements reported by laboratories. Only a logo or endorsement showing accreditation to Guide 25 or equivalent for specific calibrations or tests denotes technical credibility and an expectation of valid results. Laboratories certified to ISO 9000 cannot make the same claim.

The Special Role of Accredited Calibration Laboratories

For more general interaction between certified quality systems and laboratory accreditation, one very significant area is the role that accredited calibration laboratories play in demonstrating traceability to national and international standards of measurement. The ISO 9000 series require that ". . . suppliers shall . . . calibrate . . . inspection, measuring and test equipment . . . . against certified equipment having a valid known relationship to nationally recognized standards."

Many calibration certificates presented to quality system auditors contain statements that the measurements or calibrations are "traceable to national standards." Some auditors also insist that suppliers' calibration documents provide cross-reference to the other reference standards used to calibrate

their own devices, to provide a documented chain of traceability back to their own country's or international standards of measurement. There may be multiple steps, involving various calibration devices, required to demonstrate traceability back to a national standard. This can therefore become a very complex and, in some perceptions, bureaucratic demonstration of traceability by a supplier. The supplier may also have no direct access to information, or influence over, the provider of calibrations for its equipment.

Concentration by auditors on documented statements of traceability of measurements can be viewed as an exercise in "paper traceability, "not "technical traceability" -- that is, the calibrations performed on their equipment have been performed by personnel competent to undertake the measurements, under controlled environmental conditions (where appropriate), using other higher accuracy equipment that is maintained and recalibrated within appropriate intervals and backed up by records and other management systems which meet the principles of good laboratory practice embodied in Guide 25. Accreditation of the laboratory providing a specialist calibration service provides such reassurance of technical traceability.

As it is a fundamental requirement for accredited calibration laboratories to have their own equipment traceable to national and international standards, both the interest and spirit of the ISO 9000 requirements are thus met when accredited calibration laboratories are used by suppliers. This principle has been recognized in the recently issued ISO Standard 10012.1-1992 where Clause 4.15 "Traceability," states that ". . . the supplier may provide the documented evidence of traceability by obtaining his calibrations from a formally accredited source."

Fundamental Difference

Quality system registration (ISO 9000) asks:

- Have you defined your procedures?
- Are they documented?
- Are you following them?

Laboratory accreditation asks the same questions but then goes on to ask:

- Are they the most appropriate test procedures to use in the circumstances?
- Will they produce accurate results?
- How have you validated the procedures to ensure their accuracy?
- Do you have effective quality control procedures to ensure ongoing accuracy?
- Do you understand the science behind the test procedures?
- Do you know the limitations of the procedures?
- Can you foresee and cope with any technical problems that may arise while using the procedures?
- Do you have all the correct equipment, consumables and other resources necessary to perform these procedures?

The registration of a laboratory's quality management system is a component of laboratory accreditation -- not a substitute. Quality system registration of a laboratory to ISO 9000 misses a key element -- technical validity and competence.

Unfortunately, quality system registration of laboratories is already being seen as an easier route to some form of recognition for a laboratory than full accreditation.

European Position

In an April 1992, statement issued by the European Organization for Testing and Certification (EOTC):

> . . . the only acceptable stand is to state that QS certification cannot be taken as an alternative to accreditation, when assessing the proficiency of testing laboratories. Not trying to underrate the QS certification procedure, it should none the less be underlined that, by being intended as a systematic approach to the assessment of an extremely broad scope of organizations and field of activity, it cannot include technical requirements specific to any given domain.

Conclusion

Before laboratories jump on the ISO 9000 bandwagon, they should understand whether this type of third-party recognition is really appropriate for the needs of their customers. From the point of view of the user of test data, the quality management systems approach to granting recognition to laboratories is deficient in that it does not provide any assessment of the technical competence of personnel engaged in what can only be described as a very technical activity, nor does it address the specific requirements of particular products or measurements. The ISO 9000 series state explicitly that they are complementary not alternatives to specified technical requirements.

Users of test data, therefore, should be concerned with both the potential for performing a quality job (quality system) and technical competence (ability to achieve a technical result). The best available method of achieving these two objectives is through laboratory accreditation bodies, operating themselves to best international practice, requiring laboratories to adopt best practices and by engaging assessors who are expert in the specific tests in which the customer is interested. Acceptance of test data, nationally or internationally, should therefore be based on the application of Guide 25 to assure the necessary confidence in the data's validity.

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A METHOD FOR ESTIMATING BATCH PRECISION FROM SURROGATE RECOVERIES

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ABSTRACT

The U.S. EPA Environmental Monitoring Systems Laboratory in Las Vegas provides quality assurance support to the Superfund Contract Laboratory Program (CLP). In part, this effort involves evaluating the effectiveness of the quality control required in analytical methods. Previous work has shown that the matrix spike/matrix spike duplicate (MS/MSD) analysis, as applied in the CLP, adds little or no added value to the CLP organic analyses. One problem with eliminating the MS/MSD analysis is that this pair of analyses provides the only estimator of analytical precision for the sample batch. The current work provides a precision estimator for the entire sample batch with no additional analyses.

Precision is generally defined as a measure of the variability around a mean value. Traditionally, in analytical chemistry, this has been measured by replicate analyses of a sample. For this approach to provide useful information, the sample chosen for replicate analysis must contain the analytes of interest, the sample must be analyzed a minimum of three times to provide a statistically valid estimate, and the sample must be representative of the sample batch. The CLP MS/MSD analysis would rarely meet these three criteria. The precision estimator that has been developed uses the surrogates that are added to every sample and blank to estimate precision for the entire sample batch. Data obtained for each surrogate may be applied to estimate recoveries and precision of chemically similar analytes, and a general precision value obtained for the entire analytical fraction may be used when a single estimate of precision is desired for the batch. Historical precision data based on over 2000 CLP sample batches are given as a reference for interpreting the precision estimate. The individual surrogate recoveries can also be compared to the average recoveries for the sample batch to identify matrix and/or laboratory problems. The adoption of the new precision estimator will yield improved information on the laboratory precision of the analyses in the entire sample batch while reducing costs by eliminating two analyses per batch.

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PROVIDING LEGALLY DEFENSIBLE DATA FOR ENVIRONMENTAL ANALYSIS

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ABSTRACT

Environmental analysis plays a very important role in the environmental protection program. Due to the possible litigation involvement, most of the environmental analyses follow stringent criteria, such as the Environmental Protection Agency Contract Laboratory Program procedures with analytical results documented in an orderly manner.

The documentation demonstrates that all quality control steps are followed and facilitates data evaluation to determine the quality and usefulness of the data. Furthermore, the tedious documents concerning sample check-in, chain of custody, standard or surrogate preparation, daily refrigerator and oven temperature monitoring, analytical and extraction logbooks, standard operation procedures, etc., also constitute a process of the lab documentation.

The fundamentals for the success of the environmental analysis is people. The knowledge and experience of people constitutes the basic element for environmental analysis. In order to grow into this new area, the ability to develop new methods is crucial. In addition; the laboratory information system, laboratory automation, and quality assurance/quality control are major factors for laboratory success. This presentation will concentrate on these areas.

QUALITY ASSURANCE PROGRAM

The implementation of a good quality assurance program within the laboratory ensures that all data generated are scientifically sound. The laboratory must follow proper quality assurance/quality control procedures throughout the process.

The consistency of quality is maintained by the laboratory with the implementation of a quality assurance program plan and detailed standard operating procedures. The quality assurance program plan should provide guidance for

laboratory personnel by documenting the daily required quality assurance/quality control performed. The laboratory should have routine audits against the Quality Assurance Program Plan. The routine audits will alert ongoing problems to be resolved and prepare the laboratory for any external audits in the future. This will also document that the laboratory follows the protocol detailed in the plan.

A thorough sample custody log-in and tracking process identifies quality assurance/quality control aspects of the project requirement prior to analysis of samples. This will enable the analysts to have a detailed recording of the quality assurance/quality control requirements as a guideline to the statement of work.

The custody log-in and tracking process can also provide quality control back-up for follow-up on meeting holding times, maintaining documented custody of the sample, the process for internal tracking of the documented analytical steps of the sample analysis, and that the proper quality control has been followed.

Quality assurance/quality control follow-up of the analytical data continues throughout the data entry process with a program that flags quality control discrepancies programmed from the Quality Assurance Program Plan and Standard Operating Procedures. Prior to submission of data to the client a validation is performed on the final package. This validation is based on the quality control specification indicated in the statement of work or client contract.

The laboratory should have routine audits against the Quality Assurance Program Plan. The routine audits will alert ongoing problems to be resolved and prepare the laboratory for any external audits in the future. This will also document that the laboratory follows the protocol detailed in the plan.

STANDARD OPERATING PROCEDURES

Standard operating procedures are for the express use of providing the user with an efficient means of providing quality data in a timely manner. They should be written in such a manner that the user will understand all aspects of each appropriate standard operating procedure and be able to follow the protocol with little or no supervision.

The standard operating procedures should detail all aspects of the environmental analysis process. Steps should be written in the standard operating procedure to cover the following:

- the process of handling samples upon receipt at the laboratory
- all custody procedures and documentation
- each analytical process required
- instrument calibration
- QA/QC requirements through the analytical process
- analytical documentation requirements
- internal laboratory audits

Continued steps required for the standard operating procedure:

- traceability of standards
- corrective action procedures and follow-up
- review and validation of data
- maintenance of equipment and records
- data reporting procedures
- training of personnel
- all forms for laboratory use and instructions
- safety requirements
- sample storage and disposal procedures

LABORATORY INFORMATION MANAGEMENT SYSTEM

In evaluating commercially available laboratory information systems the options for analytical laboratories are limited. Clients require different criteria and needs based on sample identifications and deliverables which make altering a commercial LIMS difficult. However, in the final analysis our decision was to customize our own version of a laboratory information system in order to achieve our needs and requirements. This system enables the laboratory to follow a tracking flow throughout the analytical process. Client information, delivery requirements, date and time of receipt, sample ID's, required analyses and special instructions are entered into our sample log-in program. The program assigns a unique work order number, assigns a one time unique sample identification as a cross reference to the client identification, adds the information to the database, generates a printed work order, determines distribution requirements for the work order based on analyses required, computes holding times and due dates, generates sample tracking, chain of custody and corrective action forms,

and initiates a billing record form. There are program modules which can search the database for specific information, determine current sample backlog and list work orders with approaching deadlines. Work is continuing on laboratory-interactive portions of the program for full sample tracking capabilities.

LABORATORY AUTOMATION

Laboratory automation includes hardware, such as gas chromatography auto samplers, and associated software for processing sample results. Some examples of this hardware will be presented in the next eight slides, which include auto samplers for GC/MS, GC, IC, GPC, AA and ICP. We have automated the sample result process for the GC/MS, GC, IC etc.

In terms of data reporting, we have several options available through the use of our Banyan Vines network. By using the network telefax/mail feature we have developed various programs which will telefax the results to the client directly from the program. Additionally, the data is transmitted directly from the instruments to a program that will provide data results to minimize and data entry errors.

LABORATORY ANALYTICAL FLOW

As indicated on the flow chart, once the client request has been approved samples are received at the laboratory from the field samplers. If any discrepancies are found the client is notified immediately. Quality Assurance approves the work order which is then submitted to the analysts who will be involved with the project. If there are any problems during the analyses the lab manager, project manager, and client are contacted for resolution. Once a decision is made the analysis is completed and submitted to the supervisor for review. The supervisor submits data for data entry which covers the quality control aspects through a program. If there are problems the lab manager and supervisor are contacted to resolve the problems. Upon completion the final data is submitted to the supervisor for a final review and returned to QA/QC

for validation. If quality control does not meet the requirements the lab manager and supervisor are notified for narrative documentation and the final package with this documentation is paginated, copied, and submitted to the client.

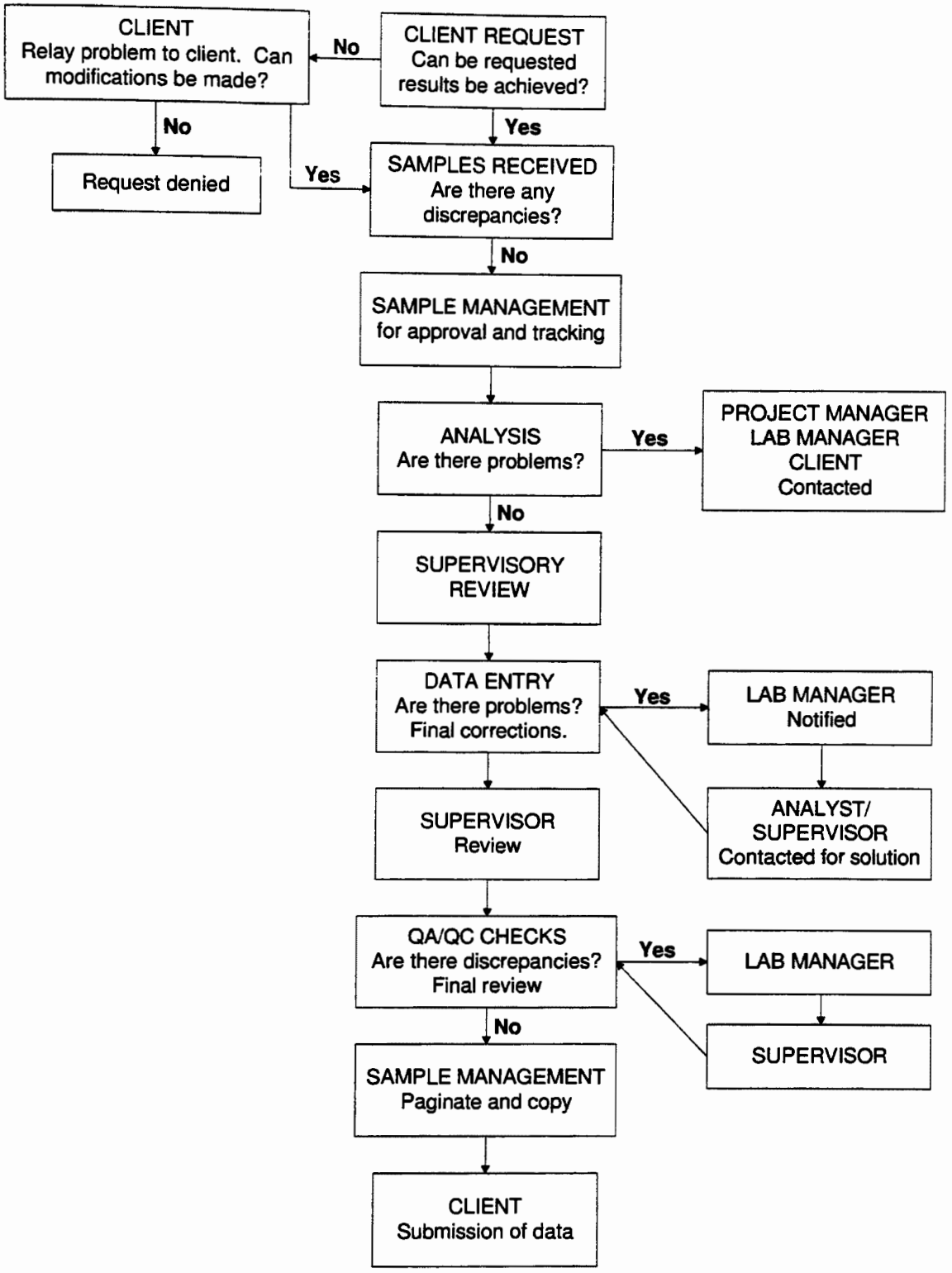
External audits will be performed by potential clients from time to time. An audit provides the laboratory with positive feedback. Laboratory personnel should improve existing procedures by implementing new suggestions and updating Quality Assurance Program Plan's and Standard Operating Procedure's. These changes continually assist in improving the quality procedures of the laboratory.

Quality assurance/quality control follow-up of the analytical data continues throughout the data entry process with a program that flags quality control discrepancies programmed from the Quality Assurance Program Plan and Standard Operating Procedures. Following the data entry process a final analytical supervisory review is performed. Prior to submission of data to the client a validation is performed on the final package. This validation is based on the quality control specification indicated in the statement of work, client contract, or method related to the analysis.

CONCLUSION:

Any project that is performed within the laboratory program, as previously discussed, will provide legally defensible data through the custody and documentation of the sample analysis. All documentation is performed according to the Good Laboratory Practice guidelines. This concept will identify all problems, corrective actions, and the affect and problems have on the quality of the data.

The program allows internal audits, tracking the sample through the system at each step beginning from receipt of the sample. With the unique identification and LIMS practices the ability to track the sample from each process and stage of analysis throughout the system. With custody and documentation that provides the ability to repeat the analysis, or steps taken throughout the process, the data provided will be legally defensible for the client.


CLIENT
Relay problem to client. Can modifications be made?
No
CLIENT REQUEST
Can be requested results be achieved?
No
Request denied
Yes
Yes
SAMPLES RECEIVED
Are there any discrepancies?
No
SAMPLE MANAGEMENT
for approval and tracking
ANALYSIS
Are there problems?
Yes
PROJECT MANAGER
LAB MANAGER
CLIENT
Contacted
No
SUPERVISORY
REVIEW
DATA ENTRY
Are there problems?
Final corrections.
Yes
LAB MANAGER
Notified
ANALYST/
SUPERVISOR
Contacted for solution
SUPERVISOR
Review
QA/QC CHECKS
Are there discrepancies?
Final review
Yes
LAB MANAGER
SUPERVISOR
No
SAMPLE MANAGEMENT
Paginate and copy
CLIENT
Submission of data

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AUDITS AS TOOLS FOR PROCESS IMPROVEMENT

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ABSTRACT

Environmental testing laboratories are audited frequently by certifying agencies and clients. This paper describes how a laboratory can take advantage of the audit by using the results as a learning experience to upgrade or refine the laboratories processes, techniques, or systems. All audit comments should be given consideration. What may seem minor to the laboratory, may be of major concern to the auditor. In this paper we discuss the different types of audits, the general criteria used, and review the different styles and techniques used by auditors. We summarize the most common findings from recently conducted audits of over 30 environmental laboratories, our information gathering process, and a trend analysis of those findings. We discuss how we used the audit process as a positive learning experience, how we upgraded our own auditing system, and how any laboratory can benefit from an audit by using benchmarking techniques to improve their quality systems. We also describe how the audit process can be used as a mentoring tool for small disadvantaged or minority-owned businesses. In summary, we demonstrate how the lessons learned from an audit can benefit a laboratory and result in cost reductions and improved efficiency of its operations.

COST-EFFECTIVE MONITORING PROGRAMS USING STANDARDIZED ELECTRONIC DELIVERABLES

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ABSTRACT

Hidden costs associated with the management of monitoring wells attributed to the assessment and archiving of analytical and field information/data have greatly inflated the overall costs of groundwater monitoring and clean-up. This article addresses elements universal to project management and proposes the cost cutting benefits of using a standardized electronic deliverable format (EDF). The Corps of Engineers North Pacific Division Laboratory (NPDL) is in the process of implementing standardization of all reported analytical data and field information in a standardized digital format.

INTRODUCTION

The Corps of Engineers North Pacific Division district offices are responsible for the overall management of groundwater monitoring and clean-up projects at various military installations. Architecture and engineering (A/E) firms are contracted to oversee the day-to-day activities and functions associated with a given clean-up project. Typically, the A/E is responsible for executing a scope of work that, amongst other criteria, clearly defines a clean-up objective, a sampling plan, a chemical data acquisition plan (CDAP), and the development of a model, based on field and analytical information and data. The analytical work is contracted out by the A/E to laboratories (if they do not have in-house capability) that are referred to as primary laboratories. The analytical data obtained from the primary laboratories is used to model the type and level of contamination.

Contaminated groundwater monitoring well programs typically span an extended period of time. It is not uncommon for a monitoring program to extend over several years. During the life of the project, it is not unusual for multiple laboratories to provide analytical data to a given A/E. It is also possible that more than one A/E firm may be involved with the project through its duration. Thus, a tremendous amount of data is being generated and processed. The tracking and management of this data is a costly and demanding undertaking.

NPDL is tasked with the responsibility of serving as a quality assurance (QA) laboratory. To assure that the government is receiving the analytical services and quality it is paying for, a minimum of ten percent of all field samples collected by an A/E firm are taken as sample splits and are analyzed by NPDL or one of its eight contract laboratories that provide analytical support. NPDL is also responsible for the generation of a quality

assurance report that comprises the evaluation of data from split samples, reported by the primary and QA laboratories. This process entails physically extracting and compiling information and data from hardcopy reports. Although performed for different reasons, the review and validation functions employed by NPDL are repeated by the A/E and the Corps of Engineers district office managing the project.

DISCUSSION

Hidden costs associated with analytical data processing are not immediately apparent but ultimately make themselves evident somewhere along the monitoring program. In short, hidden costs are attributed to the irreplaceable commodity of time in the singling out and correction of errors reported by laboratories in hardcopy reports and manual database entry. For example: the review and validation process associated with hardcopy reports is tedious and time consuming. Contacting the laboratories responsible for the analysis for clarification of ambiguous data or data that are not supported with the correct or sufficient amount of quality control (QC) takes time, especially after a laps of time between the generation of the report and the review process at NPDL, the A/E or the Corps field district office. All too often, analytical reports contain the ambiguous use of flags and qualifiers, erroneous field identification information, improper use of significant figures, misprints and miscalculations. The absence of method of preparation identification, initial and/or continuous calibration information or the revision date for the QC criteria used for evaluation can greatly undermine the integrity and validity of the data. When such information is questionable or missing, a good deal of time can be spent in its clarification or acquisition.

For the purpose of modeling, the data from hardcopy reports must be manually keyed into a database system by the A/E. To assure error free data, it is common to see the time consuming practice of double entry for the same data by two different data entry personnel. In the case where different A/Es overlap the life of the project, there is the need and potential cost for matching database platforms and structures. Similarly, the Corps district field offices must compile their own archival databases for a given project, based on hardcopy reports. It is conceivable that at a minimum, three separate database systems for three separate functions, maintained at three separate locations will be generated from hardcopy reports.

In an effort to standardize the exchange of data and information between the A/Es, the primary and QA laboratories, and the managing Corps district field offices, NPDL has developed an electronic deliverable format package that is currently being used by NPDL and its eight contract laboratories. The intent is for future distribution of EDF to A/Es and their contract laboratories and contractually require that all analytical data provided to NPDL and Corps district field offices be in a standardized EDF.

EDF is loosely based on the Air Force's Installation Restoration Program Information Management System (IRPIMS). EDF uses the basic IRPIMS (1) valid value dictionary (VVD) as a foundation for analytical methods and parameter labels because it lends itself well to EPA SW-846 (2) methodologies. EDF is based on an ASCII, field delimited, relational database structure that comprises five files (see Tables 1-5). The additional fields and modifications to IRPIMS that comprise EDF reflect NPDL's focus on the need to monitor sample custody/control as well as in-house laboratory QC.

The EDF package comprises the VVD, an electronic data loading tool (COELT) and an electronic data constancy check tool (EDCC). The COELT is used to parcel the data into the required five files by taking information and data that has been processed by a laboratory's laboratory information management system. The EDCC tool is used to validate the consistency of the reported data/information in terms of structure, format, the correct use of valid values, and completeness. An error report is generated by the EDCC to identify consistency or completeness problems. An EDF report is not considered valid unless it has been run through the EDCC and is accompanied with the error free report. NPDL will only accept valid EDF reports.

In addition to providing a consistent formatted and structured report (both digitally as well as hardcopy), the use of EDF forces the laboratory to provide required QC, initial and ongoing calibration information, revision dates for the QC criteria being used, identification of sample preparation and analytical batches, unique and consistent flags and qualifiers, codes that identify analytical work subcontracted out, codes to identify secondary column confirmation for positive hits for gas chromatograph analysis, dilution factors, etc.

NPDL has set up an electronic bulletin board system for the bi-directional exchange of information and data between its laboratories, consultants and Corps district field offices. The use of EDF will eliminate the need for manual database entry. To provide support, NPDL has set up a help desk to field questions and resolve potential problems associated with EDF and its ancillary tools.

CONCLUSION

Although it is in its infancy stage, the use of a standardized EDF is beginning to provide benefits in the elimination of transcription errors. EDF is forcing the laboratories to provide complete, error free, standardized reports. Because the COELT is capable of generating hardcopy output, the hardcopies that are being generated at NPDL from the contract laboratories EDF reports are uniform and identical in structure and format. It is anticipated that in the future, EDF will greatly help in the reduction of hidden costs associated with data and information management from groundwater monitoring programs. EDF will lend itself towards the automation of data review, processing, the

elimination of transcription errors, and will facilitate immediate transport and exchange via telephone lines. Because EDF is based on an accepted and supported platform, the archiving of data will be straight forward. In the interest of data integrity, plans are underway to investigate the potential and feasibility of having one database repository for a given project that will be accessible to NPDL, the managing Corps field office, the A/E and the contract laboratories.

Acknowledgments: The authors are grateful to Arsenault and Associates, the primary architects of EDF and Ms. Ruth Abney for her exhaustive efforts in the de-bugging process of EDF and its output product. The authors acknowledge the efforts of Dr. R. Bard for the review and proofing of the manuscript.

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TABLE 1

SAMPLE INFORMATION

Field Name	Description
LABCODE	Analytical laboratory
LOCID	Location Identification
LOGCODE	Log code
LOGDATE	Log date
LOGTIME	Log time
MATRIX	Sample matrix
CNTSHUNUM	Control sheet number
NPDLWO	Work order number
PROJNAME	Project Name
SAMPID	Field assigned sample ID

BOLD = IRPIMS Fields

TABLE 2

TEST INFORMATION

Field Name	Description
ANADATE	Date of analysis
ANMCODE	Analytical method code
BASIS	Wet/dry weight
EXMCODE	Extraction method
EXTDATE	Extraction date
LABCODE	Analytical laboratory
LABLOTCTL	Laboratory control number
LABSAMPID	Laboratory assigned ID
LOCID	Location Identification
LOGCODE	Log code
LOGDATE	Log date
LOGTIME	Log time
MATRIX	Sample matrix
QCCODE	Quality control type
RUN_NUMBER	Analysis run
APPRVD	Approved by
COCNUM	Chain of Custody No.
EXLABLOT	Extraction control number
LAB_REPNO	Laboratory report No.
LNOTE	Laboratory notes
MODPARLIST	Modified parameter list
PRESCODE	Preservation
RECDATE	Date received
REP_DATE	Date of report
SAMPID	Field assigned sample ID
SUB	Subcontracted test

BOLD = IRPIMS Fields

TABLE 3

RESULTS INFORMATION

Field Name	Description
ANADATE	Date of analysis
ANMCODE	Analytical method code
EXMCODE	Extraction method
LABCODE	Analytical laboratory
LABDL	Lab detection limits
LABSAMPID	Laboratory assigned ID
MATRIX	Sample matrix
PARLABEL	Parameter code
PARUN	Parameter uncertainty
PARVAL	Analytical result
PARVQ	Parameter value qualifier
PVCODE	Parameter value class
QCCODE	Quality control type
RUN_NUMBER	Analysis run
UNITS	Units of measure
CLREVDATE	Control chart revision date
DILFAC	Dilution factor
LNOTE	Laboratory notes
REPDL	Reported detection limits
REPDLVQ	Rep. det. limit qualifier
RT	TIC retention time
SRM	Standard reference material

BOLD = IRPIMS Fields

TABLE 4

QUALITY CONTROL INFORMATION

Field Name	Description
ANMCODE	Analytical method code
LABCODE	Analytical laboratory
LABLOTCTL	Laboratory control number
LABQCID	Quality control sample No.
MATRIX	Sample matrix
PARLABEL	Parameter code
QCCODE	Quality control type
UNITS	Units of measure
EXPECTED	Expected parameter value
LABREFID	Reference sample number

TABLE 5

CONTROL LIMIT INFORMATION

Field Name	Description
ANMCODE	Analytical method code
EXMCODE	Extraction method
LABCODE	Analytical laboratory
MATRIX	Sample matrix
PARLABEL	Parameter code
CLCODE	Control limit code
CLREVDATE	Control revision date
LOWERCL	Lower control limits
UPPERCL	Upper control limits

BOLD = IRPIMS Fields

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PERFORMANCE OBJECTIVES AND CRITERIA FOR FIELD SAMPLING ASSESSMENTS

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ABSTRACT

The Analytical Services Division, Office of Environmental Management (EM-263) has developed and is implementing an assessment program to evaluate EM's environmental sampling and analysis activities. To support these goals the Environmental Measurements Laboratory has developed Performance Objectives and Criteria (POCs) for Field Sampling Assessments.

The performance objectives address the key elements necessary for effective programmatic control of sampling services. They are intended to guide an assessment team in evaluating the effectiveness of the sampling program and the system used by the facility to establish and implement QA standards for sampling activities.

Performance Objectives and Criteria were developed in the following areas:

- QA Project Plans and Sampling and Analysis Plans
- Standard Operating Procedures
- QA for Sample Collection
- Sample Management
- Operator Training
- Operational Criteria
- Maintenance and Decontamination

The performance criteria emphasis policies and programs that must generally be defined and implemented to achieve the performance objective. Several performance indicators have been identified for each criteria. These indicators are examples of concrete, verifiable practices and activities that provide positive indications that the facility is meeting the performance objectives. They are indicators of the facility's approach to comply with the performance objective.

Primarily the POCs serve as guidance for DOE program managers, field offices and contractors to establish self-assessment programs for improving their field sampling programs. They also provide direction to technical personnel who function as technical specialists (auditors) conducting assessments of sampling activities. Assessments findings may be based on a performance objective itself or a failure to satisfy one or more of the ojective's criteria.

SMART SEQUENCING ENVIRONMENTAL GC/MS IN A CLIENT/SERVER ENVIRONMENT

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ABSTRACT

Smart sequencing of gas chromatography/mass spectrometry (GC/MS) analytical systems allow results from data analysis to control the data acquisition system without operator intervention. Intelligent sequencing of this type adds more reliability and efficiency to environmental testing. A failed quality control limit, such as decafluorotriphenylphosphine (DFTPP) tune criteria, pauses data acquisition of a set of samples referenced to that particular DFTPP run. Corrective action is possible; the system may tune itself and re-inject DFTPP. Traditionally, environmental smart sequencing for GC/MS is limited to standalone computer systems, where a single computer operates the instrument and analyzes the data. Today, computers operate on local area and wide area networks, and share tasks. Client/server environments partition jobs among the various processors. This work describes a client/server application for environmental GC/MS. A PC client computer runs the GC/MS, and a UNIX server computer analyzes the data. The client runs the samples and sends the data files to the server. The server analyzes the data and checks integrity according to EPA rules. Using the results from the server, the client makes intelligent decisions concerning data acquisition, and thus, can either abort a system out of control, or take corrective action. This sets the operator free for more productive tasks. Intelligent instrument control minimizes incorrect testing decisions and keeps operating costs low.

INTRODUCTION

Intelligent control of GC/MS analytical systems allows response from quality-control (QC) check samples to control the autosampler without user intervention. This adds more reliability and efficiency to environmental testing. A failed quality control limit, such as DFTPP tune criteria, halts data acquisition of samples in a batch job called a shift. All the samples in a particular shift are referenced to the same DFTPP run. Corrective action may be possible. The system may tune itself and re-inject DFTPP, or merely stop. Traditionally, environmental smart sequencing for GC/MS is limited to standalone computer systems, where a single computer operates the instrument and analyzes the data. Today, computers operate on local area and wide area networks, and share tasks. Client/server environments share jobs among the various processors. In the analytical laboratory, the client computer runs the samples and sends the data files to the server computer, which analyzes the data and checks QC integrity according to EPA rules. Using the results from the server, the client has information for which to make intelligent decisions concerning data acquisition.

It can either abort a system out of control, or take corrective action. Operators are free to do more productive tasks. Intelligent instrument control minimizes incorrect testing decisions, and keeps costs low.

Smart control of an autosampler for environmental GC/MS applications first appeared in 1988 for use with the Hewlett Packard Real Time Executive (RTE) Aquarius system(1). It was developed in an Environmental Protection Agency (EPA) contract lab where strict tuning and calibration criteria must be met before any samples can be run. This software enhancement allows feedback from QC check samples to control the autosampler during a twelve hour sequence run. The logic relies on 1986 US EPA contract laboratory program (CLP) requirements(2). The results of a QC run are used in a decision-making process that instructs the autosampler to do one of three things: reanalyze the QC sample, continue with the next sample, or stop the sequence all together. It attempts to remedy a system that is out of control. The system becomes 'smart' enough to conclude data acquisition if either the EPA mass spectrometry tuning criteria or the calibration criteria are out of control. See Figure 1 for the basic algorithm. This software evolved in 1992(3) to check for the newer CLP rules(4), and accommodate laboratories abiding by Federal Register(5) or SW-846(6) guidelines. It ran only on the proprietary RTE system that performed both data acquisition and data analysis. Hewlett Packard moved away from the mature RTE to faster, modern processors. These platforms rely on open operating systems, such as UNIX and WINDOWS. This move demanded a new generation of intelligent sequencing software.

The newer computing technologies added benefits to intelligent autosampler control. The initial experiments with the new systems duplicated the earlier RTE/Aquarius work. PC based systems ran environmental application software under the Microsoft WINDOWS operating system and included smart sequencing for environmental GC/MS as a standard feature. This was still a single computer solution, and very similar to the original RTE work. Hewlett Packard combined client/server expertise and measurement technology to create a UNIX based server for environmental target compound analysis. Client/server smart sequencing became possible.

A simple model of client/server computing is the distribution of tasks between two or more computer applications. See Figure 2. The model has three parts: a client, a server, and the slash that binds the client to the server(7). The client runs the client side of the application, and often sends data to the server. The client in return requests information or resources from the server. The more powerful server provides information or resources to clients. The slash is the middleware that runs on both the client and the server sides of the application. An example of middleware is the well-known TCP/IP transport stack used to transport files from the client to the server.

The client/server application of interest here is smart sequencing of environmental GC/MS instrumentation. The system consists of a WINDOWS client and a UNIX server. The

client runs batch data acquisition jobs and sends raw GC/MS data files using TCP/IP to the server for processing. It needs information back from the server to control the batch autosampler. The server gets the data file from the client, then performs the analysis. It communicates to the client if the QC samples passed or failed the EPA criteria. The middleware is the network communications software packages NFS, PC/NFS, and TCP/IP. The computers connect with standard Ethernet hardware. The application software consists of user-contributed macros running on both the client and the server that add functionality to the basic product. The client macro pauses the autosampler after a QC run, sends the data to the server, searches for a response from the server, then makes the appropriate decision about the autosampler. The server macro uses the results of the environmental targeting software on the server and intelligently decides if the QC sample has passed or failed criteria. The server macro signals the client macro about the QC result. Finally, the client controls the autosampler. There are no limits, as far as the application is concerned, as to the number of client systems that are to a particular server.

EXPERIMENTAL

The experiment consisted of one Hewlett Packard model 4920 server using a 735 processor and the standard amount of core memory and hard disk space. There were two PC clients. Each ran the Hewlett Packard WINDOWS based GC/MS software. The instrumentation for each client consisted of a Hewlett Packard 5970B mass spectromter and a 5890 gas chromatograph. The clients sent semivolatile data to the server for processing there with the Hewlett Packard Target III server based software. Hewlett Packard versions of NFS and TCP/IP ran on the server, and PC/NFS and TCP/IP ran on each client. The network backbone was Ethernet 10 BASE-T.

System modifications were minor. The custom macro running on the PC clients, named smart_seq.mac, ran automatically after data acquisition. Similarly, the custom macro named "TuneCCalcheck.mac" ran automatically at the server following data analysis. These additional macros were the only modifications required to the standard systems. The client and server systems each provide services to run custom user macros automatically.

See Figure 3 for the basic algorithm of client/server smart sequencing. The first step is to make a sequence file describing the samples. Each sequence run must have a tune run and daily calibration run. The run typically can only last twelve hours, as mandated by the EPA methods. There are sequence keywords and sample types that trigger special computations by the client/server intelligent control software. A "BFB" or "DFTPP" sample type, for example, causes the sequence to halt until the client gets the message back from the server concerning the quality of the QC data. A "daily calibration" sample type similarly stops the sequence. The server gets the daily calibration data file sent to it by the client, and automatically analyzes it. Then the macro TuneCCalcheck.mac decides if the QC criteria for daily calibration have been satisfied. It creates a text file called "passed.smt" if the

system is in QC compliance, or one called "failed.smt" if the system is out of control. The macro places them in the data file directory on the server's hard drive. Smart_seq.mac continually monitors the data directory for the result. When smart_seq.mac detects the result, it either halts the autosampler, or continues with the run.

RESULTS AND DISCUSSION

Smart sequencing with one server and two clients worked. The entire process took about twenty seconds. Time depends upon network traffic. It rarely took more than forty seconds. A big advantage that this computing scenario has over single computing systems is the ability to distribute the tasks logically. A PC fits well on the lab bench and is well suited for chromatographic data acquisition that does not require a very powerful computer. Data analysis requires more power due to the floating point calculations. It is a process better suited for a powerful server. Client/server computing offers other benefits besides intelligent sequencing and logical job partitioning. The main advantage allows the easy transfer of information among various computers connected on a network. A Laboratory Information Management System (LIMS) computer contains all the information about a sample from the time it is sampled in the field, to the time results are released. Sample information can be downloaded as a text file to the PC running the GC/MS, and be used by the client to construct a sequence file. This saves time and eliminates typing mistakes. See Figure 4 is a text file used to automatically create a sequence with the proper keywords necessary for smart sequencing. No typing is required by the chemist at the bench, and information does not have to be entered twice. Acquisition occurs, then the data files go to the server for analysis. The quantitative results move from the server to the LIMS as formatted text files. Networked laboratory systems share information and process samples together, with minimum operator intervention.

CONCLUSION

It is simple to incorporate the user-contributed macros at the PC controlling the autosampler and the server performing data analysis. Client/server smart sequencing saves time for the operator, and lets a computer take over tedious data validations. It halts a system that has gone out of control. This saves wear and tear on GC columns and mass spectrometer sources by avoiding unnecessary injections of contaminated waste samples. A cleaner system gives more reproducible data. The server part of client/server computing is better suited for the large floating point calculations involved in environmental target compound analysis. The client is better suited for the lab bench and data acquisition. This logical partitioning of computer tasks adds to laboratory efficiency. There is no cost for the user-contributed smart sequencing macros, and they are available from the author.

There is a future for intelligent control of lab systems. Computer systems will use response from data analysis to adjust acquisition parameters for both the chromatograph and the mass spectrometer. Self correcting analytical systems could keep themselves in QC

control. Failed tune runs can signal the mass spectrometer to tune itself and inject DFTPP again. Deviations from allowed retention times and response factors will flag the system to correct itself. Advances in computer technology advance smart control of analytical systems. The current Ethernet client/server framework will most likely give way to another era in which proximity does not matter. Improved communications will link mobile lab PC's and powerful servers. Object technology will effect the data and the processing. A sample run becomes an object, not just data, but data with an associated action. A DFTPP object for example would consist of the GC/MS data, the action to check EPA criteria, and the final QC result. Object technology allows a busy computer to send an object to another computer for processing help. This would be like sending to a friend's house all the ingredients and the recipe to bake a cake. Environmental laboratory computers networked across the hall, or across the world, could assist each other to control instruments and validate data simply by passing objects.

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(2) "Chemical Analytical Services for Organics Applying GC/MS Techniques", WA-87-J001, (US EPA Contract Lab Program, November 24, 1986)

(3) Koch, C. A., LC/GC, 1992, 9, 709

(4) "US EPA CLP Statement of Work for Organic Analysis for Multimedia and Multiconcentration", Document 01M01.1 (US EPA Contract Laboratory Program, Washington, D.C., 1990).

(5) Federal Register, 49, 153, October 26, 1984

(6) "Test Measurements for Evaluation of Solid Waste by Physical and Chemical Methods", (SW-836, US EPA, Washington, DC, 3rd ed., 1990), Section 1B

(7) Orfaldi, R, Harkey, D, and Edwards, J., Byte, 1995, 4, 108-122

Figure 1 The Smart sequencing GC/MS algorithm

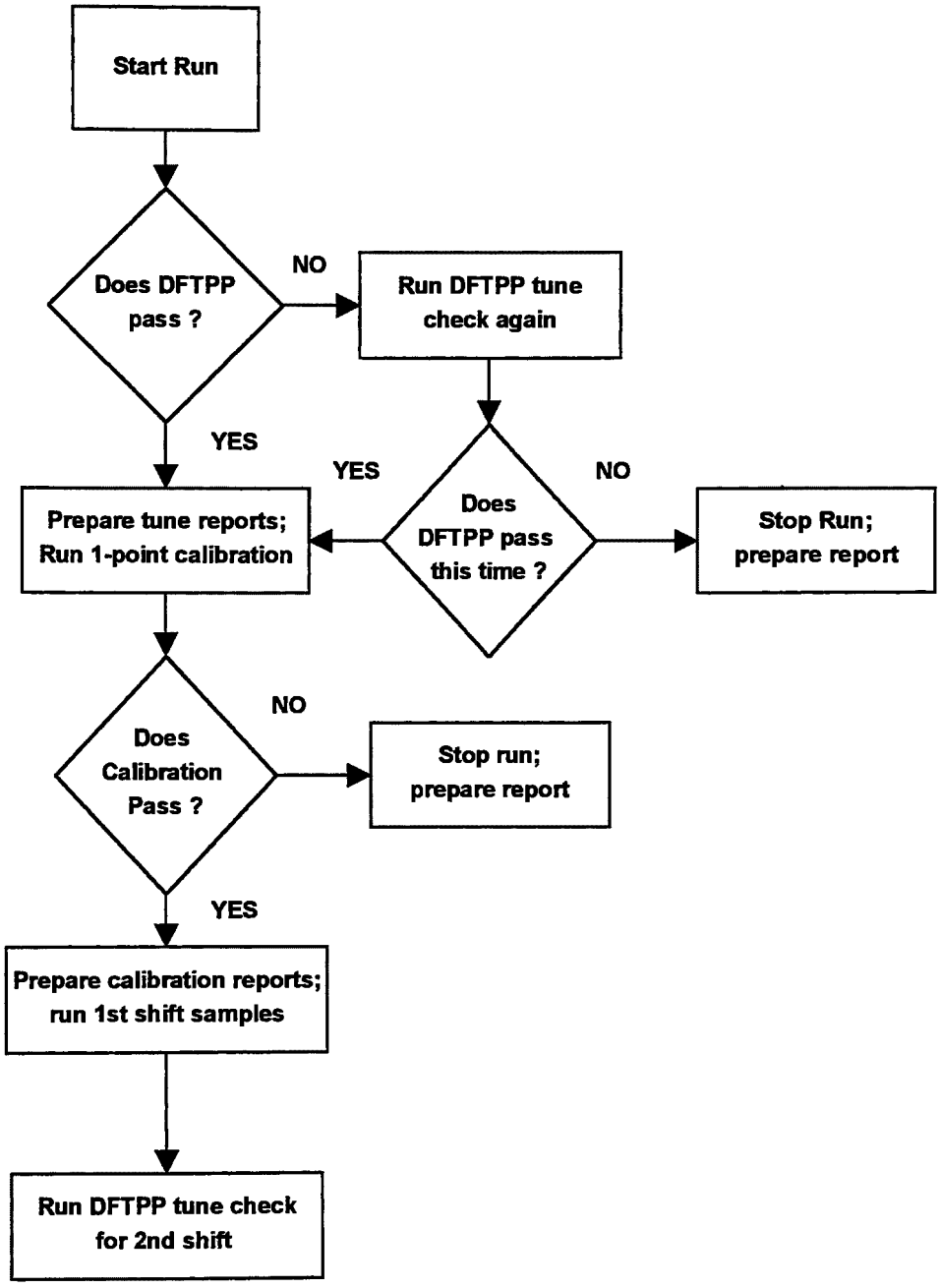

Figure 2 The Client/Server model

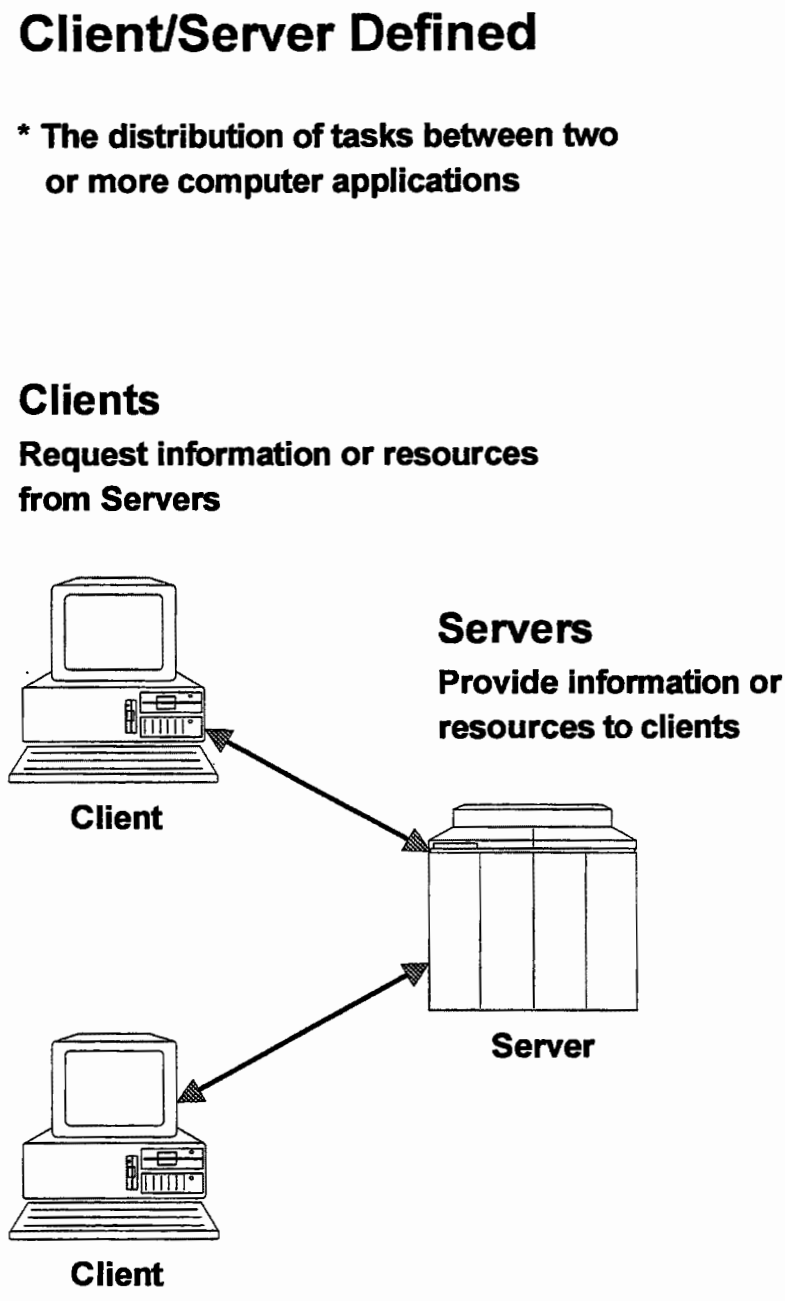

Figure 3 The Client/server smart sequence algorithm

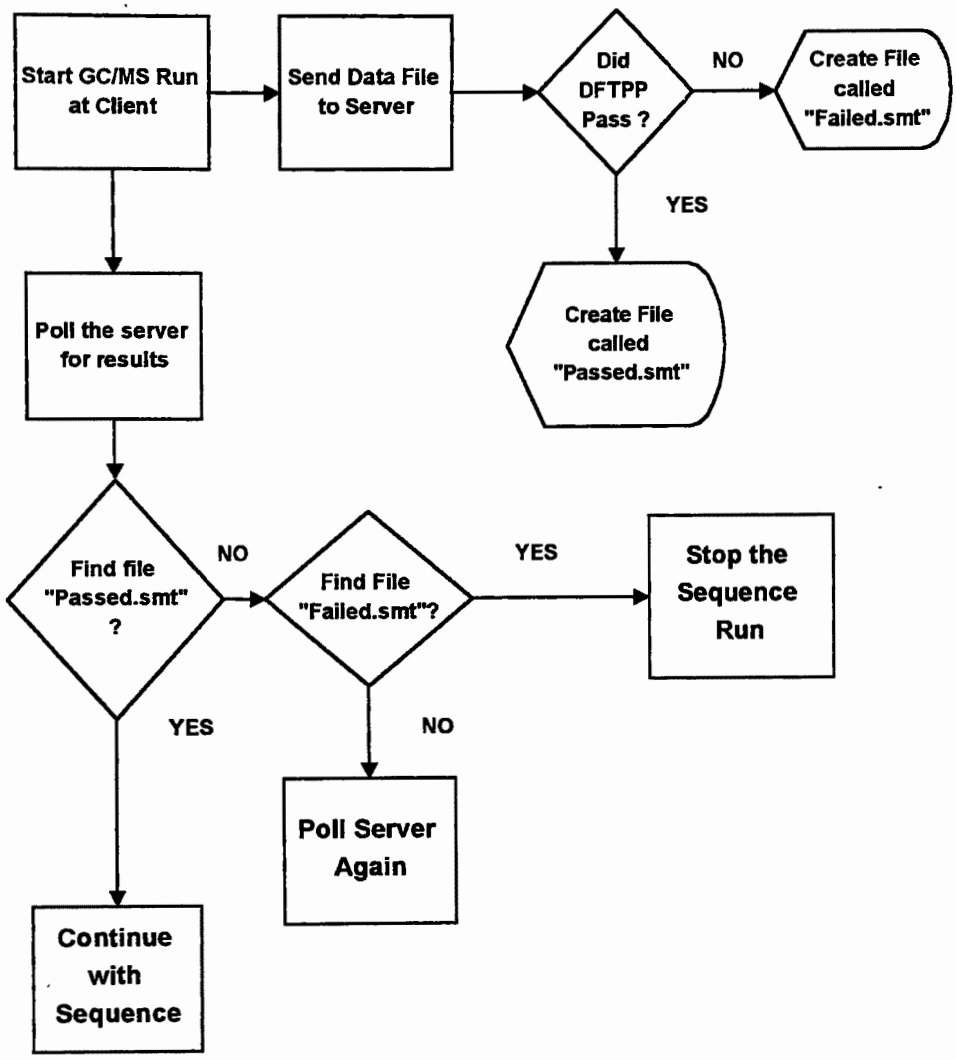

Figure 4 The LIMS text file used to construct the smart sequence file at the client PC

```
[SEQUENCE_HDR]

        SEQPATH=c:\hpchem\1\sequence
        SEQFILE=start.s
        SEQFILENEW=smart.s
        SEQCHECKBAR=0
        SEQSKIPACQ=0
        SEQOVERWRITE=1
        SEQCOMMENT=smart sequence for tune and daily cal runs
        SEQOPERATOR=operator name
        SEQDATAPATH=c:\hpchem\1\data\
        SEQPRESEQCMD="              "
        SEQPOSTSEQCMD="              "
        STARTLINE=1
        STOPLINE=8

[LINE 1]
        VIALNO=1
        DATAFILE=
        ACQMETHOD=On_Flag
        TYPE=6
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=STOP
        SAMPLEMISC=
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=

[LINE 2]
        VIALNO=1
        DATAFILE=dummy1
        ACQMETHOD=default.m
        TYPE=8
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=
```

Figure 4 (cont.)

```
[LINE 3]
        VIALNO=2
        DATAFILE=dummy2
        ACQMETHOD=default.m
        TYPE=4
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=

[LINE 4]
        VIALNO=3
        DATAFILE=dummy3
        ACQMETHOD=default.m
        TYPE=1
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=

[LINE 5]
        VIALNO=4
        DATAFILE=dummy4
        ACQMETHOD=default.m
        TYPE=1
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=
```

Figure 4 (cont.)

```
[LINE 6]
        VIALNO=5
        DATAFILE=dummy5
        ACQMETHOD=default.m
        TYPE=1
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=

[LINE 7]
        VIALNO=6
        DATAFILE=dummy6
        ACQMETHOD=default.m
        TYPE=1
        CALLEVEL=1
        UPDATEQI=1
        UPDATERF=1
        UPDATERT=1
        SAMPLEID=sample name stuff here
        SAMPLEMISC=sample misc stuff here
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=
[LINE 8]
        VIALNO=7
        DATAFILE=dummy7
        ACQMETHOD=Label
        TYPE=6
        CALLEVEL=7
        UPDATEQI=2
        UPDATERF=2
        UPDATERT=2
        SAMPLEID=STOP
        SAMPLEMISC=
        SAMPLEAMT=0
        DILFACTOR=1
        PREMACRO=
        POSTMACRO=
```

How the U.S. Environmental Protection Agency Region 2 RCRA Quality Assurance Outreach Program, Office of Research and Development, and Office of Enforcement and Compliance Assurance are Helping Industry to Minimize Environmental Compliance Costs

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) Region 2 Resource Conservation and Recovery Act (RCRA) quality assurance outreach program is cooperating with the EPA Office of Research and Development (ORD), and Office of Enforcement and Compliance Assurance (OECA) to help the regulated community minimize costs when complying with environmental regulations.

The OECA computer bulletin board system (BBS) recently merged with ORD's pollution prevention BBS. This new BBS is named Enviro$ense. The three goals of the Enviro$ense BBS are to prevent pollution, increase compliance with environmental regulations, and reduce environmental compliance costs.

The Enviro$ense computer bulletin board system will contain compliance and pollution prevention files from EPA program offices. This will allow "multi-media, one stop shopping" for compliance and pollution prevention information. For example, Enviro$ense can scan file titles and abstracts for the key words "cadmium in water", and list all compliance and pollution prevention files that contain those key words. The files of interest can then be downloaded. Enviro$ense will be accessible directly or via the Internet.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Region 2 Resource Conservation and Recovery Act (RCRA) quality assurance outreach program is cooperating with the EPA Office of Research and Development (ORD), and Office of Enforcement and Compliance Assurance (OECA) to help the regulated community minimize costs when complying with environmental regulations.

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The Enviro$ense computer bulletin board system will contain compliance and pollution prevention files from EPA program offices. This will allow "multi-media, one stop shopping" for compliance and pollution prevention information. For example, Enviro$ense can scan file titles and abstracts for the key words "cadmium in water", and list all compliance and pollution prevention files that contain those key words. The files of interest can then be downloaded. Enviro$ense will be accessible directly or via the Internet.

The BBS, which became fully operational in April, will assist industry minimize compliance costs by providing:

1. Program specific (Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, etc) regulations, guidances, and strategies for reducing environmental compliance costs; program specific quality assurance guidances and strategies for reducing environmental compliance costs; and industry specific (mining, manufacturing, petroleum, etc) regulations, guidances, and strategies for reducing environmental compliance costs. These regulations, guidances, and strategies may be downloaded by anyone who has a modem and a computer.

2. Weekly updates of EPA's Federal Register notices.

3. The EPA Region 2 seminar, symposia, and workshop schedule.

4. Quality assurance project plan guidances by program and by region.

5. Information about SW-846 analytical issues, including: data validation, method updates, performance evaluation studies, immuno assay methods, and the Office of Solid Waste Quality Assurance Newsletter.

6. Information about EPA's July 1995 Waste Testing and Quality Assurance Symposium, in Washington, DC (seminars, workshops, call for papers, etc).

7. The EPA Region 2 quality assurance standard operating procedures (SOPs), toxicity characteristic leaching procedure (TCLP) manual, and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) manual.

8. Information about air and water quality assurance issues.

9. Information on hazardous waste identification, characterization, and sample transportation.

The EPA Region 2 Office is coordinating the "ASK EPA" forum on the BBS. The ASK EPA forum will consist of question and answer forums, where people post questions and EPA experts post answers within a few days. Other individuals interested in the topic can read the questions and answers.

ASK EPA forums on the following topics will be offered:

1. Ground Water. Hosted by Bill Stelz, EPA, Washington DC.

2. How to Use EPA's Decision Error Feasibility Trials (DEFT) Software to Reduce Monitoring Costs. Hosted by Nancy Wentworth, EPA, Washington DC.

3. EPA Region 2 CERCLA quality assurance policies on data validation, routine analytical services (RAS) and non RAS methods. Hosted by Peter Savoia, EPA, Edison NJ.

4. EPA Region 2 NPDES policies. Hosted by John Kushwara, EPA, New York NY.

5. EPA Region 2 RCRA quality assurance policies. Hosted by Leon Lazarus, EPA, Edison NJ.

6. Mobile labs and robotics. Hosted by Vernon Laurie, EPA, Washington DC.

The Ask EPA forum will describe how to download the following files from Enviro$ense:
1) EPA hot line and help line telephone numbers on EPA policies, guidances and monitoring methods.
2) Monthly summaries of questions commonly asked on EPA hot lines and help lines.

USING ENVIRO$ENSE

The following discussion explains how to utilize the Enviro$ense computer bulletin board system:

Modem Settings

Speed	1,200, 2,400, 4,800, 9,600, or 14,400 baud
Data	8 bits
Parity	None
Stop	1
Duplex	Full
Emulation	VT-100 or ANSI or BBS
Phone #	703-908-2092

After logging on and selecting a password, files may be uploaded or downloaded.

UPLOADING FILES

Any type of PC file can be uploaded onto the BBS. However, the vast majority of BBS files are text files. The authors recommend that text files be uploaded in one of the following formats: 1) DOS based ASCII text, or 2) WordPerfect 5.1/5.2 files. ASCII text files may be generated by using the "Save As" or "Text Out" commands in most word processors. WordPerfect files are compatible with most word processors.

Uploaded files should be compressed unless the users wants BBS callers to be able to read the files on-line. All large files must be compressed. Compressed files must be downloaded before they are read. Compression reduces the amount of disk space utilized by a file, and reduces the time required to upload or download a file. Files may be compressed by using PKZip utilities. PKZip utilities may be obtained from the Enviro$ense BBS by downloading file "PKZ204G.EXE". After downloading this file, its name is typed at the DOS prompt. This will decompress the PKZ204G.EXE into a number of files, including a software documentation file. The PKZip documentation file explains how to use PKZip utilities. This documentation file may be accessed in any word processor.

If the user wants a text file to be readable on-line, it must be saved as an ASCII file or WordPerfect file, and its name should end with the TXT extension (i.e., MYFILE.TXT). All files other than these TXT files should be compressed using PKZip. Compressed files will always have the file extension ZIP (i.e., MYFILE.ZIP). Therefore, when preparing a file for uploading, it should have either the TXT or ZIP extensions. However, small files with different extensions are acceptable.

Placing a file to be uploaded on a hard drive accelerates the uploading. The hard drive is usually designated as the "C:" drive.

To upload a file onto the Enviro$ense BBS, the user must identify and locate a specific file, and instruct the user's communications software to transfer the file. To notify the Enviro$ense BBS that a file is to be uploaded, the user selects "U" from the main menu, and presses enter. The Enviro$ense BBS will ask for the name of the file to be uploaded. It must have the same name as the file that has been prepared for uploading (i.e., MYFILE.TXT or MYFILE.ZIP). After verifying that the BBS does not already have a file with that name, the user will be asked to briefly describe the file. The file description may be up to 10 lines of 45 characters each. The first line should describe the file. Subsequent lines should describe the file in more detail, utilizing as many key words as possible. BBS users may easily scan all file descriptions for key words. When uploading files, the agency/company that produced the file, and a contact name and phone number should be included to allow people to obtain additional information. After receiving the file description, the Enviro$ense BBS will grant permission to transfer the file. At this time, the users communications software should transmit the file to the Enviro$ense BBS.

The communications software manual illustrates how to transfer a file. Some communications programs utilize the "Page Up" key to transfer files. In order for a file to be transferred, it must be properly named and located on a specific drive. While the file is being transferred, an indicator of transfer progress can be viewed on your screen. Depending on the size of the file and the modem speed at which the user connected, uploading may take a few seconds or many minutes. Once the upload is completed, the Enviro$ense BBS will thank the user, and scan the upload for viruses. If viruses are not present, the file will be placed in the an appropriate topic directory of the files section. The key words used in the file description will determine the appropriate file directory.

For information about the Enviro$ense BBS, please contact Myles Morse at 202-260-3161 or Jeff Kelly at 202-260-2809. For information about the ASK EPA forum, please contact Leon Lazarus at 908-321-6778.

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QUALITY ASSURANCE AND QUALITY CONTROL LABORATORY AND INSITU TESTING OF PAPER MILL SLUDGES USED AS LANDFILL COVERS

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ABSTRACT

Paper mill sludges have been successfully used as an alternative to clays as landfill cover material for the past decade. Although paper mill sludges are approximately 50% kaolinite clay, the geotechnical properties of paper mill sludges differ from a typical clay. Paper mill sludges are characterized by a high water content and organic content in comparison to a typical clay which contribute to the variations in the geotechnical properties. The purpose of this paper is to give regulators a better understanding of the geotechnical properties of paper mill sludges which are used as landfill cover material.

Laboratory tests were conducted on seven paper sludges to obtain the geotechnical properties such as the Atterberg limits, compaction characteristics, water content, organic content, and shear strength. Typical laboratory procedures used for clays were altered for paper sludge due to the high initial water content. Standard procedures for the laboratory testing of the geotechnical properties of paper sludges and insitu sampling are discussed.

Hydraulic conductivity (permeability) and compressibility test were conducted on the various paper sludge. A direct relationship between organic decomposition, water content, and compressibility was established. Laboratory permeability tests were conducted on insitu samples taken from an actual paper sludge landfill cover layer.

The permeability varied considerably among the paper sludges. Factors which influence the permeability include water content, consolidation, and organic content. Although a paper sludge may not initially meet the regulatory requirement for permeability (when the sludge cover system is constructed at the natural water content), the change in void ratio that results from consolidation and dewatering under a low effective stress can reduce the hydraulic conductivity to an acceptable value.

INTRODUCTION

The high price of solid waste disposal has sparked interest in the development of alternative uses for waste sludges (paper mill sludges and water treatment plant sludges). Compactable to a low permeability in spite of high water contents and low solid contents in comparison to clays, paper mill sludges can substitute for clays in landfill

covers. Since 1975, paper mill sludges have been used to cap landfills in Wisconsin and Massachusetts (Stoffel and Ham, 1979; Pepin, 1984; Aloisi and Atkinson, 1990; Swann, 1991; Zimmie et al., 1993). This paper establishes design criteria for landfill covers using paper sludge.

Seven sludges were used in this study. Sludge A is a wastewater treatment plant sludge from a deinking recycling paper mill. The treatment plant receives 96% of the flow from the paper mill and 4% of the flow from the town. Sludge B is a blended sludge from a wastewater treatment plant which receives its effluent from a recycling paper mill and the neighboring community. Sludge C is a blended sludge from an integrated paper mill and is comprised of kaolin clay, wood pulp and organics. Sludge C was mined from a sludge monofill landfill which was in operation since 1973. Samples were collected from different sections of the monofill to represent different sludge ages: one week (C1), 2-4 years (C2), and 10-14 years (C3). Sludge D is a primary wastewater treatment plant sludge from a recycling paper mill. Sludge E is a primary wastewater treatment plant sludge from a non-integrated paper mill.

GEOTECHNICAL CLASSIFICATION

The geotechnical classification of paper mill sludges is not like that of typical clays used in landfill cover systems. For example, Atterberg Limits tests are very difficult to perform on paper sludges and the results may not be meaningful in terms of classical geotechnical classification (Zimmie and Moo-Young, 1995). Organic content, specific gravity, natural water content, and permeability appear to be the major physical properties of interest.

The ranges of natural water contents, organic content, specific gravity, and permeability are summarized in Table 1. Water contents were determined according to American Society for Testing and Materials (ASTM) procedure D2974. The organic contents of paper sludges were determined according to ASTM procedure D2974, method C for geotechnical classification purposes. Specific gravity tests were performed on the sludges according to ASTM procedure D854. Permeability tests were conducted on remolded specimens of the various sludges using ASTM procedure D5084. Paper sludge specimens were remolded at various water contents in the range of the initial moisture content. Average initial permeability values were measured at a low confining stress of 34.5 kPa.

MATERIAL WORKABILITY

Proctor tests were performed following ASTM procedure D698-78. Because of the high water content, tests were conducted from the wet side rather than from the dry side as recommended by ASTM. When water was added to dry sludge, large clods formed, the clods were difficult to break apart, and the sludge lost its initial plasticity.

During the drying process, the sludge was passed through the number 4 sieve and placed in a pan to air dry. Many trials were conducted to reach the optimum moisture content and density.

Figure 1 shows the Proctor curve, optimum moisture content, and dry density for the various sludges. The Proctor curves show a wide range of moisture contents on the wet of optimum portion of the curve and a small range of water contents on the dry of optimum portion of the curve. At higher water contents, the dry density obtained from the Proctor curve for the various sludges is similar. At the optimum density and moisture content, the sludge is dry, stiff, and unworkable. A very high water content is desirable, if the sludge is to be used as a landfill capping material (Zimmie et al., 1993). These test results compare favorably to research conducted on water treatment plant sludges (Raghu et al., 1987; Alvi and Lewis, 1987; Environmental Technology Inc., 1989; Wang et al., 1991).

During the construction of the Hubbardston landfill in Hubbardston, Massachusetts and Erving Paper mill test plots in Erving, Massachusetts, different types of equipment were used to place the sludge cap. Four types of equipment were used: a small ground pressure vibratory drum roller, a vibrating plate compactor, a sheepsfoot roller, and a low ground pressure track dozer. The sheepsfoot roller which is generally used to compact a clay liner clogged immediately due to the cohesive nature of the sludge and the high water content. The vibratory methods did not provide homogeneous mixing and did not compact the sludge effectively. The small ground pressure dozer provided the best method for placement and compaction. This equipment successfully eliminated large voids from the sludge material and kneaded the material homogeneously.

CONSOLIDATION BEHAVIOR

The water content of paper sludge is the most useful parameter in predicting consolidation behavior. The sludge samples are assumed to be fully saturated so that the void ratio is equal to the specific gravity of the sludge multiplied by the water content. To simulate insitu consolidation behavior, water contents were kept as close as possible to the initial value. Higher initial water contents result in higher initial void ratios which increase the potential consolidation.

Consolidation tests were performed on sludge A at various water contents to show the highly compressible nature of the paper sludge and to establish a relationship between consolidation behavior and initial water content (Figure 1). The change in void ratio per log cycle of pressure (C_C-Compression Index) increases due to higher initial water contents as shown in Figure 2. Higher initial water contents will result in higher void ratios, which account for the increasing magnitude of compression with increasing water content.

Consolidation tests were also performed on the other sludges at their natural water content. The compression index was plotted against the initial water content for the paper sludges and for water treatment sludge (Wang et al., 1991). The relationship between the compression index and water content is as follows:

$$Cc = 0.009w_O \quad (1)$$

The relationship between the compression index and void ratio is as follows:

$$Cc = 0.39e_O \quad (2)$$

Landva and LaRochelle (1983) established a relationship between compression index and water content for peats which is similar to the one obtained for paper mill sludges.

INFLUENCE OF ORGANIC CONTENT ON COMPRESSIBILITY

Consolidation tests were performed on the seven sludges to obtain a relationship between compressibility and organic content. Paper mill sludges are composed of 40-60% organics. Twenty two consolidation test were conducted to obtain a relationship between Figure 2 Consolidation Test on Sludge A at Various Water Contents
organic content and compressibility. Paper sludges were tested at an initial water content ranging from 109% to 224%. Sludges tested had an average water content of 166.4% with a standard deviation in the water content of 37%. The compression indices (Cc) which is the change in void ratio per logarithm cycle of the vertical stress and the coefficients of compressibility (Av) which is the change in void ratio per change in vertical stress were computed for the various test specimens. The correlation coefficient between the organic content and the compression index and coefficient of compressibility are 0.47 and 0.53, respectively, which indicates that there is a positive correlation between the variables.

Figure 3 plots the compression index and the organic content for various sludges. The relationship between the compression index and the organic content from Figure 3 is as follows:

$$C_c = 0.027\ O_c \quad (3)$$

Figure 4 plots the coefficient of compressibility and the organic content for the various sludges. The relationship between the coefficient of compressibility and the organic content is as follows:

$$A_v = 0.000263\ O_c \quad (4)$$

Previous research indicates that there is little to no data relating the organic content to compressibility for sludges. A relationship can be developed to predict the permeability of paper sludge from the organic content.

INSITU SAMPLING PROCEDURES FOR PERMEABILITY ANALYSIS

The best sampling procedure was discovered through trial and error using Shelby tubes. Slow static pressure (pushing the Shelby tube into the sludge layer with a constant vertical force) compressed the sludge during the sampling process and led to low recovery rates. A dynamic sampling process, like striking the Shelby tube with a hammer, resulted in high rates of recovery and minimal disturbance. Apparently, due to the fibers and tissues in the sludge matrix, a sharp blow was needed to cut through the sludge. The normal field procedure was to place the Shelby tube on the sludge, place a wood block on top of the Shelby tube, and strike the block with a hammer. This procedure resulted in the highest rates of recovery and the least disturbance (Moo-Young, 1992).

Laboratory permeability tests were conducted on undisturbed sludge A samples taken from the Hubbardston Landfill on five occasions: July 1991, October 1991, April 1992, January 1993, and July 1993. All laboratory permeability tests in this study were performed following the procedures of ASTM D5084 for measuring the hydraulic conductivity of saturated porous material using a flexible wall permeameter with backpressure. Samples were tested at a low confining stress of 34.5 KPa to simulate the worst case, that is the highest permeability.

In general, the samples met the 1×10^{-7} cm/sec regulatory requirement for a low permeability landfill cover system in Massachusetts. Table 2 summarizes the permeabilities of the samples. The water contents of the samples 1, 2, and 4 taken from the landfill after construction varied from 150% to 220%. In general all specimens taken from various sections of the landfill immediately after construction either met the regulatory requirement for permeability or were very close.

Sample 3, taken after 9 months, was dewatered and consolidated under an eighteen inch overburden. It was markedly stiffer and denser than samples obtained shortly after construction. The permeability for the sample meets the regulatory requirements of 1×10^{-7}cm/sec. Sample 5 was taken from the same section of the landfill as sample 3, eighteen months after placement. Permeability tests yielded an average permeability of 3.4×10^{-8} cm/sec at a water content of 107 %, which easily meets the 1×10^{-7} cm/sec standard for landfill cover design. After 18 months of consolidation the sludge layer met the regulatory requirements. The sludge layer performs as an adequate hydraulic barrier at a water content of 107% and a void ratio of 2.1. Sample 6 was taken two years after placement from the same section of the landfill as samples 3 and 5.

Sample 6 meets the permeability requirement. Thus, time, dewatering and consolidation have reduced the permeability of sludge A.

HYDRAULIC CONDUCTIVITY

A major factor in the design of a paper sludge landfill cover is the estimation of the permeability after initial settlement (approximately six months to one year). There are three major factors that contribute to the permeability characteristics of paper sludges: water content, organic content, and consolidation. Zimmie and Moo-Young (1995) have conducted research on the hydraulic conductivity of various paper sludges. In general, the water content and permeability relationship for paper sludges reveals that the permeability increases near the optimum moisture content (40% to 60%). The minimum permeability for paper sludges occurs approximately 100 percent wet of the optimum water content. When constructing a paper sludge landfill cover, a high water content is desirable, usually

at the natural water content, ranging from 150-250% (Zimmie et al, 1993).

Figure 5 shows a relationship between the organic content and permeability. The organic content and the permeability were plotted for the various sludges. The organic content ranged from 25% to 73%. For the average permeability line, the hydraulic conductivity ranged from 2×10^{-8} to 2×10^{-7} cm/sec. The 95% prediction interval is shown to give a range of values for the permeability and organic content relationship. The upper prediction interval ranges from 4×10^{-7} to 1×10^{-5} cm/sec, and the lower prediction interval ranges from 1×10^{-9} to 2×10^{-8} cm/sec. As the organic content decreases, there is a decrease in permeability. Points outside of the prediction interval indicate that the prediction interval is only an estimated range for the permeability.

The consolidation characteristics of paper sludges are well documented (Zimmie and Moo-Young, 1995; Zimmie et al., 1993; Wang et al., 1991; Alvi and Lewis, 1987; Raghu et al., 1987). Paper sludge is a highly compressible material with a compression index of 1.1 to 1.5 (Moo-Young, 1992). Sludges with higher initial water contents have steeper decreases in void ratio under equivalent changes in effective stress. The amount of reduction in void ratio under a given change in effective stress directly effects the magnitude of change of permeability. A typical paper sludge shows approximately one order of magnitude decrease in permeability while a clay shows a reduction of a factor of two over the same range of pressures (Zimmie and Moo-Young, 1995). These results (a decrease in permeability resulting from an increase in effective stress on a sample) are comparable to the results obtained from studies conducted on organic clays and peats (Landva and LaRochelle, 1983).

Figure 6 shows the effects of a change in void ratio on the permeability of samples of sludges A, C1-C3, and D which were molded at various water contents. It is of interest to examine the curves for sludges A and D. These sludges were selected for comparison

due to their similar organic contents, water contents, and compression properties. Permeability tests were performed at 34.5 kPa, 69 kPa, and 138 kPa. Although the two sludges do not have permeabilities of the same magnitude, they show nearly equivalent changes in void ratio per log cycle change in permeability. Sludge C3 and C1 which were molded at higher water contents have a steeper change in void ratio and a larger reduction in permeability.

The void ratio-permeability relationships were also established for sludges C (Figure 6). Sludges C1 and C3 were molded at 250 % water content and show similar changes in void ratio. Sludge C2 was molded at 190% water content which is identical to one of the sludge D samples. Sludges C2 and D show similar compressive behavior, and the change in void ratio per log cycle change in permeability are comparable.

LANDFILL COVER DESIGN FOR PAPER SLUDGE

For landfill cover design, one of the common stipulations is that the cover should include a barrier layer with a permeability less than or equal to 1×10^{-7} cm/sec. Most sludges in this study (C1, C2, D, and E) do not initially meet that regulatory requirement for permeability when tested at the natural water content under a low confining stress (Table 1). In general, most of the sludges meet the 1×10^{-7} cm/sec permeability requirement when tested at higher consolidation pressures (Moo-Young, 1992; Zimmie and Moo-Young, 1995). The time for this reduction in permeability must be short in duration for the material to be considered as the low permeability material of a landfill cover system. Short term laboratory tests take consolidation effects into account but are not capable of judging long term effects such as organic degradation. However, the use of higher effective stresses to measure the permeability of paper sludges yields conservative results, since organic decomposition also reduces the permeability (Figure 2).

The estimated load at the mid-point of a typical paper sludge landfill cover system is approximately 23.9 kPa. At higher water contents (166-190%), the minimum change in void ratio (from the initial void ratio to a vertical pressure of 23.9 kPa) ranges from 0.5 to 1.0 (Zimmie and Moo-Young, 1995). Using the minimum change in void ratio, the change in permeability can be predicted for the various sludges using Figure 6. A maximum change in permeability of approximately one order of magnitude can result from the consolidation of the paper sludge cover. Initially most of the sludges (C1, C2, D, and E) do not initially meet the 1×10^{-7} cm/sec regulatory requirement (Zimmie and Moo-Young, 1995). However, large changes in void ratio ($\Delta e = 1$ or greater) that may occur within one year will reduce the hydraulic conductivity of the sludge to an acceptable value of 1×10^{-7} cm/sec or less.

The laboratory permeability tests on the insitu samples (Table 2) can be used to illustrate the change in insitu hydraulic conductivity that results from a change in void

ratio. For the Hubbardston Landfill, the average initial permeability, water content, and void ratio were 1.06 x 10^{-7}, 190%, and 3.72, respectively. After nine months, the permeability, water content, and void ratio were 4.47 x 10^{-8}, 106%, and 2.1, respectively. There is a decrease in water content of 86% and a change in void ratio of 1.62. The resulting change in permeability was approximately one half an order of magnitude, which compares favorably to the observed changes in laboratory compacted samples.

CONCLUSION

Paper sludges are characterized by high water contents, organic contents, and compressibilities, and are compactable to low permeabilities. A high water content is recommended for the construction of a paper sludge cap, since paper sludge is stiff and unworkable near the optimum water content. For best insitu compaction, a low ground pressure dozer is recommended for the construction of a paper sludge cap.

One dimensional consolidation tests revealed a direct relationship between the water content and the compression index and between the organic content, the compression index, and the coefficient of compressibility. Paper mill sludges were characterized by high strains and large reductions in void ratio. Higher water contents resulted in higher void ratios and increased the compressibility.

Permeability tests were performed on the various sludges. The minimum permeability of paper sludge occurs far wet of the optimum moisture content. Organic content, water content, and compressibility are the key parameters which affect the permeability of paper sludges. Paper sludges yield a decrease in permeability five times that for a typical clay for an effective stress range of 34.5 to 138 kPa. Observations of the municipal landfill using a 91 cm layer of sludge A as the impermeable barrier indicate that it is providing an adequate hydraulic barrier.

When designing a landfill cover system using paper sludge as the impermeable barrier, the sludge layer should be constructed at the natural water content. Initially at the natural water content, the sludge may not meet the regulatory requirement for permeability of 1 x 10^{-7} cm/sec or less. However, the change in void ratio that results from the application of an overburden pressure (i.e., drainage layer and vegetative support layer) can reduce the permeability to an acceptable value.

ACKNOWLEDGMENTS

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Table 1 Summary of Water Content, Organic Content, Specific Gravity, and Average Initial Permeability

SLUDGE	WATER CONTENT (%)	ORGANIC CONTENT (%)	SPECIFIC GRAVITY	AVERAGE INITIAL PERMEABILITY (cm/sec)
A	150-230	45-50	1.88-1.96	1.0×10^{-7}
B	236-250	50-60	1.83-1.85	1.0×10^{-7}
C1	255-268	50-60	1.80-1.84	1×10^{-6}
C2	183-198	45-50	1.90-1.93	3×10^{-7}
C3	222-230	40-45	1.96-1.97	1×10^{-7}
D	150-185	42-46	1.93-1.95	1×10^{-6}
E	150-200	40-45	1.86-1.88	5×10^{-6}

Table 2

Summary of Laboratory Permeability Tests on Insitu Samples

SAMPLE	DATE	PERMEABILITY (cm/sec)	WATER CONTENT (%)
1	JULY 1991	1.06×10^{-7}	190
2	OCTOBER 1991	4.0×10^{-8}	185
3[a]	APRIL 1992	4.47×10^{-8}	106
4	APRIL 1992	4.2×10^{-7}	220
5[b]	JANUARY 1993	3.4×10^{-8}	107
6[c]	JULY 1993	3.8×10^{-8}	91.5

[a] nine months
b eighteen months
[c] twenty four months

FIGURE 1 PROCTOR CURVE FOR VARIOUS SLUDGES

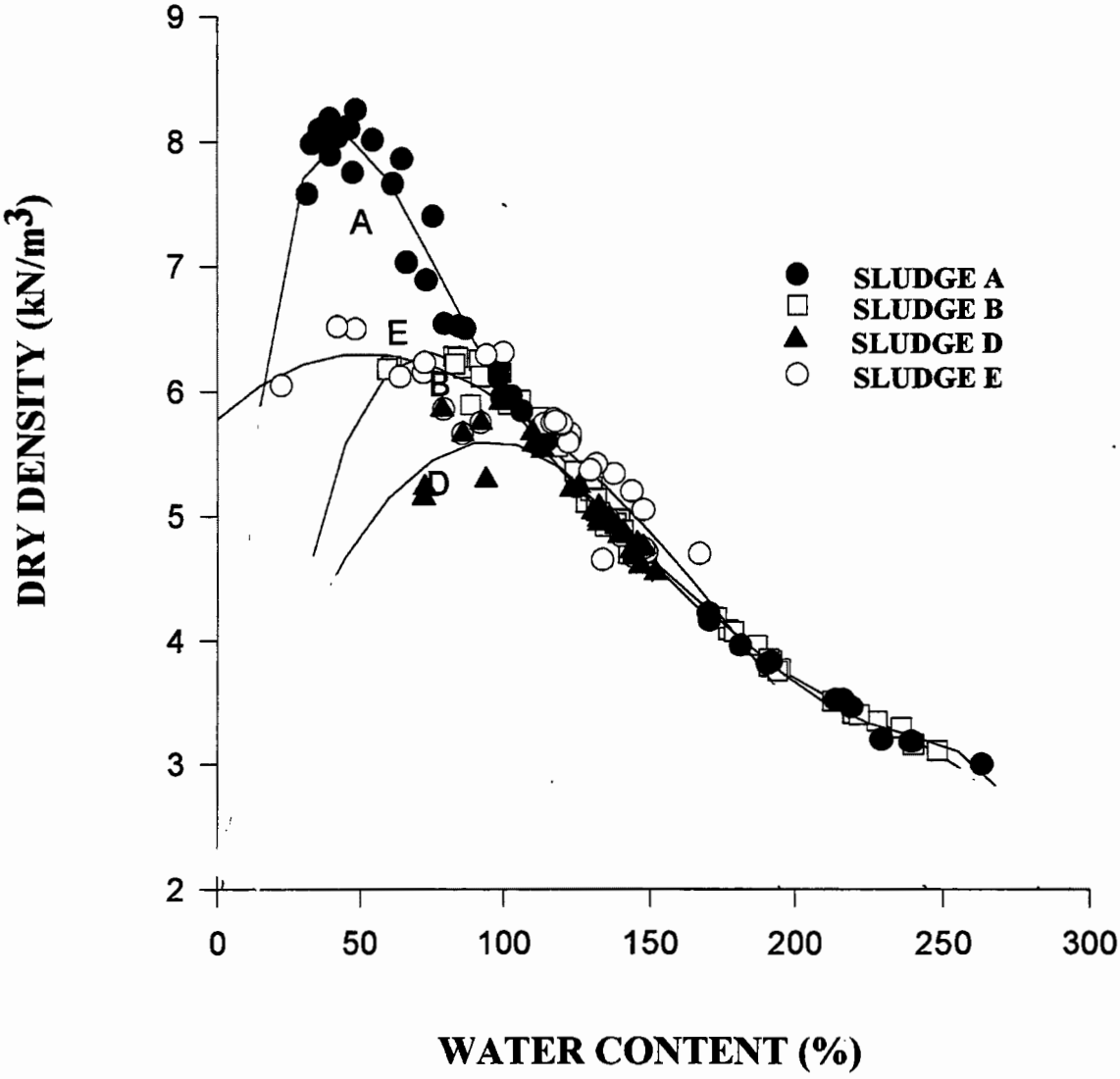


FIGURE 2 CONSOLIDATION TEST ON SLUDGE A

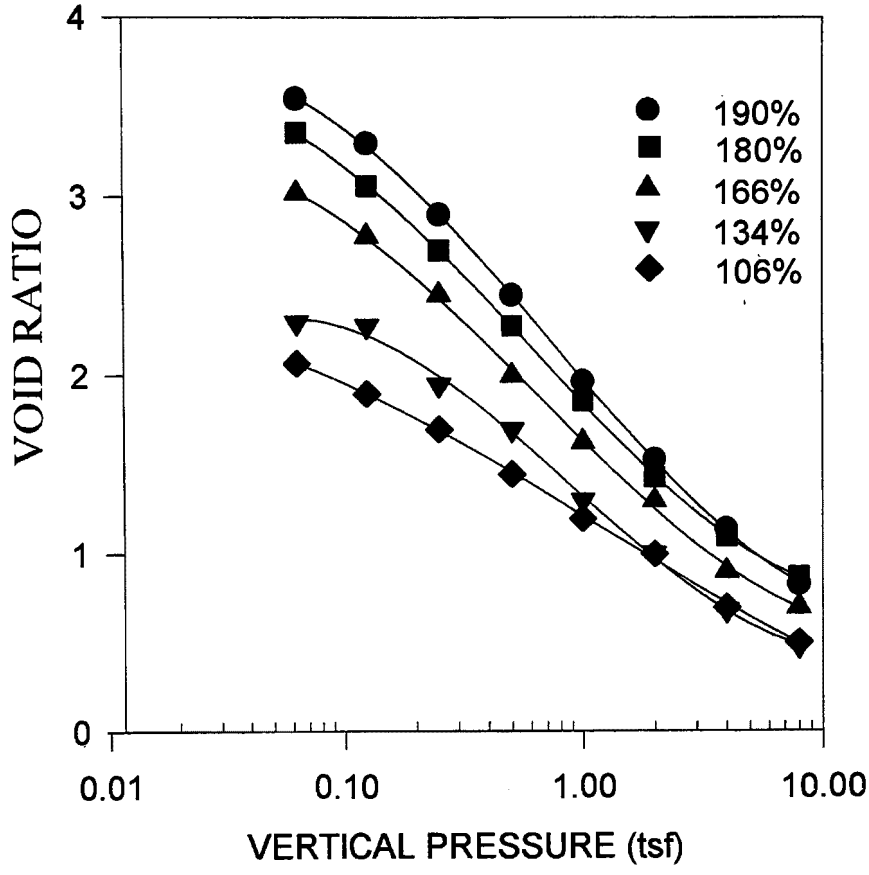


FIGURE 3 COMPRESSION INDEX AND ORGANIC CONTENT RELATIONSHIP

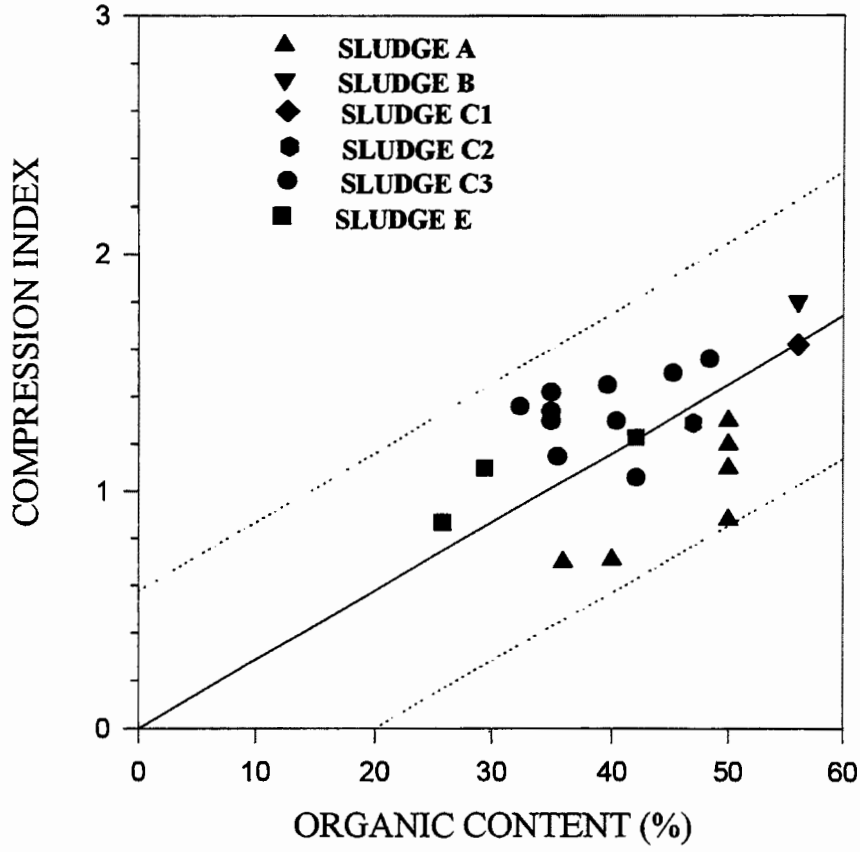


FIGURE 4 COEFFICIENT OF COMPRESSIBILITY AND ORGANIC CONTENT RELATIONSHIP

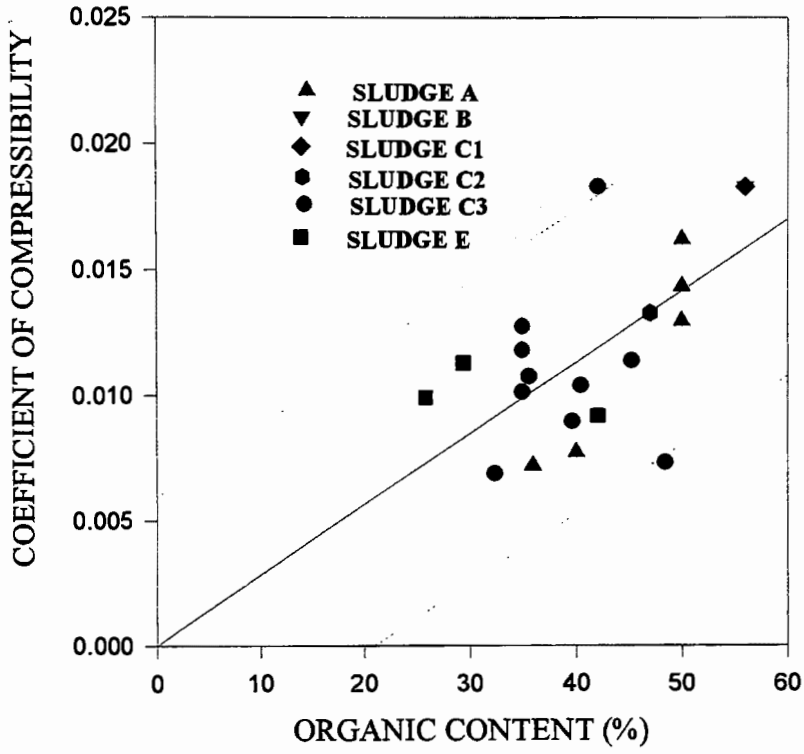


FIGURE 5 RELATIONSHIP FOR THE ORGANIC CONTENT AND PERMEABILITY

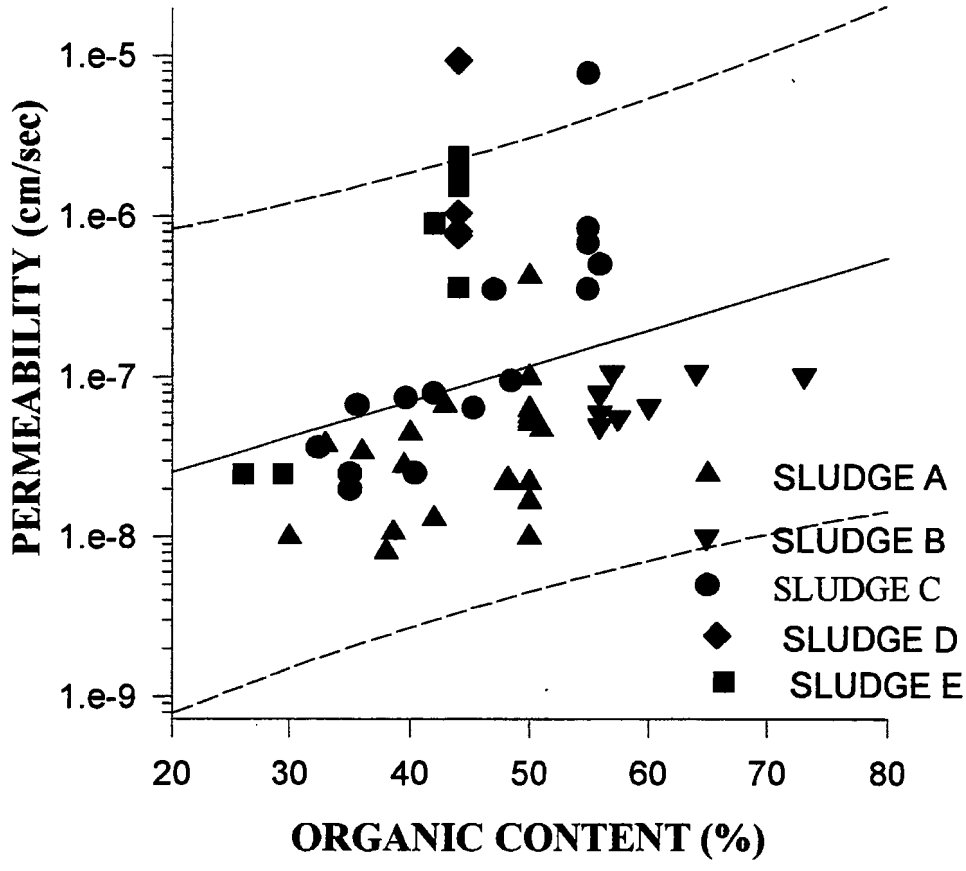
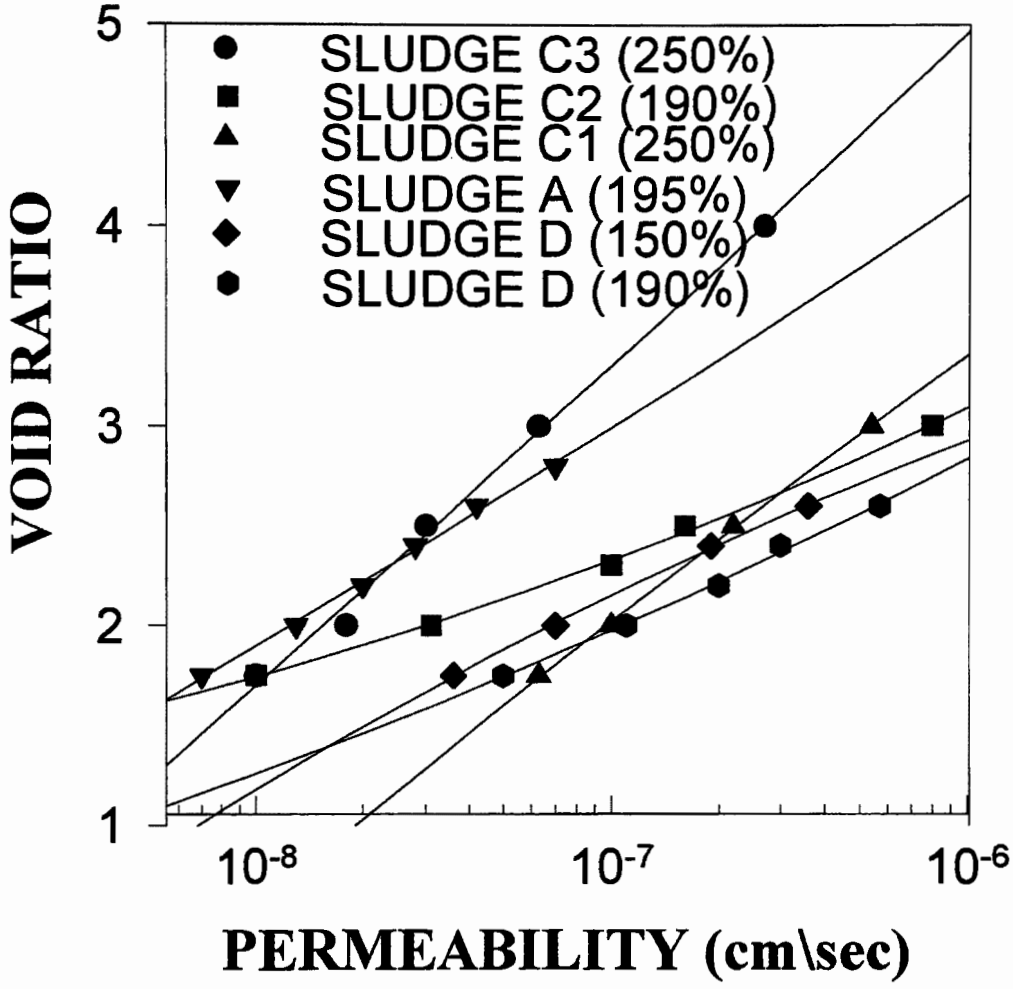


FIGURE 6 PERMEABILITY VS. VOID RATIO RELATIONSHIP



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DETERMINATION OF CONTROL LIMITS FOR ANALYTICAL PERFORMANCE EVALUATION IN U.S. DOE'S RADIOLOGICAL QUALITY ASSESSMENT PROGRAM

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ABSTRACT

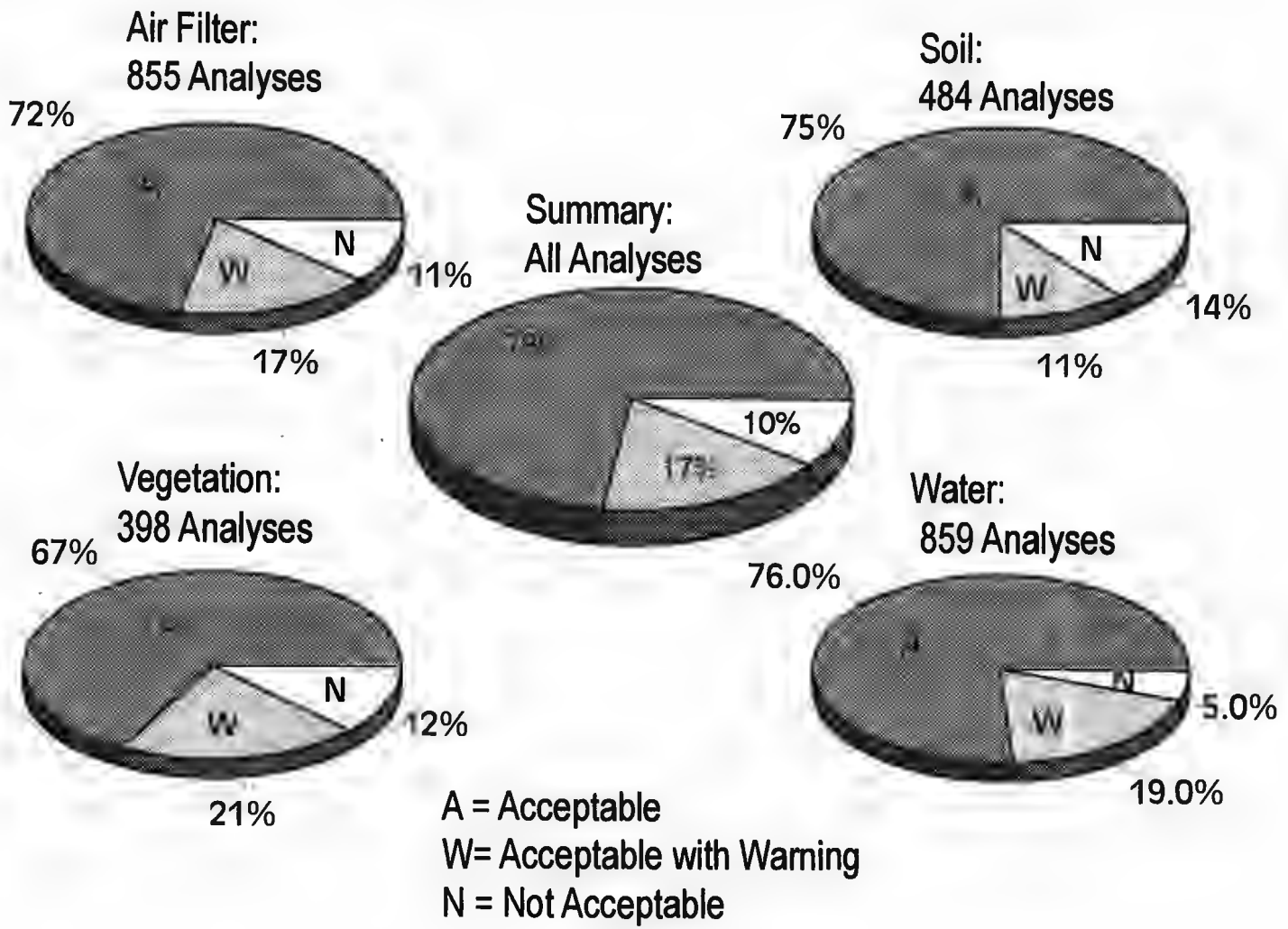
The Environmental Measurements Laboratory (EML) administers a semi-annual Quality Assessment Program (QAP) for the U.S. Department of Energy to assess the quality of environmental radiological data that are generated by its contractors. Participation in EML QAP is required under DOE Order 5400.1 for all laboratories providing monitoring and/or surveillance support to DOE sites. Furthermore, analytical laboratories supporting DOE/Environmental Management (EM) Program activities are required to participate in QAP under an EM memorandum issued in 1993 (P. Grimm, Memorandum March 5, 1993). Beginning with QAP41 (9/1994), all participants' analytical QAP performance will be evaluated based on control limits derived from EML's historical radioanalytical QAP data from 1982 through 1992.

The historical data comprise performance-based analytical measurements of radionuclides in environmental matrices of air filter, soil, vegetation, and water. The analytes for air filter are: ^{7}Be, ^{54}Mn, ^{57}Co, ^{60}Co, ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{234}U, ^{238}U, ^{238}Pu, ^{239}Pu and ^{241}Am; for soil are: ^{40}K, ^{90}Sr, ^{137}Cs, ^{226}Ra, ^{234}U, ^{238}U, total U, ^{238}Pu, ^{239}Pu and ^{241}Am; for vegetation are ^{40}K, ^{60}Co, ^{90}Sr, ^{137}Cs, ^{234}U, ^{238}U, ^{238}Pu, ^{239}Pu and ^{241}Am; and for water are: ^{3}H, ^{54}Mn, ^{57}Co, ^{60}Co, ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{234}U, ^{238}U, total U, ^{238}Pu, ^{239}Pu and ^{241}Am. These radioanalyte/matrix pairs are evaluated on the basis of reported variations among intercomparisons with time as well as on possible correlations of variations with activity levels. Results from the data analysis show that environmental matrices show wider variability range in the order soil > vegetation > air filter > water. This order may be due to the structural complexities of soil and vegetation which are natural matrices, whereas air filter and water matrices are spiked synthetic matrices (no interferences).

The QAP control limits are established from percentile distributions of cumulative historical reported values that are normalized to EML's values. The operational criteria developed for QAP performance are based on observed analytical capabilities for individual radioanalyte/matrix pairs over a ten year history of the program. The middle 70% of all historical reported values per analyte/matrix has been established "acceptable" and the next 10% on both sides of the 70% are "acceptable with warning". Reported values less than the 5th percentile and greater than the 95th percentile are established to be "not acceptable." These control limits derived from the historical radioanalyte/matrix

percentiles have been used to evaluate the QAP41 (9/1994) data (Figure). Results of the evaluation show that performance proportions observed for QAP41 data are consistent with those of previous QAP intercomparisons using $\pm 20\%$ and $\pm 50\%$. Further discussions on this topic are in Pan, V. (1995) Analysis of EML QAP Data from 1982 -1992: Determination of Operational Criteria and Control Limits for Performance Evaluation Purposes, U.S. DOE Report, EML-564, New York.

9/1994 QAP Summary of Evaluations of 2596 Reported Analyses



EM QUALITY ASSURANCE ASSESSMENTS FOR ENVIRONMENTAL SAMPLING AND ANALYSIS

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ABSTRACT

The collection of credible and cost-effective environmental data is critical to the success of environmental management (EM) programs at DOE facilities. A well-established and supported assessment program is critical to the success of the characterization, remediation and post-closure monitoring activities at DOE facilities. The Office of Environmental Management, Analytical Services Division (EM-263), along with the DOE's, Environmental Measurements Laboratory (EML) and the Radiological and Environmental Sciences Laboratory (RESL), has developed a comprehensive program to conduct independent assessments of EM analytical laboratory and field sampling activities and the associated quality assurance (QA) implementation. The assessment is designed to address both compliance and performance issues. This balanced approach will assess the existence, adequacy, implementation and effectiveness of the QA elements.

The program was developed for technical and QA, sampling and data manager assessors. It employs a line of inquiry interview approach rather than the more common checklist approach of a compliance audit. Assessment standards for the interviews related to laboratory and sampling activities have been developed. The two most important features of the program are: (1) The use of technical and management assessors ; and (2) That it is not regulatory compliance driven (i.e. no checklists). The end result will be the production of quality data as a result of improvement of the technical and QA processes.

In order to provide guidance that is comprehensive enough to address the various aspects of environmental sampling and analysis activities and to provide criteria leading to consistent EM assessments across the DOE complex, six separate documents were issued. Performance objectives and criteria have been developed which establish the basis for assessment findings. The performance objectives also provide criteria for

consistent assessment. The performance objectives and associated criteria are directly related to QA guidance for laboratory and sampling activities which was promulgated by the Department to support EM activities. This QA guidance was developed to ensure that the quality of environmental data produced is systematically documented and can be easily verified, making the data readily acceptable to regulatory agencies and to the public.

The assessment program is designed to assess appropriate DOE field organizations and EM contractors. It can also serve as guidance for the assessment program at any facility performing analytical laboratory and field sampling activities.

A PATTERN RECOGNITION BASED QUALITY SCORING COMPUTER PROGRAM

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ABSTRACT

QC criteria for environmental data often have explicitly delineated acceptance windows. When data is out of a stipulated tolerance, various penalties might be applied that require sample reanalysis or a payment penalty. When such problems arise, and the criteria are not technically based, as is often the case, everyone loses. Data quality decision dilemmas of this nature are not uncommon, and they result in adverse economic impact on regulators, analytical laboratories, and others. It is a true lose-lose situation when perfectly acceptable data is classified as out of specification because the criteria are incorrect. This quandary often arises due to nature of the approach taken to score the data quality criteria. Essentially, the "in vs. out" nature of the specification is binary in form. However, the data is multivariate in nature, and does not fit the binary decision model.

In this presentation, we demonstrate a simple new software tool that employs pattern recognition techniques that allow one to compare analytical data across organic and inorganic results for standards and samples. We demonstrate how data can be "resurrected" using a pattern recognition approach that provides alternate scales of comparison for multivariate data sets, be they in or out of specification. We show how a quality matching factor system can be employed to score the results for any set of environmental data. We demonstrate how the program uses a point-and-click approach to transform, weight, and otherwise modify organic, inorganic, and other data types to easily provide alternate perspectives on the information. We show how a more informed data perspective results from such comparisons. We demonstrate how, through this approach, one can bring common sense to environmental data analysis and save significant funds by using alternate data quality classification schemes. We discuss the powers and limitations of a pattern recognition based quality scoring approach and we propose the adoption of such a technique for examining environmental data quality scoring when traditional data analysis methods incorrectly classify data.

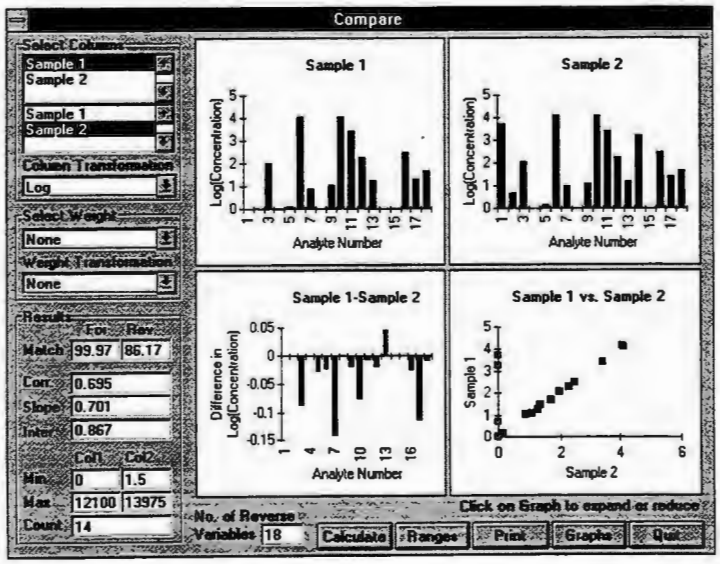

Figure 1 - Comparison of analysis of two actual soil samples by ICP/AES. The top two graphs show the analyte number vs. log of concentration. The lower left graph shows the difference plot of analyte vs. log of concentration, and the lower right graph is a scatter plot of log of concentration for Sample 1 plotted against log of concentration for Sample 2. All graphs can be displayed full screen and can be edited by the user.

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Automated Data Assurance Manager (ADAM)

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ABSTRACT

Data management and data quality assessment are inexorably linked functions that are the most important aspect of any environmental analysis monitoring program. Data management begins with preparation of sampling documents, proceeds through data quality assessment, and finishes with storage and retrieval of technically valid, legally defensible data of known and documented quality. Data quality assessment is a determination of the suitability of the data for the intended use and includes the four major tasks of data management, data validation, data qualification/review (flagging), and finally, the determination of suitability which must be consistent with the intended use of the analytical data. We have developed a software system, called ADAM, which provides automated data management and data quality assessment functions. ADAM is the first comprehensive sample data management system to include all of the following outstanding major features:

1) cradle-to-grave sample documentation using pre-printed forms
2) field data entry
3) analytical data importing (manual, electronic, or combined)
4) automated data validation and qualification
5) data reduction and reporting
6) data storage/archiving
7) laboratory invoice checking.

ADAM operates in Microsoft Windows® and utilizes software that will be industry compatible for many years into the future (Microsoft Visual Basic® and the Microsoft Access® relational database). ADAM is a state-of-the-art system that can be easily tailored to any site or project through a user-friendly menu system. ADAM relies heavily on dictionary or maintenance tables which reduce repetitive data entry. The data validation performed by ADAM includes all QC checks (calibration response, internal standard area reproducibility, surrogate recovery, precision, accuracy, etc.) for the major analysis methods (SW-846, EPA-CLP, Standard Methods, and EPA's 200, 300, 500, and 600 series). Data qualification can be performed in accordance with the EPA's Functional Guidelines for laboratory data review or any project specific guidelines. ADAM operates on the direct data output of the laboratory instrumentation thus reducing transcription and calculation errors. The design of ADAM provides for maximum flexibility and includes procedures that (1) accommodate different QC sample naming protocols by different laboratories, (2) allow for entry of client-specific analytical method protocols, and (3) handle varying degrees (levels) of QC.

ADAM is an invaluable tool to support the task of determination of suitability of analytical data for its specified intended use. The design, construction, and implementation of ADAM provides a range of benefits unavailable in any other commercial software system. The major benefits of ADAM include flexibility, improved data defensibility, open database connectivity, and improved efficiency which results in lower costs.

1.0 INTRODUCTION

In recent years the environmental arena has expanded dramatically, pushing technology to new limits and encouraging innovation in an ever changing regulatory atmosphere. One environmental issue dominates all aspects of this dynamic arena - the science of identifying and quantitating regulated chemical species or, laboratory analysis. A tremendous amount of resource and capital is expended based on laboratory analytical results and the legal aspects surrounding environmental issues make it imperative that these results be "of known and acceptable quality". To achieve this goal, data quality assessment procedures which are standardized and uniform must be applied to all environmental analysis data. The only practical means of attaining complete, uniform data quality assessment is to use an automated software application that processes electronic laboratory analysis results for QC and environmental samples. Any such automated software application must be able to provide efficient sample data management and tracking, process data from any laboratory, validate to control limits for all the major environmental methods, incorporate new methods or project specific control limits, accommodate different QC protocols and agency standards, securely maintain large volumes of data, and easily communicate with other software. The Automated Data Assurance Manager (ADAM) which utilizes Microsoft Visual Basic and the Access relational database in a Windows environment, is such a software application.

2.0 MAJOR FEATURES

Data quality assessment is the determination of the suitability of chemical analysis data for the intended use and includes four major tasks:

1) Data Management - sample documentation and tracking.
2) Data Validation - verifying that the laboratory has complied with all QC data quality requirements (QC Checks) of the specified analytical method.
3) Data Qualification/Review - flagging the data to reflect any failures to meet the data quality requirements according to a set of pre-established functional guidelines.
4) Suitability Determination - determining the suitability of the qualified data for the intended use.

ADAM is a comprehensive automated system which includes the following major features to support these tasks:

1) Project Data Management
2) Importing of Analytical Data
3) QA/QC Data Validation
4) QA/QC Data Reduction
5) QA/QC Data Flagging
6) Completeness Calculations
7) Laboratory Invoice Checking
8) QA/QC Reporting
9) Data Storage and Archiving

Figure 1 shows the Main Menu used to access the major features. Each feature is designed to provide for maximum flexibility while insuring the integrity of existing functions and allowing for easy incorporation of new functions. System flexibility and integrity are provided through the use of "maintenance" tables. These tables define analytes, analytical method control limits, parameters, parameter groups (e.g. RCRA metals), project detection limits, QC levels, and utility information such as company addresses and laboratory analysis costs). User-friendly entry screens make it easy to customize the maintenance tables for a particular project. Once set up, the tables are used to reduce the amount of repetitive data entry thus reducing errors and providing consistency.

Incorporation of new functions is facilitated by the use of "system" tables. Instead of hard code, these tables are used to define procedural elements such as processing order and processing steps to be included. Like the maintenance tables, the system tables can be customized on a project or system level.

Each major feature is discussed in more detail in the following sections.

2.1 PROJECT DATA MANAGEMENT

Centralized data management is essential to the success of an environmental project and must include cradle-to-grave sample documentation and tracking. ADAM is designed to facilitate the preparation of sample control documentation; tracking of samples from collection through disposal; acceptance of field and analytical sample data; data searching, sorting, and editing; data storage and security; transfer of data; and reporting of data.

Sample tracking is initiated in the system by creating a Chain-of-Custody (COC) record and continues via manual entry of completion dates (i.e. when samples are received by the laboratory, analytical results are received by the project, validation report is submitted to the user, samples are disposed of, etc.). A COC record is created for both internal sample sets and extant sample sets. For internal sample sets, the COC record is used to print an Analysis Request/Chain-of-Custody (ARCOC) report which is given to the sampler and executed in the field. For extant sample sets, the COC record is used to enter information off a report from another system, i.e. the laboratory's or project's, that is needed for sample tracking and QA/QC processing.

To create a COC record, ADAM begins by assigning a unique ADAM COC Number and Set Number. (For extant sample sets, the extant numbers are also carried.) ADAM Sample Numbers are assigned by adding an incrementer to the Set Number. The ADAM Set Number includes a four-character Set Group Code which is assigned by the database manager. This can be used to provide for easy recognition of sample sets and to group data for statistical calculations.

Wherever possible, all remaining information for the COC record is entered using maintenance tables (see Figure 2 and Figure 3). This includes project and laboratory addresses, SOP references, the QC level, and parameters requested. Additionally, existing container lists, sample information, or entire COCs can be used to create a new unique COC. In this manner, the database manager can set up a "template" to be used for recurring sampling events such as quarterly well monitoring.

Any field on the COC record can be left blank and a partially completed ARCOC report printed and given to the sampler as instructions. For some projects, it is helpful to pre-print Armcos for all sampling events scheduled for the week and forward them to the sampling team to direct their efforts. By creating COC's in the system for scheduled sampling events, it is also possible to develop reports showing projected laboratory analytical costs.

2.2 IMPORTING OF ANALYTICAL DATA

The common practice of manually entering analytical data into a computer database greatly increases the error and effort for a project. Importing electronic analytical data facilitates data manipulations such as statistical calculations, graphing, etc. and, most importantly, automated QA/QC data validation and review. The ADAM system includes applications of an importing software which can import virtually any electronic laboratory analysis results and QC data formats. This includes data for analyses on four different instrument types: GCMS including air volatile organic compounds (VOC), volatile, and semi-volatile organic analyses; GC including PCB, pesticide, and herbicide analyses; Metals including ICP, AA, and cold vapor analyses; and Miscellaneous Parameters including a variety of wet chemical tests.

ADAM is designed to handle either "raw" analytical data such as a GCMS quantitation report produced by the instrument data system or "calculated" analytical data such as a results report produced by the laboratory data management system, CLP software, etc. In addition to the analytical data, ADAM requires sample-to-QC sample references. This data can be imported from a laboratory report or taken from the instrument run log and extraction lab log.

All data is first imported into holding tables. If electronic analytical data is not available, these tables can be used for manual entry of the analytical data. The import routine includes procedures that verify no duplicate records exist and check data formats by applying validation expressions and/or numerical ranges. Procedures are also included that assign a Sample Type (i.e. CCAL, MS, BLANK) to each sample analysis and the ADAM Set Number and Sample Number to each extant sample analysis. Sample Types, which are used be ADAM for QA/QC processing, are defined in an ADAM system table and thus can be varied depending on a particular laboratory's naming convention. Finally, ADAM copies the data into permanent tables. Figure 4 shows an example of a GCMS quantitation report downloaded as an ASCII text file from a Finnigan data system and Figure 5 is the resultant Access table obtained from the import routine.

2.3 QA/QC DATA VALIDATION

Data validation is a process to verify that the laboratory has complied with all QC data quality requirements (QC Checks) of the specified analytical method. The QC Checks are defined in terms of data quality objectives (DQOs) which include both procedural requirements, such as calibrating the instrument each shift and numerical requirements, such as accuracy and precision control limits. ADAM performs an automated QA/QC data validation for analyses on four different instrument types: GCMS, GC, Metals, and Miscellaneous Parameters. The system includes procedures in the code and control limits in the maintenance tables for all of the QC Checks in Table 1. The coded procedures are based on the USEPA's National Functional Guidelines for Data Review The maintenance tables include control limits for the major analytical methods listed in Table 2. Updates to these methods or the addition of control limits for new or project-specific methods are easily accomplished via control limit entry screens.

ADAM performs the QA/QC data validation in two steps: QA/QC Pre-processing and QA/QC Processing. Both steps are completed for the current Set Number for each sample and parameter and at the QC Level indicated on the COC. Based on the QC Level, an ADAM system table is used to define which QC Checks are to be included and for each QC Check which type of QC Sample is required (see Figure 6).

The first step, QA/QC Pre-processing, verifies that all procedural requirements have been met by checking that all sample results, both environmental and QC, have been received from the laboratory and that maximum sample-to-QC sample ratios have not been exceeded. ADAM uses the system table mentioned above to determine which types of QC Samples are required (i.e.

MS, LCS, CCAL, etc.). If any data if found to be missing or invalid, an exception report is printed. If no data is found to be missing, the Set Number is ready for QA/QC Processing.

QA/QC Processing verifies that all numerical requirements have been met by adjusting the units of the analytical data to those specified in the control limits, calculating the necessary QC Elements (e.g. %RSD) using raw analytical data or retrieving them from calculated analytical data, and comparing each to the control limit. QA/QC processing is performed in a sub-database which includes only the imported data and the required maintenance tables. This design feature results in a fixed processing time regardless of the data stored in the system. Again, ADAM uses the system table mentioned above to determine which QC Checks are to be included. All outcomes for the QA/QC Process are printed to a QC Failure Report or the QC Summary Report (see Section 2.8) and stored for use in QA/QC Data Reduction, Flagging, and Reporting.

2.4 QA/QC DATA REDUCTION

Data Reduction is the process of performing calculations on the analytical data to obtain reported amounts that are printed on the QA/QC Reports and exported to the user. Presently, the ADAM system includes Data Reduction Steps for calculating an analysis detection limit which is the reported amount for non-detects and for combining an original and diluted analysis pair into a single set of reported amounts. Analysis detection limits are calculated using the sample correction factor and the Method Detection Limit. This step is essential if raw analytical data from a quantitation report that shows only hits is received and imported. The combination of an original and diluted analysis is performed analyte-by-analyte taking the result that is within the calibration range. Like QC Checks, Data Reduction Steps are defined in an ADAM system table based on the QC Level. Therefore, it is easy to incorporate new functions such as blank subtraction or Air front plus back tube addition as needed for project customization.

2.5 QA/QC DATA QUALIFICATION/REVIEW (FLAGGING)

Data qualification or data review, also known as data flagging, is a process to apply qualifying flags to each sample to reflect any failures found in QA/QC Data Validation according to a set of functional guidelines. QA personnel can then determine if the qualified data is suitable for the intended use. Presently, ADAM includes procedures for data flagging according to the USEPA's National Functional Guidelines for Data Review (i.e. using U,J,D,B,N,R). The procedures include flagging each sample to reflect any failure for the sample itself and any failure of a QC sample referenced to the sample. Like QC Checks and Data Reduction Steps, Data Flagging is defined in an ADAM system table making it easy to incorporate different functional guidelines for flagging as needed for project customization.

2.6 COMPLETENESS CALCULATIONS

Completeness is the yardstick of any Quality Assurance program. Completeness is defined as the percentage of samples which pass a specific QC Check. ADAM calculates completeness for all QC Checks included in the QA/QC Data Validation and prints a completeness report. The calculations are performed on a select group of samples chosen by parameter, Set Group Code, collection date, laboratory, project, client, etc. The ADAM system includes a mechanism by which QA personnel can reject data for a sample analysis with gross QC failures and thus exclude it from export to the user and completeness calculations.

2.7 LABORATORY INVOICE CHECKING

The ADAM system includes an invoice checking feature which calculates invoices using the number of samples and parameters called out on the COC, the laboratory analysis costs stored in the maintenance tables, and any applicable penalties or surcharges. Invoice subtotals and totals are calculated and a invoice report is printed for comparison to the laboratory invoice. The

calculations are performed on a select group of samples chosen by Set Number, analysis date, project, client, etc. The ADAM system includes a mechanism by which QA personnel can reject the invoice for a sample analysis with gross QC failures.

2.8 QA/QC REPORTING

ADAM can print or export a QC Summary Report that is specific for each instrument type (GCMS, GC, Metals, Miscellaneous Parameters). The report is intended as an aid to QA personnel making the suitability determination. It is printed by Set Number and includes all types of environmental and QC samples, as specified in an ADAM system table, in order of analysis. Table 3 shows an example of the GCMS QC Summary Report for an environmental sample. Custom report formats can easily be created from stored data in the ADAM system.

2.9 DATA STORAGE AND ARCHIVING

ADAM is designed to provide facilities for data storage and manipulation during the active phase of a project. Although not designed to provide trend analysis and long-term data archival, the system may be equipped with sufficient disk capacity to support these functions. Since the system stores unprocessed as well as processed (flagged) data, many useful project data summaries may be generated using Microsoft Access query and reporting tools. Due to the open database connectivity (ODBC) supported by Microsoft Access, users may also select from a growing number of third-party applications for reporting and statistical functions.

3.0 CONCLUSIONS

We have found ADAM to be an invaluable tool to support the task of determination of suitability of analytical data for its specified intended use. The design, construction, and implementation of ADAM provides a range of benefits unavailable in any other commercial software system. The major benefits of ADAM include flexibility, improved data defensibility, improved efficiency which results in lower costs, and communicability with most commercial software.

Flexibility is realized through ADAM's ability to handle virtually any analytical method, set of QC Checks (QC Level), or laboratory electronic reporting format and a user friendliness which allows easy setup of the desired protocol. Maximum data defensibility is achieved by cradle-to-grave documentation, using unprocessed laboratory data, minimizing manual data manipulation, making it practical (from the standpoint of cost) to validate and review all QC and sample data, and the resultant elimination of errors of omission prior to archiving of data. Increased efficiency and lower costs result from the significantly lower labor costs needed for automated as compared to manual data validation and review; and the accurate cost/work control which derives from the sample tracking, scheduling, and invoice checking features. ADAM provides an ideal environment for evaluation of historical data by the engineer/scientist or QA personnel through its open database connectivity. QC and sample data can be easily imported to other software for statistical calculations, graphing, trend analysis, etc.

TABLE 1

ADAM QC CHECKS

		GCMS	GC	Metals	Misc
Holding Times	Leach	x	x	x	x
	Extraction	x	x	x	x
	Analysis	x	x	x	x
	Tube (Air)	x	x		
Instrument Performance	Tune %RA	x			
	Tune Frequency	x			
	PEM Concentration		x		
	PEM RPD		x		
	PEM %Breakdown		x		
	ICS %R			x	
	ICS Frequency			x	
	Analytical Spike %R			x	
	MSA Coefficient			x	
	Serial Dilution %D			x	
Initial Calibration	Concentrations	x	x		
	%RSD / %R	x	x	x	
	RRF	x			
	RT vs. ICAL Average	x	x		
	Peak# / RT vs. Establ'd	x			
	Frequency			x	
Continuing Calibration	Concentration	x	x		
	%D / RPD / %R	x	x	x	
	RRF	x			
	RT vs. ICAL Average	x	x		
	Peak# / RT vs. Establ'd	x			
	Frequency	x	x	x	
Blanks	Contamination	x	x	x	x
	Frequency	x	x	x	x
Surrogates	Recovery	x	x		
	RT vs. ICAL Average		x		
	RT vs. CCAL	x			
	Corrective Action	x			
MS/MSDs	Spike Level	x	x	x	x
	Recovery	x	x	x	x
	RPD	x	x	x	x
	Frequency	x	x	x	x
	Corrective Action	x	x		x
Duplicates	RPD			x	x
	Absolute Difference			x	
	Frequency			x	x
Lab Control Samples	Recovery	x	x	x	
	RPD	x	x	x	
	Frequency	x	x	x	
Internal Standards	Area	x			
	RT vs. CCAL	x			
	Corrective Action	x			
Compound Identification	RT vs. ICAL Average		x		
	RT vs. CCAL	x			
Compound Quantitation	Ion	x			
	Amount	x	x		

TABLE 2

ADAM ANALYTICAL METHODS

Instrument	Analysis Type	CLP	EPA 100-400 Series	EPA 500 Series	EPA 600 Series	Standard Methods	SW-846
GCMS	AIR		*				
	VOA	x		x	x	x	x
	SVA	x		x	x	x	x
GC	PCB	x		x	x	x	x
	Pest	x		x	x	x	x
	Herb			x		x	x
METALS	AA	x	x			x	x
	CV	x	x			x	x
	ICP	x	x			x	x
MISC	BOD		x			x	
	Bromide		x			x	
	Chloride		x			x	x
	COD		x			x	
	Coliform					x	x
	Fluoride		x			x	
	Gross A					x	x
	Gross B					x	x
	NH3N		x			x	
	Nitrate		x			x	x
	Nitrite		x			x	
	Nitrate/ Nitrite		x			x	
	Odor		x			x	
	O & G		x			x	x
	Phosph		x			x	
	Radium					x	x
	Sulfide		x			x	x
	Sulfate		x			x	x
	Surfact					x	
	TDS		x			x	
	TKN		x			x	
	TOC		x			x	x
	TOX					x	x
	TPH		x			x	x
	TSS		x			x	
	Turbid		x			x	

* Method TO1 and TO2 in "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", EPA-600/4-84-041.

TABLE 3
EXAMPLE GCMS QC SUMMARY

Quality Assurance Associates
QAA, L.C.

Set Number:	WELL000003	Page:	1 of 2
Instrument Type:	GCMS	Date Printed:	5/20/95
Analysis Type:	VOA	Time Printed:	11:45
Analytical/Prep Method:	5030A/8240A	User:	TGS

	COC	Last Analyzed:	Y
		Reject Data:	N
Sample Number:	WELL000003 02	Reject Invoice:	N

Location:	P1 Out	Collection Date:	5/15/95	Lab Name:	Laboratory
Grab/Comp:	Grab	Leach Date:	NA	Lab Number:	95050124
Sample Type:	Env	Extraction Date:	NA	Instrument:	F14
Sample Matrix:	water	Analysis Date:	5/18/95	Analyst Initials:	PLS
Moisture %:	NA	Analysis Time:	09:05	Smpl Amt (ml/g)	5
Corr Factor:	1.0	Analysis Level:	NA	Ext Final Vol (ul):	NA

Sample's EBLK	NA	Sample's MS:	WELL000003 01	Sample's MSD:	WELL000003 01
Sample's CS:	NA	Sample's CSD:	NA		

Chloromethane	10	U	ug/l
Bromomethane	10	U	ug/l
Vinyl chloride	7	J	ug/l
Dichloromethane	100	JB	ug/l
Carbon Disulfide	110	J	ug/l
1,1-Dichloroethene	5	U	ug/l
trans-1,2-Dichoroethene	50	R	ug/l

TYPE	SURROGATE	AREA	RECOVERY	1st LIMIT	2nd LIMIT
Mand	d8-Toluene	80123	89	88 - 110	
Mand	4-Bromofluorobenzene	79627	90	86 - 115	
Mand	d4-1,2-Dichloroethane	55592	88	76 - 114	
Mand	MAXIMUM FAILURES ALLOWED			0	

TYPE	INTERNAL STANDARD	AREA	RECOVERY	1st LIMIT	2nd LIMIT
Mand	Bromochloromethane	200593	210	50 - 200 *	
Mand	1,4-Difluorobenzene	94952	110	50 - 200	
Mand	d5-Chlorobenzene	109008	135	50 - 200	
Mand	MAXIMUM FAILURES ALLOWED			0 *	

TYPE	INTERNAL STANDARD	RT	LIMIT
Mand	Bromochloromethane	305	300 - 330
Mand	1,4-Difluorobenzene	373	350 - 380
Mand	d5-Chlorobenzene	606	580 - 610

	ACTUAL	LIMIT		ACTUAL	LIMIT
Shift Window (hrs):	3.5	12	Analysis Hold Time (days):	3	14
Leach Hold Time (days):	NA		Extract Hold Time (days):	NA	

* QC Failure
W Waived

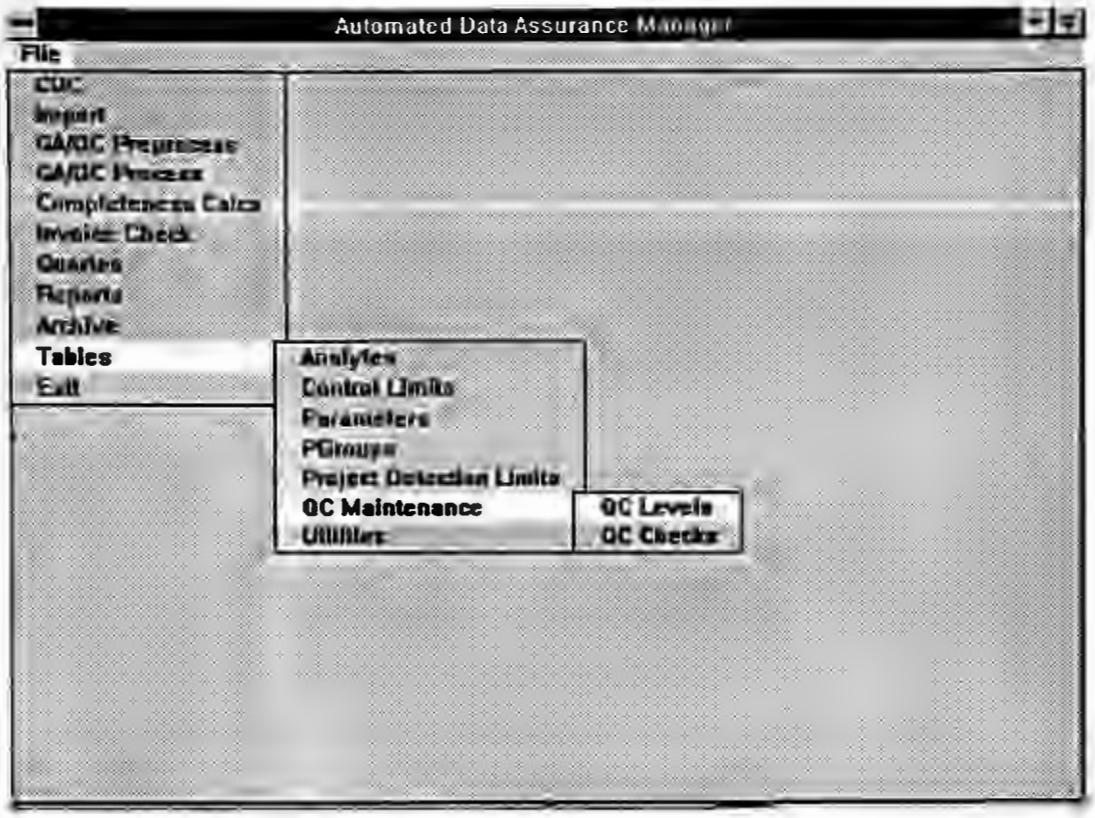
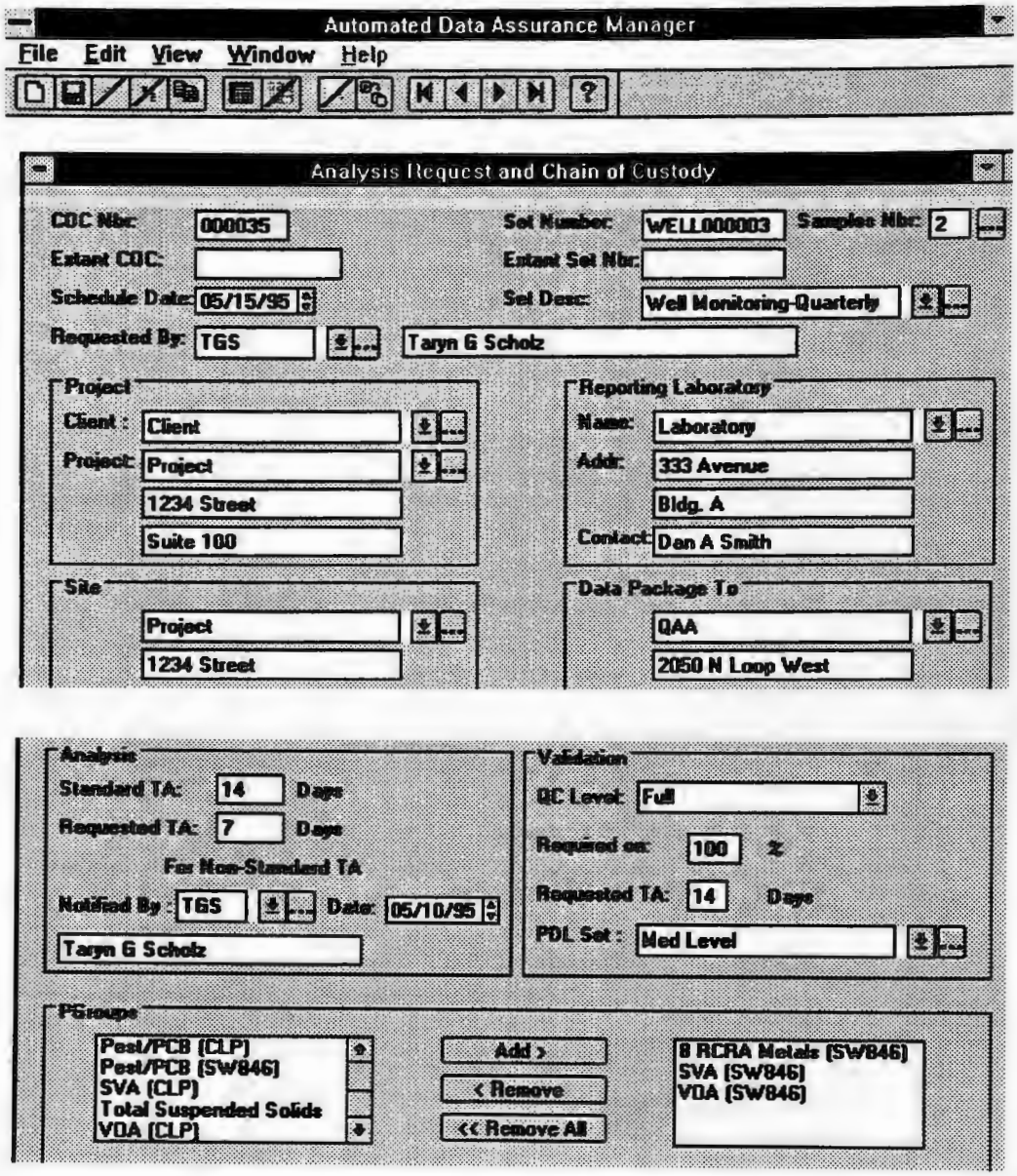


Figure 1.

ADAM Main Menu



Indicates items entered using the maintenance table

Figure 2.

Typical Entry Screens for ADAM COC

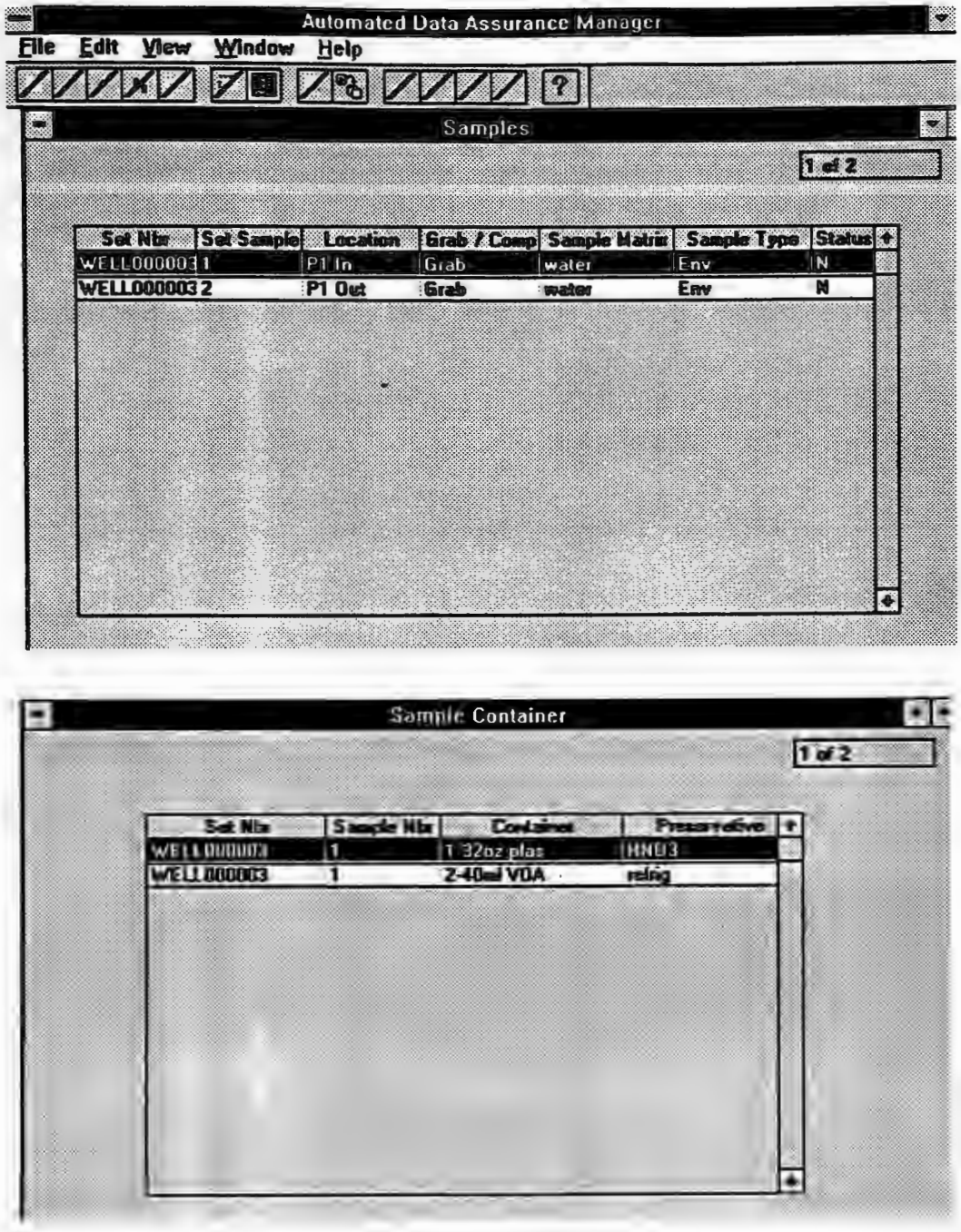


Figure 3.

Sample and Container List for ADAM COC

Quantitation Report File: H50004V01A

Data: H50004V01A.TI
03/10/95 10:47:00
Sample: H5000401
Conds.: 03/08/95
Formula: 03/04/95 Instrument: TX4020 Weight: 200.000
Submitted by: RUST REM Analyst: PDD Acct. No.: UG/L

AMOUNT=AREA * REF AMNT/(REF AREA * RESP FACT)
Resp. fac. from Library Entry

No	Name
1	CI35 PENTAFLUOROBENZENE **IS1**
2	CI10 1,4-DIFLUOROBENZENE **IS2**
3	CI20 D5-CHLOROBENZENE **IS3**
4	CI30 1,4-DICHLOROBENZENE-D4 **IS4**
5	CS15 D4-1,2-DICHLOROETHANE **SU1**
6	CS05 D8-TOLUENE **SU2**
7	CS10 P-BROMOFLUOROBENZENE **SU3**
8	C150 TRICHLOROETHENE
9	C220 TETRACHLOROETHENE

No	m/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	168	299	4:59	1	1.000	A BB	67592.	10.000 UG/L	9.98
2	114	354	5:54	2	1.000	A BB	78869.	10.000 UG/L	9.98
3	117	607	10:07	3	1.000	A BB	71253.	10.000 UG/L	9.98
4	152	836	13:56	4	1.000	A BB	34972.	10.000 UG/L	9.98
5	65	319	5:19	2	0.901	A BB	20463.	9.574 %	9.56
6	98	476	7:56	2	1.345	A BB	80312.	10.390 %	10.37
7	95	720	12:00	2	2.034	A BB	39620.	11.252 %	1.23
8	130	374	6:14	2	1.056	A BB	28387.	8.589 UG/L	8.57
9	166	531	8:51	3	0.875	A BB	81962.	20.368 UG/L	20.33

No	Ret(L)	Ratio	RRT(L)	Ratio	Amnt	Amnt(L)	R.Fac	R.Fac(L)	Ratio
1	5:17	0.94	1.000	1.00	10.00	10.00	1.000	1.000	1.00
2	6:14	0.95	1.000	1.00	10.00	10.00	1.000	1.000	1.00
3	10:24	0.97	1.000	1.00	10.00	10.00	1.000	1.000	1.00
4	14:08	0.99	1.000	1.00	10.00	10.00	1.000	1.000	1.00
5	5:39	0.94	0.906	0.99	9.57	10.00	0.259	0.271	0.96
6	8:16	0.96	1.326	1.01	10.39	10.00	1.018	0.980	1.04
7	12:15	0.98	1.965	1.03	11.25	10.00	0.502	0.446	1.13
8	6:34	0.95	1.053	1.00	8.59	10.00	0.360	0.419	0.86
9	9:10	0.97	0.881	0.99	20.37	10.00	1.150	0.565	2.04

Figure 4.

Unprocessed ASCII Results File from Finnigan GCMS.

SetNbr	SmplNbr	SmplID	SmplSuf1	SmplSuf2	LabFile	SmplTyp	SmplSTyp	AnalyTyp
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA
H50004	01	0000H5000401			H50004V01A	COC		VOA

AlytMNbr	PrepMNbr	CasNbr	CNbr	Scan	Area	Amt	Units	me	Flag	SpikeAdd	SpikeUnt
8260	8260		C135	299	67592	10	UG/L	168		""	UG/L
8260	8260		C110	354	78869	10	UG/L	114		""	UG/L
8260	8260		C120	607	71253	10	UG/L	117		""	UG/L
8260	8260		C130	836	34972	10	UG/L	152		""	UG/L
8260	8260		CS15	319	20463	9.574	%	65		""	UG/L
8260	8260		CS05	476	80312	10.39	%	98		""	UG/L
8260	8260		CS10	720	39620	11.252	%	95		""	UG/L
8260	8260		C150	374	28387	8.589	UG/L	130		""	UG/L
8260	8260		C220	531	81962	20.368	UG/L	166		""	UG/L

Figure 5.

Datasheet View of Imported Data from Microsoft Access

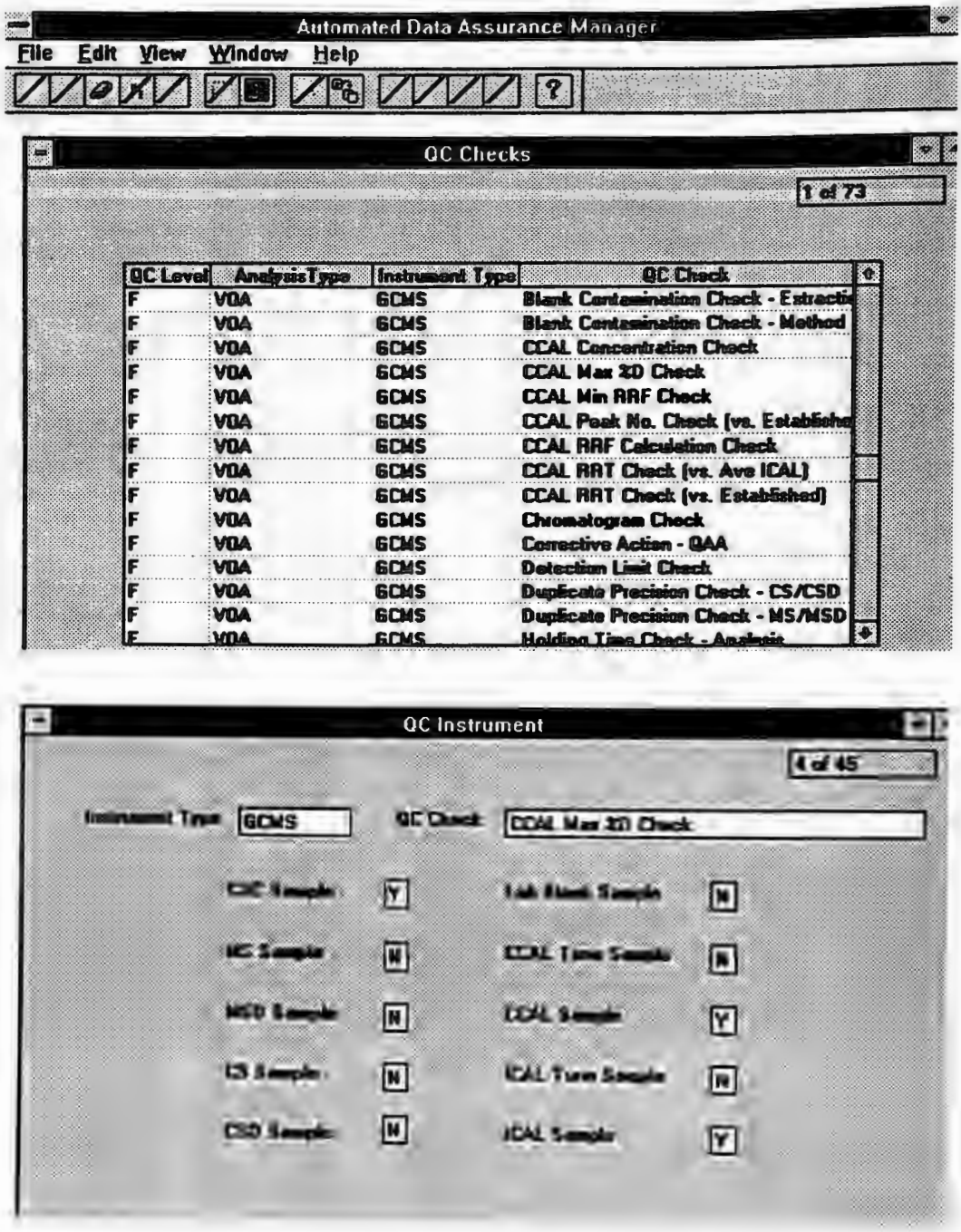


Figure 6.
Typical Entry Screens for ADAM QC Levels

THE DISKETTE DATA DILEMMA

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ABSTRACT

The growing trend in analytical data reporting includes a submittal of the data in an electronic format (on diskette). Laboratories generally feel this is a minor request; however, laboratories need to re-evaluate this process. Often discrepancies are found in the data, results submitted on hard copy **do not match** the data submitted on diskette.

Why are these discrepancies getting to the client? The stringent quality control procedures applicable to bench chemists are generally not the same, or do not exist for "computer people" generating the diskette.

The potential impact is enormous if these discrepancies are not detected. At a minimum, resampling is initiated. It is very important that the laboratory community understand the importance for accurate analytical results.

What should labs be doing to avoid this problem? Quality control procedures applicable to data reporting for bench chemist should be similar to those for computer personnel - someone needs to check their work. This final quality control check should include a comparison of hard copy results to diskette results. Laboratories should have Standard Operating Procedures (SOPs) for producing diskette deliverables; if they don't have these SOPs they should not attempt diskette reporting.

INTRODUCTION

Major decisions are made based on environmental data, therefore the quality of this data is very important. Many types of QA/QC precautions may be incorporated into a project with a Quality Assurance Project Plan (QAPP) and rigorous data validation procedures; however, if hard copy data is not check against electronically submitted data, reporting discrepancies can occur.

How can reporting discrepancies affect the data? If only rounding problems occurred on the project, the problem may be minor; however, when positive results are reported incorrectly, the analytical results may jeopardize the project. The severity of the discrepancy on the project, depends on the magnitude of error in results reported.

The purpose of this paper is to make data users aware of problems that may occur with electronic data submittal. Examples of reporting errors are given, a discussion of the benefits of data validation, the regulations associated with analytical data reporting and

possible solutions to the discrepancies found between hard copy data and data submitted electronically.

EXAMPLES

There are many different types of errors found during data reporting. Most of these errors can be detected through the data validation process. The first type and most often encountered type of reporting error is the rounding error. Reports generated from instruments and external software packages (for CLP reporting) may not be the same as the diskette deliverables generated from the Laboratory Information Management System (LIMS). An example of rounding error follows:

On a recent project, a laboratory reported results on CLP forms, on laboratory generated reports (from LIMS), and on diskette. All three reports had different quantitation limits. How did this happen? It appears that the CLP forms were generated from the instrument (GC/MS), the laboratory generated hardcopy reports were generated from LIMS and results rounded, while results submitted on diskette did not undergo rounding. Although rounding discrepancies may not be as severe as other error types, they should not be occurring. The data user should not have to decide which number is correct; this may be a time consuming task.

The second type of error is generated when an analyst changes a value that has been already reported to the client. For example, the laboratory generated hard copy reports, after these hard copy results were generated the analyst changed the results; the diskettes were then generated and results between hard copy and diskette did not match. There should be a mechanism at the laboratory to prevent analyst from changing results; results should be final before submittal to the client.

An example of the third type of error occurs during QA review. The laboratory QA officer reviewed the hard copy CLP package; results were corrected manually on the hard copy data, however, these changes were not incorporated to the electronic submittal of data. This type of problem is easily found during data validation if the reviewer is also checking electronic data. This is a crucial step during data validation and should not be over looked.

The fourth type of error occurs when an analyst makes an error by failing to report a result correctly. The fourth type of error can be detected by an experienced data reviewer. These types of errors include misidentification of compounds, wrong dilution factors, and missing peaks on the chromatogram (due to peak shape or extreme saturation).

It is seldom that projects get through the validation process without finding at least one problem with the results reported.

DATA VALIDATION

Data validation is a rigorous review of analytical data reported. During the review, the data validator reviews raw data packages and assesses the severity of quality control noncompliances and determines if data is acceptable for project use. The reviewer also determines if sample bias has been induced on reported results do to the out-of-control QC results. Qualifiers (codes) are placed on the data to make the data user aware that problems may be associated with the data.

The review is based of the following USEPA guidelines:

USEPA, February 1994. "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", Office of Solid Waste and Emergency Response. EPA-540/R-94/012.

USEPA, February 1994. "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", Office of Solid Waste and Emergency Response. EPA-540/R-94/013.

In addition, each EPA regional office may have specific standard operating procedures for validating data within their region.

The level of expertise required by the data reviewer includes five years of GC including GC/MS experience for the organic data reviewer and three years of experience with inorganic instrumentation (AA, GFAA, and ICP) for the inorganic reviewer. It is very important to have qualified reviewers who are very experienced with instrumentation and have the ability to target areas where mistakes often occur.

A thorough review will include a review of chain-of-custody documentation, a review of the raw instrument data, a check on calculations, and a check on electronic data.

REGULATIONS

At this time, environmental laboratories are regulated at the state level. Each state has its own certification program for environmental laboratories. Large laboratories who do work in many states may have to go through the certification program for each state it does analysis for. Certification programs generally entail analysis of performance evaluation (PE) samples and an audit by the regulatory agency.

The National Environmental Laboratory Accreditation Program (NELAP) has been created to provide a national set of environmental laboratory accreditation standards, if the national standards are met, individual states are to provide reciprocity. The individual states would continue to enforce accreditation; however, laboratories would only have to

analyze one set of PE samples and undergo only one audit.

The proposed NELAP can be found in the Federal Register (volume 59, No. 231). This standard thoroughly discusses the reporting of data via hardcopy; however, this standard does not specifically discuss electronic submittal of data. The NELAP discusses SOPs and says laboratories "shall maintain standard operating procedures (SOPs) that accurately reflect all phases of current laboratory activities including assessing data integrity". Such a statement would include an SOP for data reported electronically.

Other regulations which discuss laboratory practices include the regulation called "Good Laboratory Practices". This regulation governs medical laboratories (21 CFR 58), agrochemical laboratories (40 CFR 130), and laboratories performing analysis under the Toxic Substances Control Act (40 CFR 792). These current regulations also thoroughly discuss the hard copy data reporting, but do not specifically address electronic data reporting.

SOLUTIONS

The attractiveness of using electronically submitted data is the ease of statistical analysis, data searching, and reporting. However, submitting data electronically benefits only if it is submitted correctly. Data validation is a tool used to review the quality of data; however, there may be more ways to encourage laboratories to report data correctly. QAPPs, contractual agreements, and review of the laboratory SOP for electronic data submittal may be key in reducing data reporting problems.

A thorough discussion of procedures used to submit electronic data and the quality control requirements associated with the electronic submittal should be discussed in the QAPP. This should be included in chapter 9 "Data Reduction, Validation, and Reporting".

Contracts are also beneficial when communicating project requirements to the laboratory. Contracts with laboratories requiring them to submit data correctly or be penalized may be an option (contractual agreements are also very helpful in defining holding time requirements and turn-around requirements).

Another option is to review the laboratories SOP for electronic submittal and include this in a QAPP appendix. If an SOP does not exist, the laboratory should not be submitting data on electronic media.

SUMMARY

Assuming data submitted electronically is valid is a dangerous mistake. Electronically submitted data must also go through a QA review to determine if results were reported correctly. A more thorough review of electronically submitted data at the laboratory

would benefit data users.

At this time, regulations do not specifically discuss electronically submitted data. However, laboratories should have SOPs regarding electronically submitted data. Communicating specific requirements to the laboratory is critical to obtaining quality data. Including laboratory reporting requirements in QAPPs and laboratory contract may help reduce discrepancies in data reported.

REFERENCES

Garner, W.Y., M.S. Barge, and J.P. Ussary, *Good Laboratory Practice Standards: Applications for Field and Laboratory Studies.* American Chemical Society, Washington, DC, 1992.

USEPA, National Environmental Laboratory Accreditation Conference (NELAC), Federal Register, Volume 59, No. 231, December 2, 1994.

USEPA, Region V Model QA Project Plan, USEPA Region V, Chicago, Illinois, May 24, 1991.

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Development of Assessment Protocols for DOE's Integrated Performance Evaluation Program (IPEP)*

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To be presented at
The Eleventh Annual Waste Testing & Quality Assurance Symposium
Washington, DC
July 23-28, 1995

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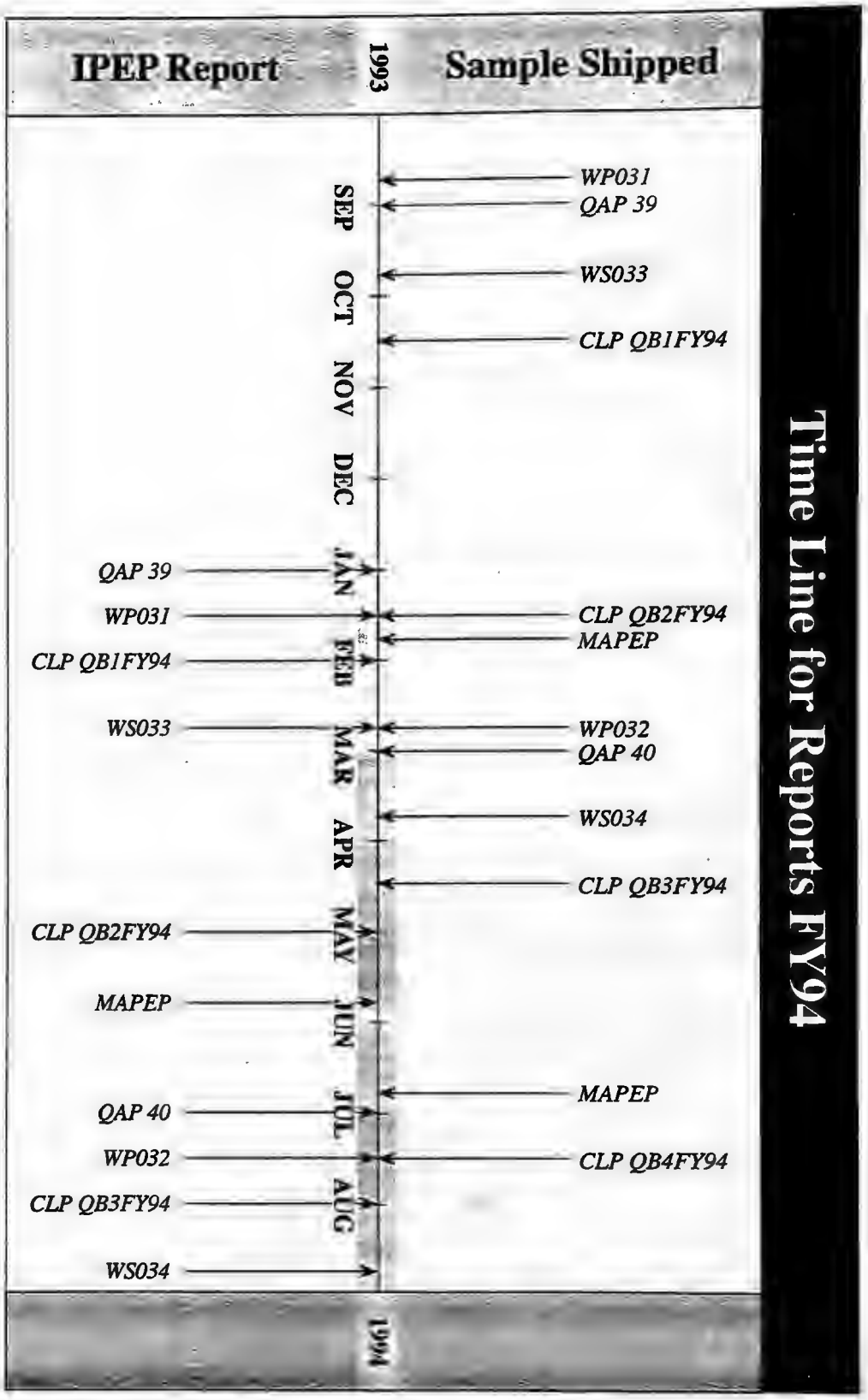
Proposed Routine IPEP Reports

Report Type	#/ Year	Audience(s)
Single Study PE Reports	16	EM-26 Laboratories
CLP Inorganic	4	DOE Offices of Sample Management
CLP Organic	4	DOE Operations Offices
WS	2	
WP	2	
EML QAP	2	
MAPEP	2	
Consolidated Reports	4	EM-26 Laboratories DOE Offices of Sample Management DOE Operations Offices
Management Reports	12	EM-26
DOE Operations Offs.	4	DOE Operations Offices
EM HQ Area Program Offs.	4	EM HQ Area Program Offices
Offices of Deputy Assistant Secretaries, EM-30, -40	4	Offices of Deputy Assistant Secretaries, EM-30, -40


Time Line for Reports FY94
IPEP Report
1993
Sample Shipped
SEP
OCT
NOV
DEC
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
1994
WP031
QAP 39
WS033
CLP QB1FY94
QAP 39
WP031
CLP QB1FY94
WS033
CLP QB2FY94
MAPEP
WP032
QAP 40
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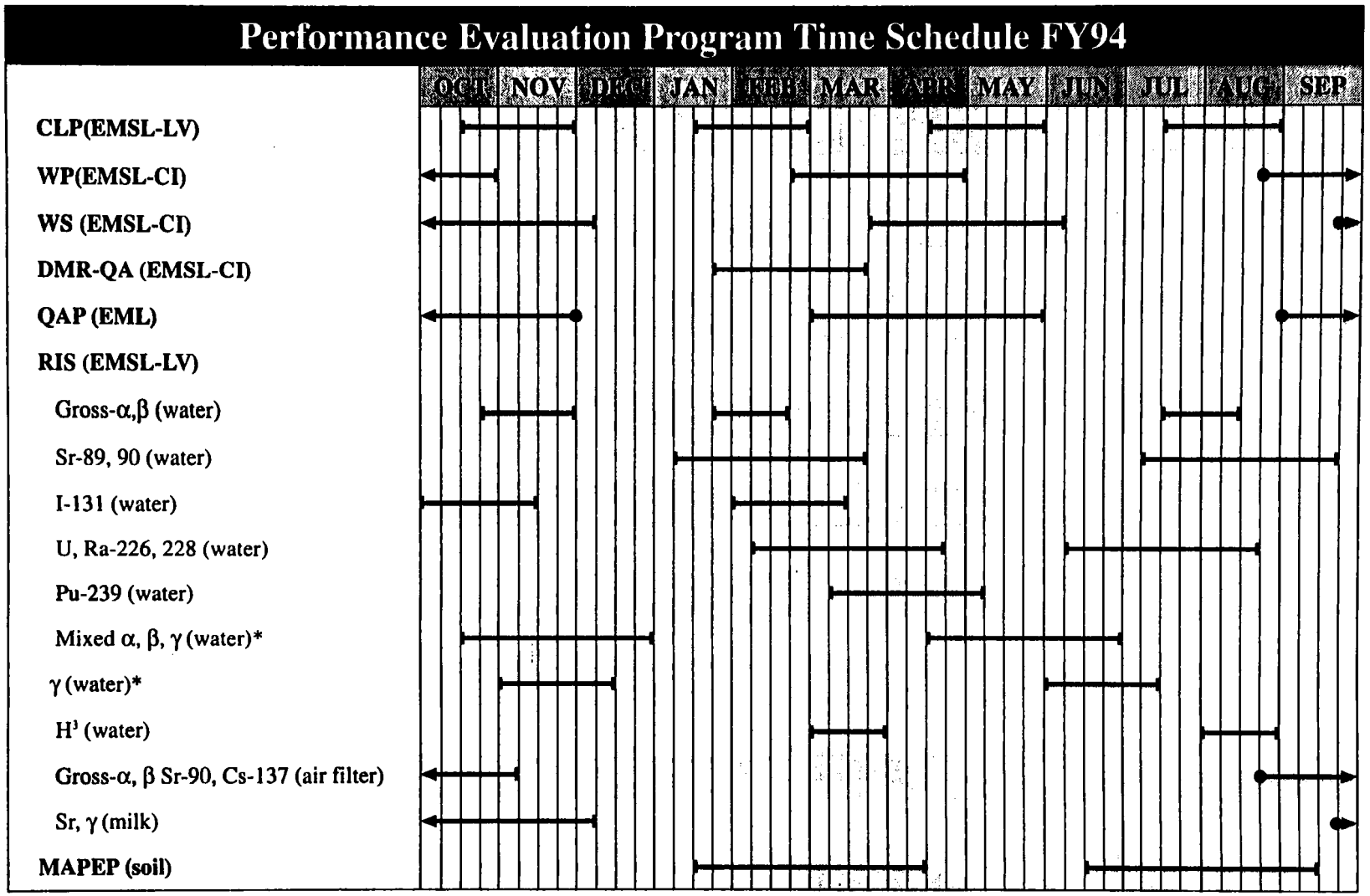
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NOV
DEC
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
CLP(EMSL-LV)
WP(EMSL-CI)
WS (EMSL-CI)
DMR-QA (EMSL-CI)
QAP (EML)
RIS (EMSL-LV)
Gross-α,β (water)
Sr-89, 90 (water)
I-131 (water)
U, Ra-226, 228 (water)
Pu-239 (water)
Mixed α, β, γ (water)*
γ (water)*
H³ (water)
Gross-α, β Sr-90, Cs-137 (air filter)
Sr, γ (milk)
MAPEP (soil)

PE Program Single Analyte Assessment Categories

IPEP	WS	WP	CLP INORGANIC	CLP ORGANIC	EML QAP	MAPEP
A (Acceptable)	**A** (Acceptable)	**A** (Acceptable)			**A** (Acceptable)	**A** (Acceptable)
W (Acceptable with Warning)		**CFE** (Check for Error)	**$** (Warning)	**(W)**[1] (Warning)	**W** (Acceptable with Warning)	**W** (Acceptable with Warning)
N (Not Acceptable)	**N** (Not Acceptable) **(U)**[2] (Unusable)	**NA** (Not Acceptable) **(U)**[2] (Unusable)	**U** (Analyzed, Not Detected) **X** (Outside Action Limits) **UX** (Element Not Identified) **#** (False Positive)	**U** (Analyzed, Not Detected) **X** (Outside Action Limits) **&** (Cmpd. Not Identified) **NS** (Required Data, Not Submitted)	**N** (Not Acceptable)	**N** (Not Acceptable)

[1] Warning limits provided by CLP, but not used in its assessment.

[2] EMSL-Ci assesses a result that is reported as a "less than" or "greater than" value as "Unusable," because it could not be quantitatively judged. However, it the true value is higher than a "less than" value, the reported result is assessed as "Not Acceptable." IPEP will assess both these situations as "Not Acceptable."

Single Study Assessment

Matrix/Analyte Class and Overall % Acceptable

Single Cell Assessment (Statistical) ----------> Qualitative Assessment (A, W, N) ----------> % Acceptable

Single Study Historical Assessment

Consolidated Report Assessments (Multiple Studies, Current and Historical Assessments)

Overall % Acceptable *or*
Matrix/Analyte *or*
Matrix/Analyte Class: _____

Total % Acceptable: _____
IPEP Assessment: _____

PE PROG/ QUARTER	CLP INORG	CLP ORG	WS	WP	EML QAP	MAPEP	% ACC	IPEP ASMT.
FY95 Q2								
FY95 Q1								
FY94 Q4								
FY94 Q3								
FY94 Q2								
FY94 Q1								
FY93 Q4								
FY93 Q3								

Single PE Program Assessments

Assessment Criterion	Current Study		3-Study History	
	Condition	IPEP Assessment	Condition	IPEP Assessment
Participation	% Participation = 100 of EM-Required Matrix/Analytes	**A:** Acceptable, No Corrective Action Recommended		
	% Participation < 100 of EM-Required Matrix/Analytes	**N:** Not Acceptable, Corrective Action Recommended - Reason for not participating, - Participation in next available study for all EM-Required Matrix/Analytes		
Overall % Acceptable	% Acceptable ≥ 90	**A:** Acceptable, No Corrective Action Recommended		
	% Acceptable < 90 ≥ 75	**W:** Acceptable with Warning, No Corrective Action Recommended*1	Overall % Acceptable < A in >1 of last 3 studies	Corrective Action Recommended for unacceptable matrix/analytes in current study
	% Acceptable < 75	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes		
Matrix/Analyte (Cell) Class*2	% Acceptable ≥ 90	**A:** Acceptable, No Corrective Action Recommended		
	% Acceptable < 90 ≥ 75	**W:** Acceptable with Warning, No Corrective Action Recommended*3	% Acceptable < A in >1 of last 3 studies	Corrective Action Recommended for unacceptable matrix/analytes in current study
	% Acceptable < 75	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes		
Single Matrix/Analyte (Cell)	Single Analyte < A	**W:** Acceptable with Warning **N:** Not Acceptable No Corrective Action Recommended	Analyte < A in >1 of last 3 studies*4	Corrective Action Recommended for unacceptable analytes
	For programs with >1 matrix per study, any analyte <A in >1 matrix	**W:** Acceptable with Warning **N:** Not Acceptable Corrective Action Recommended		

Notes:

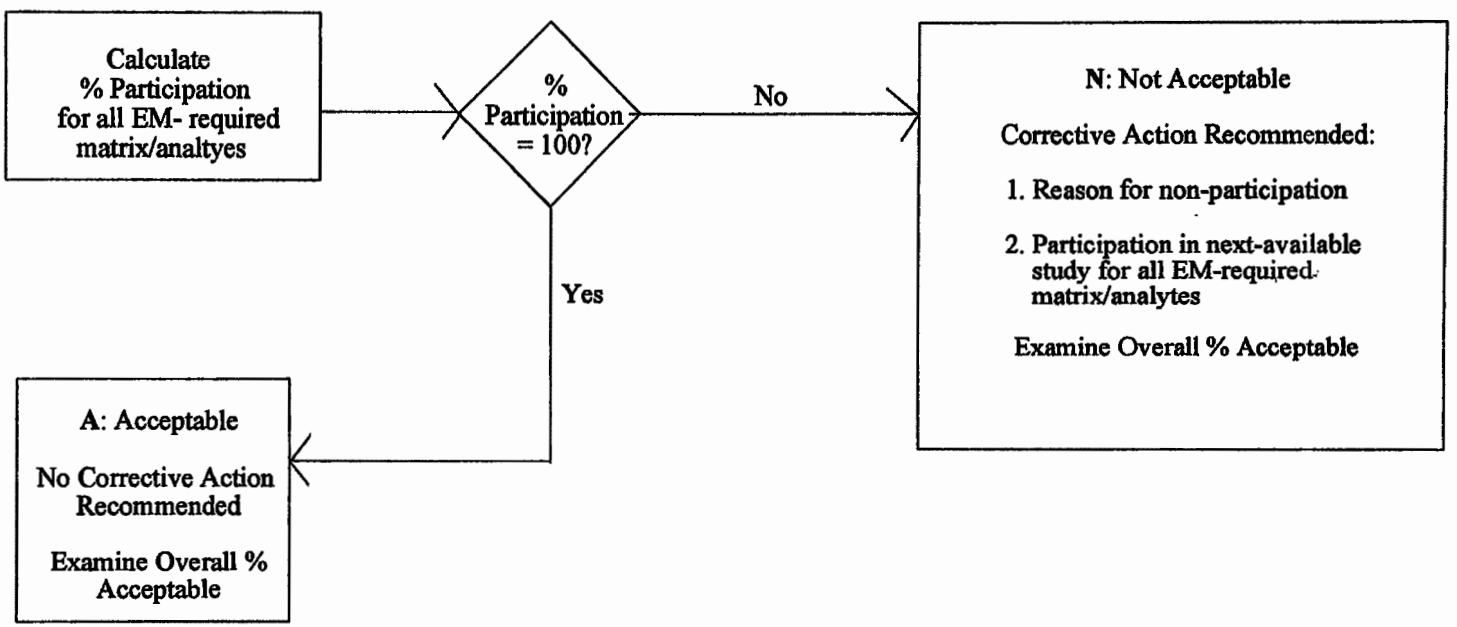
*1: If a laboratory has only participated once in a given PE program, corrective action should be performed on unacceptable analytes, to provide stricter oversight of new laboratories.

*2: If there is only one analyte in the matrix/analyte class, use the single matrix/analyte assessment as the matrix/analyte class assessment.

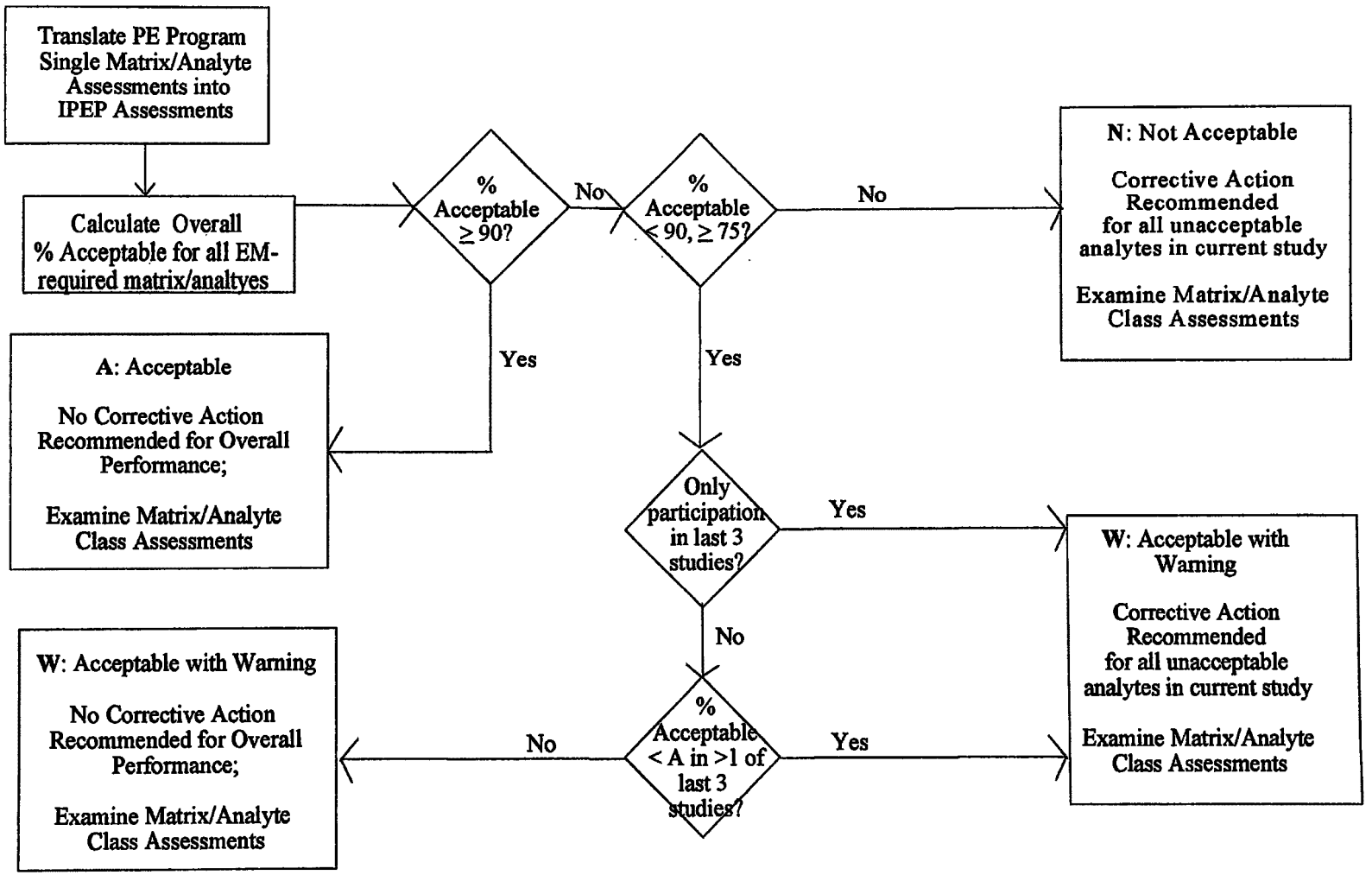
*3: If a laboratory has only participated once, corrective action should be performed on unacceptable analytes if the class assessment is < A, to provide stricter oversight of new laboratories.

*4: If a laboratory has only participated once, corrective action should be performed on unacceptable analytes if the cell assessment is < A, to provide stricter oversight of new laboratories.

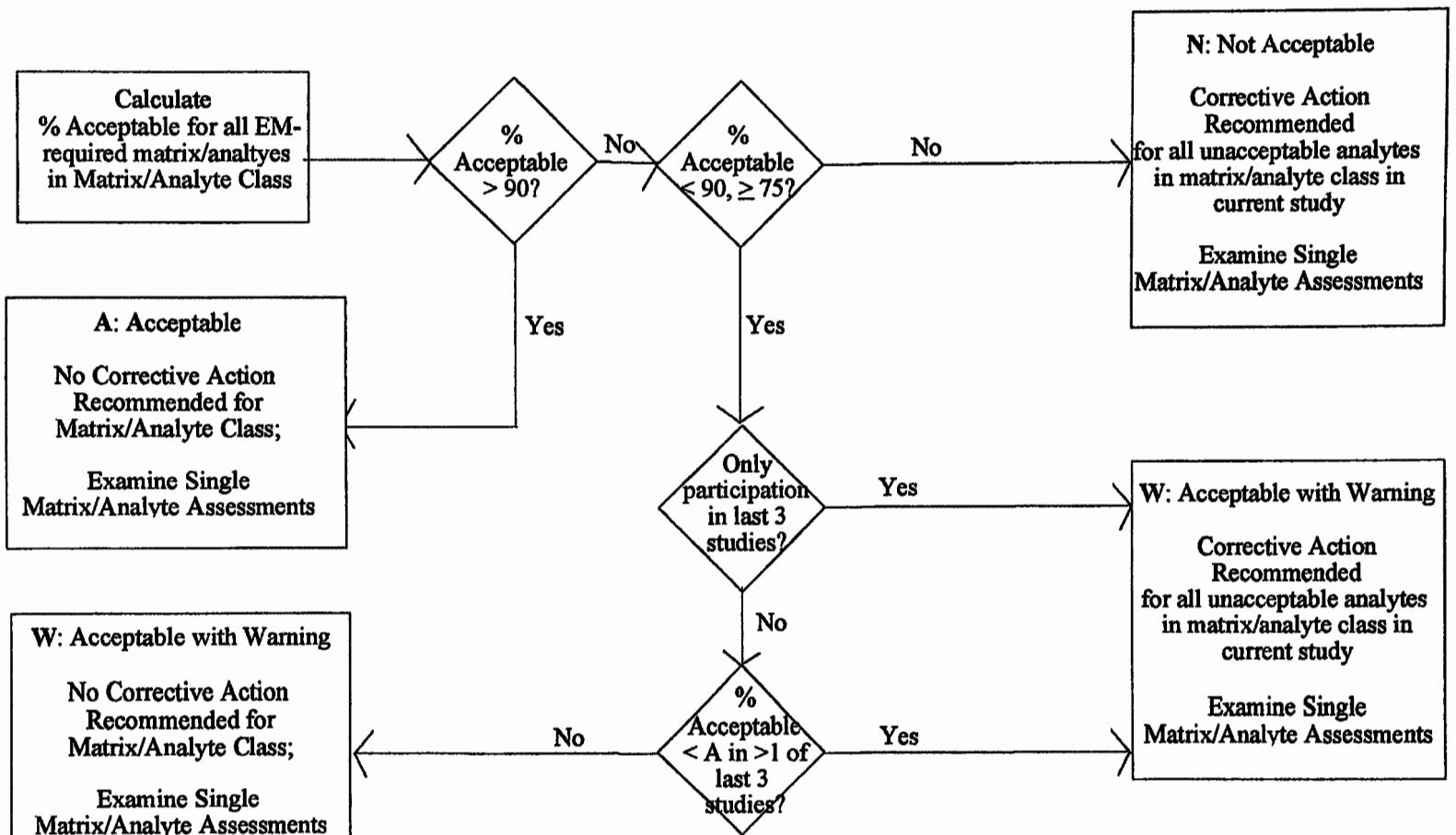
Assessment of Participation, Single PE Studies



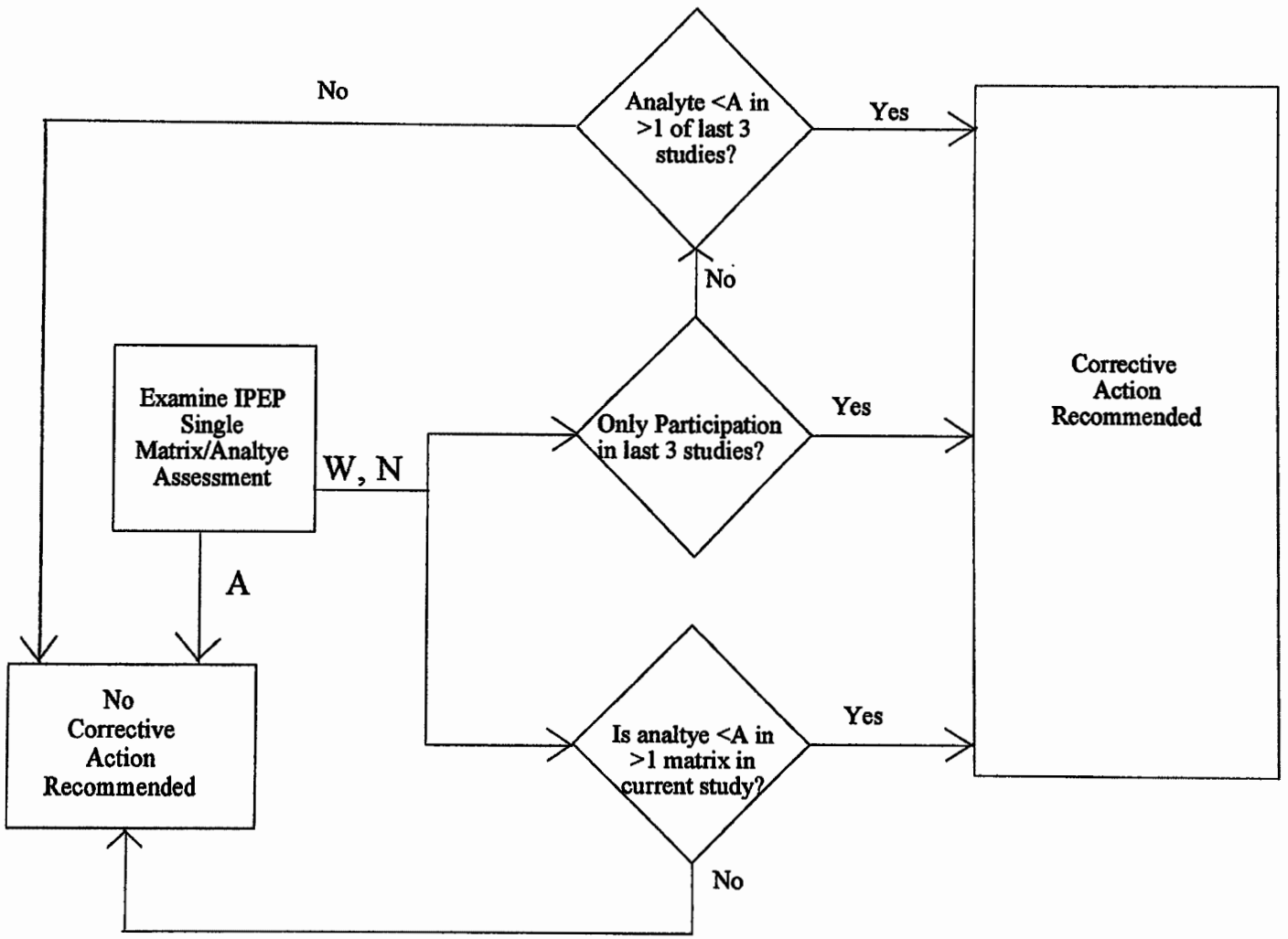
Assessment of Overall % Acceptable, Single PE Studies



Assessment of Matrix/Analyte Class, Single PE Studies



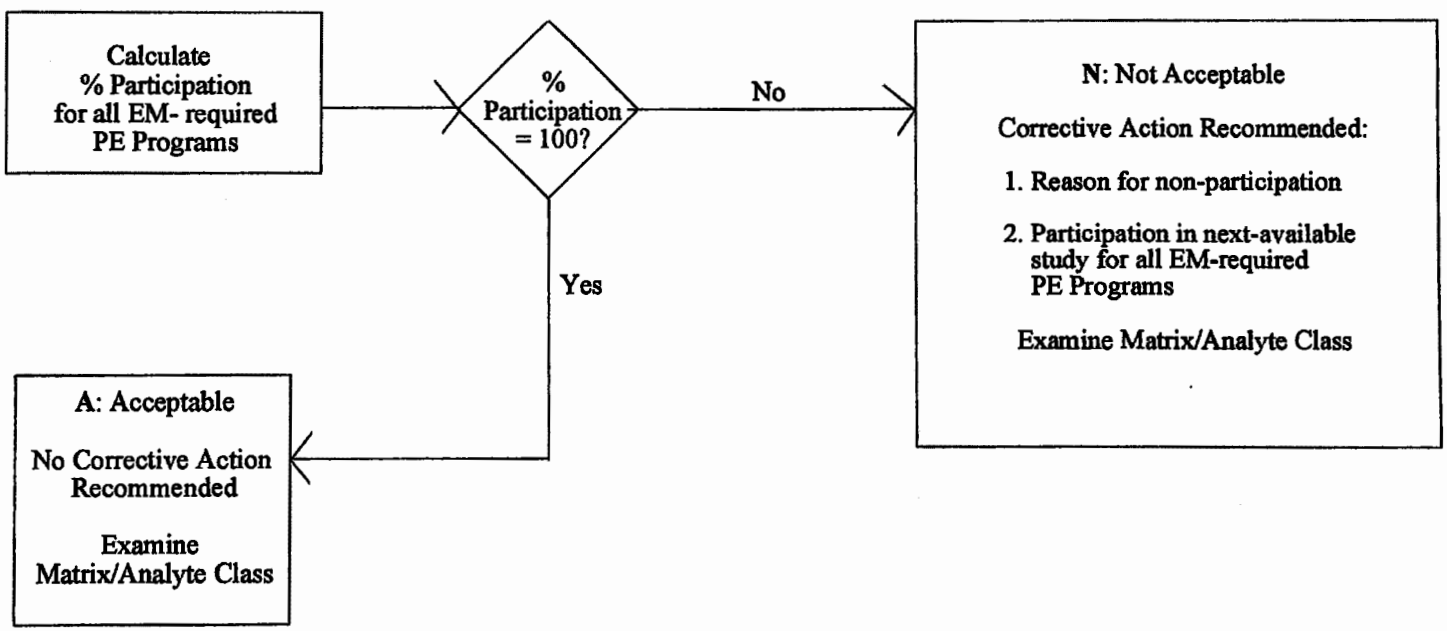
Assessment of Single Matrix/Analyte, Single PE Studies



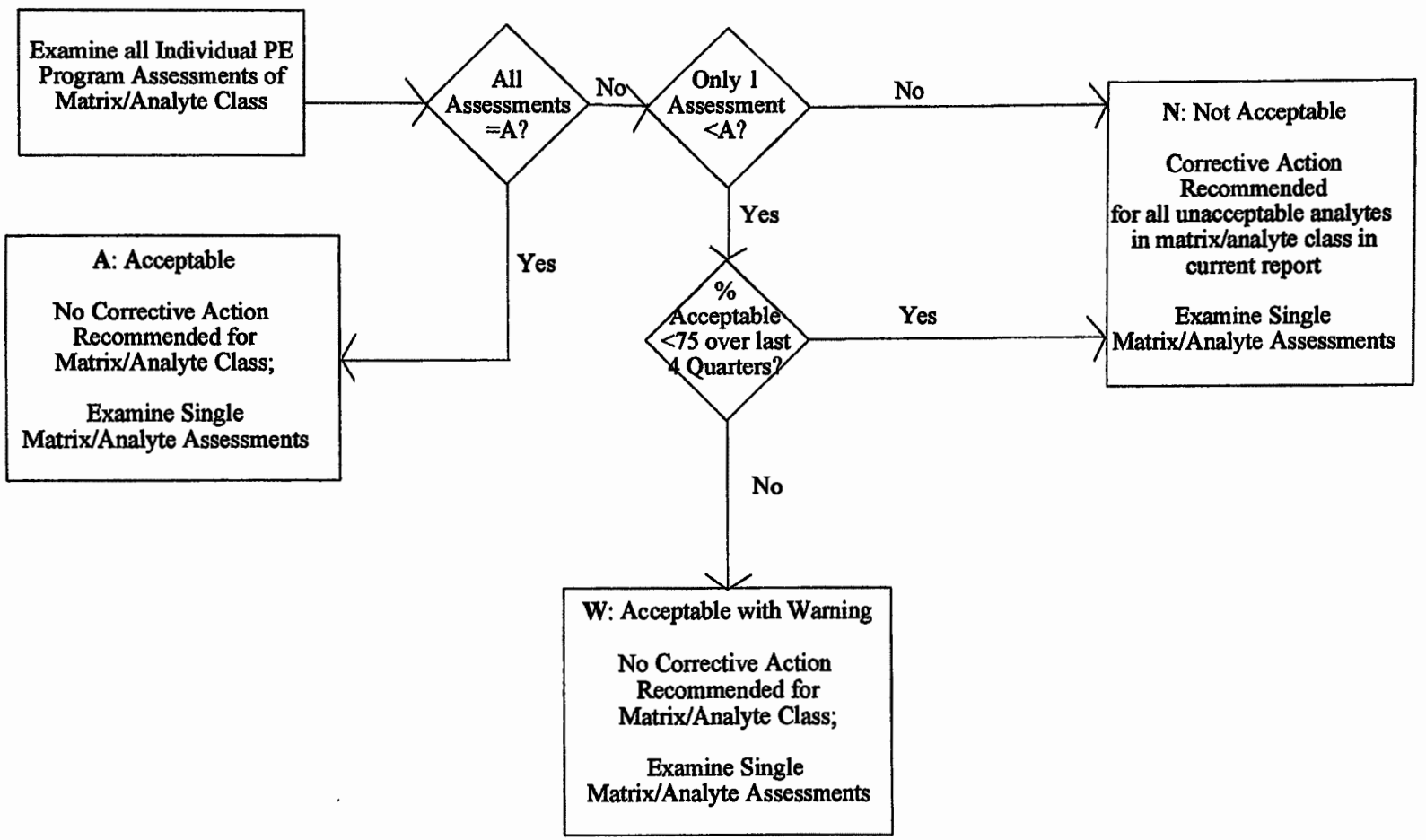
Assessments for Quarterly Consolidated Reports

Assessment Criterion	Current Study		4-Quarter History	
	Condition	IPEP Assessment	Condition	IPEP Assessment
Participation	% Participation = 100 of EM-Required PE Programs	**A:** Acceptable, No Corrective Action Recommended		
	% Participation < 100 of EM-Required PE Programs	**N:** Not Acceptable, Corrective Action Recommended - Reason for not participating, - Participation in next available study		
Matrix/Analyte (Cell) Class	All individual PE Assessments of Matrix/Analyte Class = A	**A:** Acceptable, No Corrective Action Recommended		
	1 Individual PE Assessment of Matrix/Analyte Class < A	**W:** Acceptable with Warning, No Corrective Action Recommended	% Acceptable < 75	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes
	>1 Individual PE Assessment of Matrix/Analyte Class < A	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes		
Single Matrix/Analyte (Cell)	All individual PE Assessments of Matrix/Analyte = A	**A:** Acceptable, No Corrective Action Recommended		
	1 Individual PE Assessment of Matrix/Analyte < A	**W:** Acceptable with Warning, No Corrective Action Recommended	% Acceptable < 75	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes
	>1 Individual PE Assessment of Matrix/Analyte < A	**N:** Not Acceptable Corrective Action Recommended for unacceptable matrix/analytes		

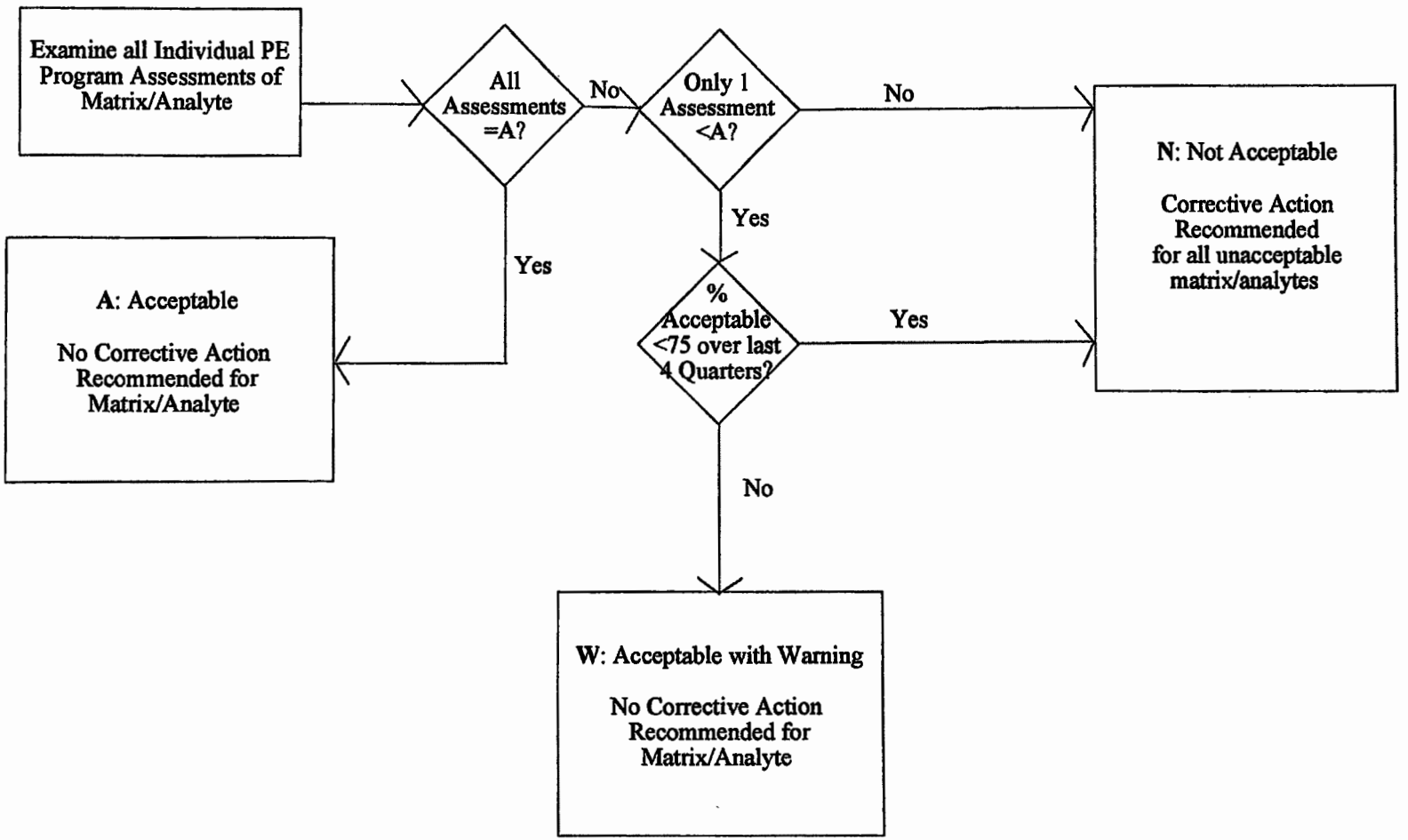
Assessment of Participation , Consolidated Reports



Assessment of Matrix/Analyte Class, Consolidated Reports



Assessment of Single Matrix/Analyte, Consolidated Reports



INTERNATIONAL AGREEMENTS IN LABORATORY ACCREDITATION

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Abstract

Internationally, there is growing pressure to provide for acceptance of test data on a worldwide basis under provisions of international and regional treaties such as the General Agreement on Tariffs and Trade (GATT), the North American Free Trade Agreement (NAFTA) and a variety of directives promulgated to establish the European Union (EU) Single Internal Market. But today's emphasis on quality has heightened awareness of the importance of good data and competent testing laboratories. Laboratory accreditation is a means to promote the acceptance of test data.

Ways that existing accreditation bodies can cooperate, through multi-lateral mutual recognition procedures, create in effect one international system, thus paving the way for worldwide acceptance of test data. Such an international laboratory accreditation system is well underway in the European Union. European nations have established the European Cooperation for Accreditation of Laboratories (EAL). The EAL approach is to create a forum for arriving at a multilateral agreement (Mutual Recognition Agreement -- MRA) among various accreditation systems. This means that appointed representatives from the laboratory accreditation systems which are members of EAL perform an assessment of an applicant laboratory accreditation system on behalf of all the systems in the agreement. If the basic requirements are met, then the accreditation is recognized by all systems party to the agreement. This model is being used as a basis for similar models in most industrial nations of the world, most recently, in the Asia Pacific area. Efforts are also being made in North America to forge a multi-lateral agreement among accrediting bodies. The private sector European Organization for Testing and Certification (EOTC) is strongly encouraging this MRA approach and has already recognized the MRA among several laboratory accreditation systems in Europe.

Introduction

The achievement of an appropriate accuracy of testing and measurement is necessary for effective quality control in industrial enterprise. To give assurance of test and measurement accuracy to the customer, it is necessary to demonstrate the capability of the laboratory. This is equally true for both domestic as well as foreign customers. To serve this purpose, many nations have laboratory accreditation systems that give industry confidence in test data through accredited services of calibration and testing. The preferred mechanism for facilitating acceptance of tests and measurements between countries appears to be the mutual recognition of national laboratory accreditation systems.

In particular, the European Union (EU) has aggressively pursued various programs to establish confidence in each country's laboratories as part of the establishment of an "internal market." Thus, the EU along with the European Organization for Testing and Certification (EOTC) and its recognition of the agreement group the European cooperation for Accreditation of Laboratories (EAL) developed a multilateral mutual recognition agreement among laboratory accreditation bodies of the EU.

The importance of test (and calibration) data in trade is increasing rapidly. Although there are many examples where test reports from countries of export have been accepted by the importer without retest, this acceptance is limited either by mutual agreement between buyer and seller or by ad hoc decisions by an importer. But 'adhocracy' is being actively discouraged by current international quality assurance standards (e.g., ISO 9000 series). Thus, the ability to sell internationally based only on reputation or salesmanship is diminishing. Unfortunately, areas where test and calibration data are not accepted internationally are growing and products are being retested in the country of import. Exporters often face a troublesome and time-consuming journey through foreign administration of testing acceptance. The delays and costs of retesting in a foreign country may even discourage the pursuit of that market.

Lack of acceptance of test data across national borders is claimed to be a very significant barrier to trade and a number of international agreements, such as the GATT Standards Code, the OECD Code of Good Laboratory Practice, and the European Union (EU) and the European Free Trade Association (EFTA) policies on testing and certification, have been developed in efforts to overcome this particular problem. If these agreements and policies are to be effective, it is essential that one can rely on tests made in other countries. No one in an importing country should accept data from an exporting country unless they are confident that these data are as reliable (or of equivalent quality) as if the instrument had been tested by a competent body in the importing country. Therefore, in order to be able to rely on foreign test results it is necessary to know, or be assured of, the competence of the laboratories providing the test data. In turn, this should provide a high degree of confidence (but not a guarantee) that the data is of the requisite quality.

Laboratory Accreditation

It is because of the difficulty as well as the growing necessity to evaluate the performance of laboratories that laboratory accreditation has developed. It is defined in ISO Guide 2 as "the formal recognition that a testing laboratory is competent to carry out specific tests or types of tests." Testing in its broadest sense includes calibration. Laboratory accreditation is usually granted:

- By an identified accreditation body to prescribed criteria;
- For specific tests or types of tests described in reference documents or otherwise defined by performance descriptors;

- After an initial on-site assessment of QA management and specific capability by qualified assessors.

Surveillance of ongoing performance by reassessment at periodic intervals and by proficiency testing or other forms of relevant auditing, is common accepted or required.

In performing accreditations of laboratories, it is recognized that they function differently from that of testing laboratories.

International Acceptance of Testing

Existing mechanisms by which test data are accepted in foreign countries are based on:

- Acceptance of foreign data without question;
- Approval of a foreign laboratory by the acceptance body or the customer of the laboratory (designated laboratories;
- Approval of a foreign laboratory through evaluation or recommendation by a third-party in either country;
- Mutual recognition agreements between laboratories; and
- Mutual recognition agreements between laboratory accreditation organizations in both countries.

Many examples of all these mechanisms are effectively in operation. But it is clear the latter offers the most universal approach to the problem. That is why the concept of laboratory accreditation has been so popular and has spread so fast in the last 15 years.

International Laboratory Accreditation Conference (ILAC)

One of the most significant factors influencing the growing acceptance of laboratories among countries, and within countries for that matter, is the existence of an informal group of laboratory accreditation system managers and interested parties known as ILAC. The first ILAC conference was held in Denmark in 1977. Since then, conferences were held in the United States, Australia, France, Czechoslovakia, Mexico, Japan, the United Kingdom, Israel, New Zealand, Italy, Canada, and Hong Kong. Future meetings are planned in Amsterdam and Sydney. ILAC has no permanent secretariat; the host acts as the secretary. There is no formal delegation procedure; interested persons from the various countries volunteer to attend and pay the modest conference fee. Conferences last one week, with reports from various task forces and committees; decisions are made by unanimous agreement on various resolutions which come out of the work of the committees and task forces.

Acceptance of the ILAC Work. In spite of this informality and the lack of a permanent secretary, ILAC has produced a number of documents which have been

adopted by other organizations to become, in effect, national as well as international standards. The International Standards Organization (ISO) has been particularly active in converting these documents to ISO Guides (see Table 1). Subjects of the guides deal with general criteria for accrediting laboratories (ISO Guide 25), requirements for the acceptance of testing laboratories (Guide 38), proficiency testing (Guide 43), guidance for operation and recognition of accrediting bodies (Guide 58). OIML has published guidelines for determining calibration intervals (International Document No. 10) based on the work of ILAC.

Table 1 - ISO/IEC GUIDES

Guide 2	General Terms and Their Definitions Concerning Standardization, Certification and Testing Laboratory Accreditation.
Guide 25	General Requirements for the Competence of Calibration and Testing Laboratories.
Guide 43	Development and Operation of Laboratory Proficiency Testing
Guide 58	Calibration and Testing Laboratory Accreditation Systems -- General Requirements for Operation and Recognition

Most if not all national systems, including the American Association for Laboratory Accreditation (A2LA) in the United States, use ISO Guide 25 as its formal criteria for accreditation.

Other international standards related to this subject are listed in Table 2.

Table 2 - INTERNATIONAL STANDARDS

ISO STANDARDS

8402	Quality -- Vocabulary.
9000	Quality Management and Quality Assurance Standards -- Guidelines for Selection and Use.
9001	Quality Systems -- Model for Quality Assurance in Design/Development, Production, Installation and Servicing.
9002	Quality Systems -- Model for Quality Assurance in Production, Installation and Servicing
9003	Quality Systems -- Model for Quality Assurance in Final Inspection and Test
9004	Quality Management and Quality System Elements -- Guidelines
10011	Generic Guidelines for Auditing Quality Systems

ILAC Committees. ILAC has four Committees to carry out its work. Table 3 lists the current work of the first three ILAC Committees. Committee 4 is the administrative committee for the conference.

Table 3 - ILAC WORK ITEMS

Committee 1. Commercial applications

Costs of Mutual Recognition Agreements and the efficiency of the process
Acceptance of test data on basis of Guide 25 or ISO 9000 for laboratories
Seminar on Guide 25 or ISO 9000 for laboratories
Uncertainty, repeatability, reproducibility
Advantages of laboratory accreditation for insurance industry
Competition in laboratory accreditation
Abuses of accredited status by laboratories
Promotion of Mutual Recognition Agreements
Legal implications of agreements on acceptance of test reports
Effectiveness of MRAs in dealing with technical barriers to trade
Agreements between laboratory accreditation bodies and certification bodies.
ILAC Handbook and Directory
Assist in Realizations of GATT Agreements
Liaison with International Trade Related Organizations
Liability in Testing
Testing, Quality Assurance, Certification and Accreditation
Guidelines on Cross-national Accreditation of Laboratories
Role of Testing and Laboratory Accreditation in International Trade

Committee 2. Laboratory Accreditation Practices

Surveillance and Reassessment of Accredited Laboratories
Assessor Qualifications and Competence
Traceability of Measurements
Measurement Uncertainty in Testing
Accreditation of Multidisciplinary Laboratories
Accreditation of Non-routine Work
Harmonization of the Rules relating to Logos
Relationship between Testing, Inspection and Product Certification

Committee 3. Laboratory Practices

Demonstration of traceability of measurements
Selection and use of reference materials
Validation and verification of test methods
Determination of uncertainties associated with test results
Test data processing and presentation: connection with declaration of compliance
Follow-up of the revision of ISO/IEC Guide 43
Follow-up of the revision of ISO/IEC Guide 25
Quality Assurance in relation with use of automated test equipment and
Implementation of laboratory information systems
Guidance for the preparation of a quality manual

ISO and IEC

The references to the International Organization for Standardization (ISO) Guides in Table 1 really should include the International Electrotechnical Commission (IEC) as well, since the IEC has taken formal action to comment on and approve these Guides. But most of the committee work has been performed by ISO CASCO, the ISO Conformity Assessment Standards Committee. CASCO has been responsible for many new ISO/IEC Guides dealing with product certification. Most of its work related to laboratory accreditation is based on the material supplied by ILAC, starting with Guide 25.

ISO has published the ISO 9000 series of standards to establish the basic requirements for generic quality management programs in the manufacturing industries. ISO 9000 provides guidelines for selection and use of quality management and quality assurance standards. ISO 9001, 9002, and 9003 are models representing three distinct forms of functional or organizational capability suitable for purchaser-supplier contractual purposes. ISO 9004 consists of a fuller description of each of the quality system elements.

The ISO 9000 series have been adopted by virtually all of the industrialized nations as their own national standards on this subject. The ISO 9000 series is having a significant effect on the revision to the laboratory accreditation criteria (ISO Guide 25).

Commission of the European Union (EC)

The European Commission (EC) has implemented various programs in its effort to achieve a "single internal market." Many of these programs involve standards-related issues and any firm doing business in Europe must keep aware of the effect of these programs and must be ready to take action to ensure equitable access to markets. The advantage of these programs is that a single internal market will be created instead of the many separate markets corresponding to the number of countries making up the European Union. The disadvantage is that the EU may implement trade restrictive policies.

In 1985, the EU decided against detailed standards for everything in favor of only regulations containing "core requirements". In the absence of EU-wide standards or directives, member states may use their own national standards. Products in compliance with these national standards would have uninhibited entry into other member countries. The EU has basically adopted the ISO/IEC Guides 2, 25, 43, and 58 as well as the ILAC work for its standards in laboratory accreditation.

Bilateral and Multilateral Agreements

The first set of bilateral agreements were signed between European bodies as well as between NATA Australia and TELARC New Zealand in the 1970's. Several more bilateral agreements emerged in the 1980's. Recognizing the substantial cost of maintaining several bilateral agreements, the accreditation community has recognized the need for multilateral arrangements, led by European systems. Table 4 lists national laboratory accreditation systems and the number of other countries systems for which they have mutual recognition.

Table 4 - LIST OF NATIONAL LABORATORY ACCREDITATION SYSTEMS

Country	System	Year Established	Number of Mutual Recognition Agreements
Australia	NATA	1946	5
Austria	OKD	1983	
Canada	SCC/PALCAN	1981	2
P.R. China	SBTS	1984	
F.R. Germany	DKD	1977	12
Finland	MSF	1980	
France	COFRAC	1969	12
Hong Kong	HOKLAS	1985	1
Hungary	MSZH	1985	5
India	NCTCF	1988	
Italy	SINALP	1977	12
Netherlands	STERLAB	1975	1
New Zealand	TELARC	1973	5
Norway	NOLA	1988	
Poland	NLMS		
Portugal	IPQ	1986	
Saudi Arabia	SASO	1987	2
Singapore	SINGLAS	1986	
South Africa	CSIR/NCS	1987	1
Spain	RELE	1986	12
Sweden	MPR	1972	12
Switzerland	SAS	1988	12
Turkey	TSE	1987	
U.K	NAMAS	1966	12
U.S.A	A2LA	1978	4
U.S.A	NVLAP	1976	3

EAL

National laboratory accreditation services have been developed mainly in Europe as early as 1966 as a tool for the efficient dissemination of standards and the confirmation of traceability of measurements to national standards. To avoid barriers to trade relating to calibration and test certificates, the laboratory accreditation systems of Western European countries are cooperating within what's called the European cooperation for Accreditation of Laboratories (EAL). EAL has set up an on-going program of technical cooperation aimed at establishing mutual confidence among systems, leading to formal declarations (multilateral agreements or MLAs) of the technical equivalence of accredited laboratories and their data. Thus the acceptance of data is being made possible through EAL. This mechanism has the potential to restrict the flow of data unless the data are generated by a laboratory accredited by one of the EAL MLA members or recognized outside bodies.

APLAC

Another multilateral arrangement is emerging in the Asia Pacific region. A formal Memorandum of Understanding (MOU), designed to reduce technical barriers to trade, was signed by laboratory accreditation bodies from 16 Asia Pacific countries, on April 4, 1995 in Jakarta, Indonesia. A total of 20 accreditation bodies signed the agreement.

The Asia Pacific Laboratory Accreditation Cooperation (APLAC) has met informally for six meetings over the past three years. At its seventh meeting on April 4, 1995, Mr. John Gilmour, Chief Executive of the National Association of Testing Authorities (NATA) in Australia, was elected Chairman. The Board of Management will consist of the chairman and members from five other countries: Hong Kong, New Zealand, Singapore, People's Republic of China, and the United States.

John Locke, President of the American Association for Laboratory Accreditation (A2LA) was named chairman of the first standing committee approved, the Mutual Recognition Agreement (MRA) Committee. The Management Board will organize additional committees for proficiency testing, the APLAC New Notes, training, the bibliography, etc., as deemed appropriate.

Full APLAC members are:

AUSTRALIA: National Association of Testing Authorities, NATA;
BRUNEI DARUSSALAM: Ministry of Development, Construction Planning and Research Unit;
CHINESE TAIPEI: Chinese National Laboratory Accreditation, CNLA;
HONG KONG: Hong Kong Laboratory Accreditation Scheme, HOKLAS;
INDIA: (National Accreditation Board for Testing & Calibration Laboratories, NABL);
INDONESIA: National Accreditation Body of Indonesia, KAN;
JAPAN: Standards Department, AIST;
Japan Calibration Service System, JCSS;
KOREA: Korean Laboratory Accreditation Scheme, KOLAS;
MALAYSIA: Laboratory Accreditation Scheme of Malaysia, SAMM, Accreditation Council, MAC, SIRIM;
NEW ZEALAND; Telarc New Zealand;
PAPUA NEW GUINEA: National Institute of Standards and Industrial Technology;
PEOPLE'S REPUBLIC OF CHINA: China National Accreditation Committee for Laboratories, CNACL
Chinese Import Export Commodity Inspection Bureau, SACI;
SINGAPORE: Singapore Laboratory Accreditation Scheme, SINGLAS;
THAILAND: Thai Laboratory Accreditation Scheme, TLAS, Industrial Standards Institute;
UNITED STATES OF AMERICAN: American Association for Laboratory Accreditation, A2LA
National Voluntary Laboratory Accreditation Program, NVLAP (at NIST)
ICBO (International Conference of Building Officials) Evaluation Service; and
VIETNAM: Directorate for Standards and Quality, DSQ.

The MOU states: "Laboratory testing is recognized as an important element in acceptance of products, and the lack of acceptance of test data accompanying traded goods has long been one of the major technical barriers to trade. APLAC's main objective is to establish a regional network in which products tested in one country need not be retested in the importing country, thereby reducing both costs and delays in shipment of the product."

By signing the MOU, laboratory accreditation bodies in the Asia Pacific Area have expressed a desire to cooperate to generally improve standards of testing and calibration in the economies of the region and to enhance the freer trade objectives promoted by the Asia Pacific Economic Cooperation (APEC).

MUTUAL RECOGNITION AGREEMENT PROCESS

The International Laboratory Accreditation Conference (ILAC) developed a document entitled, "Guidelines for Establishment and review of Mutual Recognition Agreements" in 1994. This document will serve as the reference document for establishing a mutual recognition agreement among accreditation bodies in the area. This document is similar in content and material to the agreement established by the European cooperation for the Accreditation of Laboratories (EAL) and now in place with 12 of the 18 member countries in the European Union recognizing each other's accredited laboratories.

The Guidelines deal with the major steps in assessing accreditation bodies:

- criteria for mutual recognition (ISO/IEC Guide 43 and 58 for the accreditation bodies, Guide 25 for the laboratories);
- the contents of a quality manual needed by the body seeking recognition
- procedures for preparing for evaluations, including the selection of the evaluation team members;
- conduct of the evaluations (both of the applicant system and representative laboratories being assessed by that system);
- the procedures for completing the agreement (including handling of discrepancies found); and
- procedure for maintaining and monitoring the agreement.

The MRA Committee will consider these guidelines and recommend adoption of a final set of guides by all members of APLAC.

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INTERNATIONAL ACTIVITIES IN REFERENCE MATERIAL CERTIFICATION

Peter S. Unger
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ABSTRACT

Interest in developing reliable reference materials for analytical measurements is growing worldwide. Serious discussions, both nationally and internationally, are underway on the need for third-party assessment of reference materials producers and the certification of their reference materials. Programs have evolved in the United States and other countries such as China.

Established in 1975, the ISO Council Committee on reference materials (REMCO) has developed guidance for definitions, categories, and levels of classification of reference materials. Similarly, the ISO Council Committee on conformity assessment (CASCO) has developed guidance for conformity assessment tools including laboratory accreditation, quality system registration (or certification) and product certification. More recently, the Cooperation for International Traceability of Analytical Chemistry (CITAC) has emerged to deal specifically with the issue of reliable reference materials so that measurements across international boundaries are comparable. The documents that these three bodies have published as well as what else is being developed or needed for certification of reference materials will be discussed.

AUTHOR'S BIOGRAPHICAL SKETCH

Peter Unger is Vice President of the American Association for Laboratory Accreditation (A2LA). Previously, he served as Associate Manager of Laboratory Accreditation at the National Bureau of Standards (now the National Institute of Standards and Technology). He has been involved with laboratory accreditation on the national level since 1978.

Mr. Unger is currently Chairman of ASTM E-36 on Laboratory Accreditation and Vice Chairman, Quality Provisions, of ASTM E-11 on Quality and Statistics.

Mr. Unger has a BS degree in systems engineering from Princeton University and a masters in environmental management from George Washington University. He is a certified lead auditor under both the RAB's ISO 9000 auditor certification program and the U.K. IQA Institute for the Registration of Certificated Assessors.

AUTOMATED SAMPLING PLAN PREPARATION: QASPER, VERSION 4.1

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ABSTRACT

The Quality Assurance Sampling Plan for Environmental Response (QASPER) software facilitates the preparation of sampling plans by prompting users, through an automated process, to consider elements which should be addressed in comprehensive QA/QC Sampling Plans for environmental response actions. The software compiles user-selected, technical text and user-provided, site-specific information into a QA/QC Sampling Plan which can be implemented to generate reliable, accurate data of known quality that will meet its intended use. More specifically, QASPER allows the user to document general site background information and data use objectives. QASPER then focuses on specific remedial units (or sampling areas) by prompting the user to define the sampling design, sampling requirements, and analytical requirements for each unit. Other elements to be identified are standard operating procedures, quality assurance and data validation protocols, deliverable formats, personnel responsibilities, and the project schedule.

QASPER, Version 4.1 is consistent with Superfund Accelerated Cleanup Model (SACM) initiatives as well as current U.S. EPA documents such as the *Data Quality Objectives Process for Superfund* (OSWER 9355.9-01) and the Removal Program representative sampling guidance documents.

U.S. EPA On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) are currently the primary users of QASPER. The software is very flexible and would prove beneficial to other regulatory, academic, and scientific organizations and their contractors.

INTRODUCTION

QASPER was developed to assist the site Project Manager in developing a timely sampling plan which includes many critical elements. Users are prompted by the program to consider elements necessary to generate a comprehensive QA/QC Sampling Plan which is consistent with current U.S. EPA guidance. QASPER creates a database of user-selected, technical text and user-provided, site-specific information which is used to generate a QA/QC Sampling Plan ready for review, approval, and implementation.

This paper will describe the Superfund data categories, define the essential components of QA/QC Sampling Plans, and describe the features of the QASPER software.

SUPERFUND DATA CATEGORIES

The Superfund program has developed the following two descriptive data categories:

- Screening data
- Definitive data

Minimum QA/QC requirements are associated with each category and a variety of analytical methods may be used to generate either type of data.

QA/QC Sampling Plans created within QASPER are developed around these two equally-important categories; therefore, a brief definition of each category follows. Screening and definitive data categories are described in greater detail in the *Data Quality Objectives Process for Superfund* (OSWER 9355.9-01).

Screening Data - These data are generated by rapid, less precise methods of analysis (e.g., field portable X-ray fluorescence, portable gas chromatography, immunoassay) with simple or minimal sample preparation steps. For example, sample preparation may be a simple procedure such as dilution with a solvent rather than an elaborate extraction/digestion and cleanup. The resulting data provide analyte identification and quantification, although the quantification may be imprecise. At least 10% of the screening data must be confirmed using more rigorous QA/QC procedures and criteria associated with definitive data.

Definitive Data - These data are generated using more exact or precise analytical methods, such as gas chromatography/mass spectroscopy or atomic absorption. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce tangible raw data (i.e., chromatograms, spectra, digital values) in the form of paper printouts or electronic files. For data to be definitive, either analytical or total measurement error must be determined.

QA/QC SAMPLING PLAN ESSENTIAL COMPONENTS

Comprehensive QA/QC Sampling Plans should include the following elements: background, data use objectives, sampling design, sampling and analytical methodologies, QA requirements, and project organization.

Background - a description of how the site was used or the cause of the contamination. This will help in choosing sampling locations, target compounds, and analytical methods. Sources of this information could include local, state, and federal files; representatives of various agencies; and previous response action reports.

Data Use Objectives - statements of the intended use of the data, questions that must be answered, or decisions that will be made based on the collected data. Examples of data use objectives are: determining the presence of contamination, determining the extent of contamination, identifying threats to humans or the environment, and verifying cleanup.

Sampling Design - discussion of the matrices to be sampled and the compounds for which they will be sampled, the sampling strategy to be implemented, a description of sampling locations and the numbers of environmental and QC samples to be collected.

Sampling and Analytical Methodologies - a description of sample handling requirements, the sampling equipment to be used, and analytical requirements. In addition, the standard operating procedures (SOPs) to be employed for sampling, sample documentation, and sample transportation should be described.

QA Requirements - a detailed description of the appropriate data quality indicators and QA/QC protocols. Data quality indicators are quantitative statistics and qualitative descriptors that are used to interpret the degree of acceptability or utility of data to the user. The principal data quality indicators are bias, precision, accuracy, comparability, completeness, and representativeness.

Project Organization - a list of personnel responsible for conducting the investigation and the laboratories responsible for analyzing the samples should be provided.

QA/QC Sampling Plans prepared using the QASPER software include all of these components.

QASPER QA/QC SAMPLING PLANS

QA/QC Sampling Plans created within QASPER include a title page and 11 sections which are based on the requirements of two documents: *Data Quality Objectives Process for Superfund* (OSWER 9355.9-01) and the *Removal Program QA/QC Guidance on Sampling QA/QC Plan and Data Validation Procedures* (OSWER 9360.4-01).

QASPER has a database of standard technical text which is utilized in an electronic "cut and paste" process with user-provided, site-specific information to create a QA/QC Sampling Plan. This allows the user to focus on critical information while the software handles the presentation and correlation of that information with data in other sections.

This process will be illustrated by "walking-through" QASPER. It is recommended that users progress in a sequential manner since the database builds on previously provided information. It is possible to skip sections or avoid input requirements, especially when information is not yet known, but it may not be possible to complete certain sections

(i.e., 3.0, 4.0, 6.0, and 7.0) without providing information in preceding sections (i.e., 1.0 and 2.0). Figure 1 depicts the menu of QASPER sections.

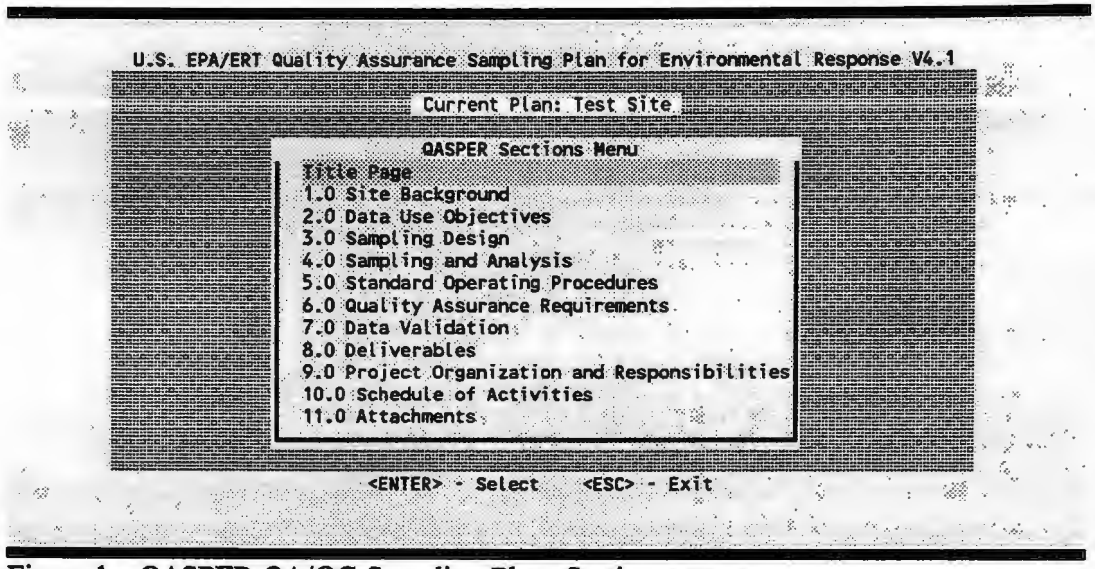

Figure 1. QASPER QA/QC Sampling Plans Sections

Title Page - This section includes basic information such as the site name, various identifying numbers, and the names and affiliations of key personnel associated with the site. Some of this information will be utilized elsewhere within the completed plan. If the user chooses not to enter the requested information, the completed plan will be assembled without the information. To add information that is not requested by QASPER, the user may edit the plan using a word processing program.

Section 1.0, Site Background - In this section, information about the site is entered, including: location and size of the site; information about the surrounding environment; status of current site activity; general types of materials that may be present; remedial units (sampling areas); specific contaminants of concern and their volumes; cause of the contamination; potential migration pathways, exposure routes, and receptors; constraints that may hinder sampling; additional information about the site; source of the information; and current stage/phase of the project.

Section 2.0, Data Use Objectives - Here the user specifies the organizational program area within which they are working and the objective(s) of the sampling event. QASPER then identifies the data category (screening or definitive) that is applicable to the project. If QASPER indicates a data category of screening (S), the user is able to upgrade it to definitive (D) by following the instructions on the screen, as shown in Figure 2. In some cases, either type of data may be collected so the user is requested to specify the category. In addition, the user specifies acceptable limits for making decision errors.

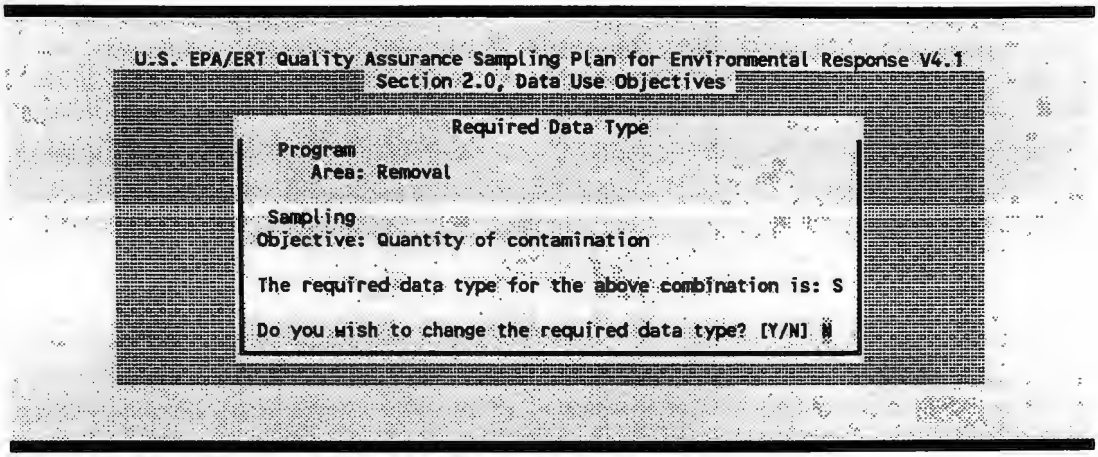

Figure 2. Data Category Upgrade Mechanism

Section 3.0, Sampling Design - In this section, for each remedial unit and its associated program area/sampling objective, the user specifies the matrix to be sampled and the parameters for which the samples will be analyzed. Users also specify the sampling approach, and the locations and numbers of samples to be collected, including background and QA/QC samples as shown in Figure 3.

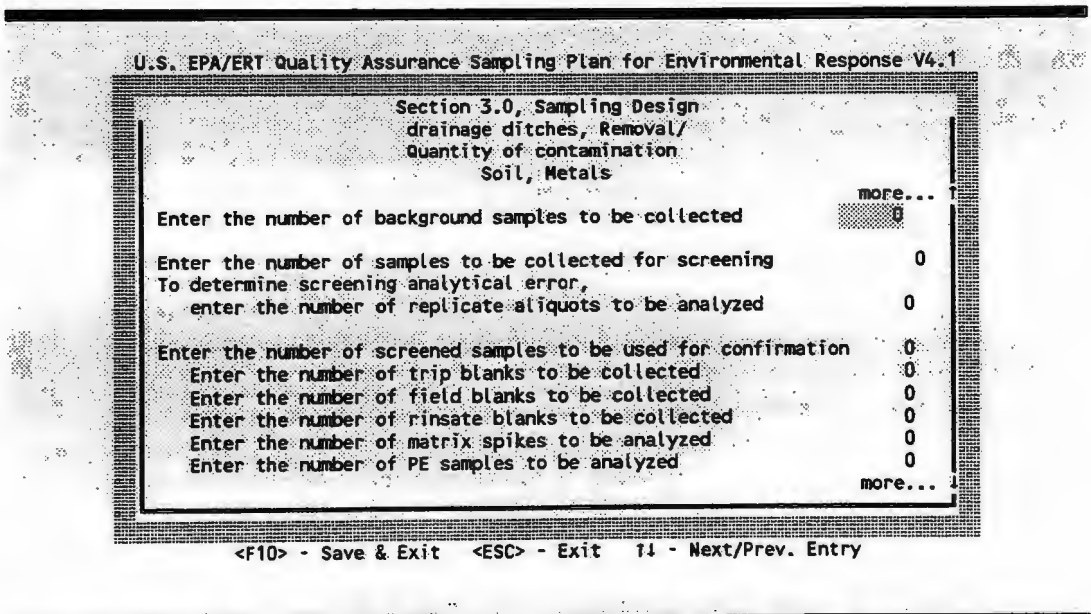

Figure 3. Numbers of Samples to be Collected

Section 4.0, Sampling and Analysis - Here users identify the sampling requirements, sampling equipment, and sample analytical information for each remedial unit, program area/sampling objective, matrix, and parameter combination as shown in Figure 4.

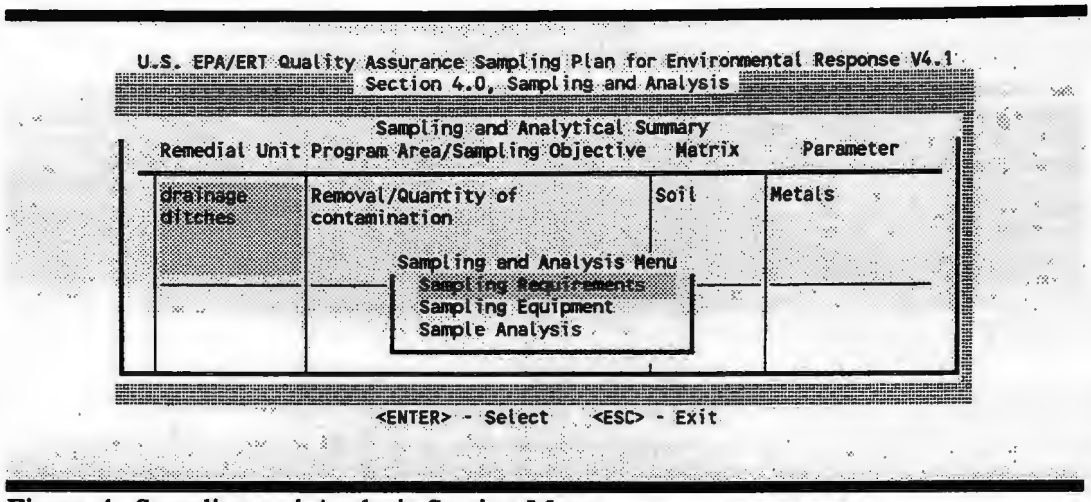

Figure 4. Sampling and Analysis Section Menu

Within **Sampling Requirements**, users specify the type and number of sampling containers, the method of sample preservation, and the holding time for the analytical parameter and matrix being sampled. If the matrix to be sampled is air, users specify the sampling flow rate and the volume to be sampled rather than the sample containers and preservative.

Within **Sampling Equipment**, users specify the equipment which will be used to collect samples. If applicable, users also specify the associated decontamination procedure.

Within **Sample Analysis**, users specify action levels and their justification, the method/instrument to be used during sample analysis, the required detection limit for the analysis, and the method-specific performance requirements. If the data category is S, this information is specified for both screening and definitive confirmation analyses.

Section 5.0, Standard Operating Procedures - In this section SOPs for sampling, sample documentation, and sample handling and shipment are available. Users may select standardized technical SOP text, modify it, or enter their own.

Section 6.0, Quality Assurance Requirements - This section receives the QA requirements text for the data categories that were identified in Section 2.0. Both sampling and analytical QA protocols are included. Users have an opportunity to view and edit the text.

Section 7.0, Data Validation - This section contains the instructions for validating the analytical data generated under this plan. The instructions are based on the data categories that were identified in Section 2.0. Users may view and edit the text.

Section 8.0, Deliverables - In this section, users specify deliverables or reports that will be produced including analyses, analytical reports, final reports, maps/figures, etc. QASPER provides standardized summary text for the deliverables shown in Figure 5. Users may choose from a picklist or enter new deliverables.

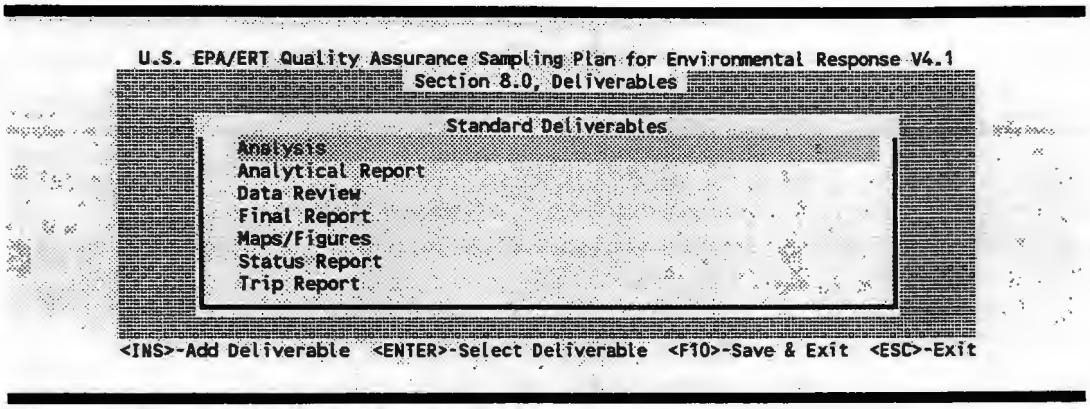

Figure 5. Standard Deliverables Available

Section 9.0, Project Organization and Responsibilities - In this section, users specify personnel who will be working on the project, their responsibilities, and the laboratories that will be analyzing the samples. Users may choose from a picklist or enter new personnel, responsibilities, or laboratories.

Section 10.0, Project Schedule - This section documents the time table for project activities. Individual project activities and their start and end dates are listed.

Section 11.0, Attachments - This section provides a list of attachments to the QA/QC Sampling Plan. This could include target compound lists, a site map, or other relevant information. Users may select from the standard picklist and may add their own attachments.

FEATURES OF QASPER

QASPER incorporates a variety of utilities that may be used to maintain the QASPER databases or to customize individual copies of QASPER.

Backup Plan - This utility is an automated feature which produces backup files of the plan databases. The corresponding Restore utility is an automated procedure that restores the databases that have been backed up.

Export Plan - This utility sends a copy of a plan database to the designated floppy disk or subdirectory. The file may be brought back into this or another copy of QASPER using the corresponding Import Plan feature, enabling users to transfer and share plans.

Maintain Lists - This utility allows additions to or deletions from the various picklists which are provided in QASPER.

Maintain Generic Text - This utility allows users to customize generic text provided in QASPER. This feature provides for variations in the text to accommodate regional or programmatic differences in policy and procedures.

Maintain Plan Text - This utility allows users to customize the format and content of the QA/QC Sampling Plan template, again allowing for variation in regional or organizational differences.

Export Modifications - This utility allows users to prepare a file which includes customized lists, generic text, and plan templates as shown in Figure 6. This file can be distributed throughout a region or an organization and imported into all regional or organizational copies of QASPER. This will ensure consistency of QA/QC Sampling Plans prepared within the region or organization.

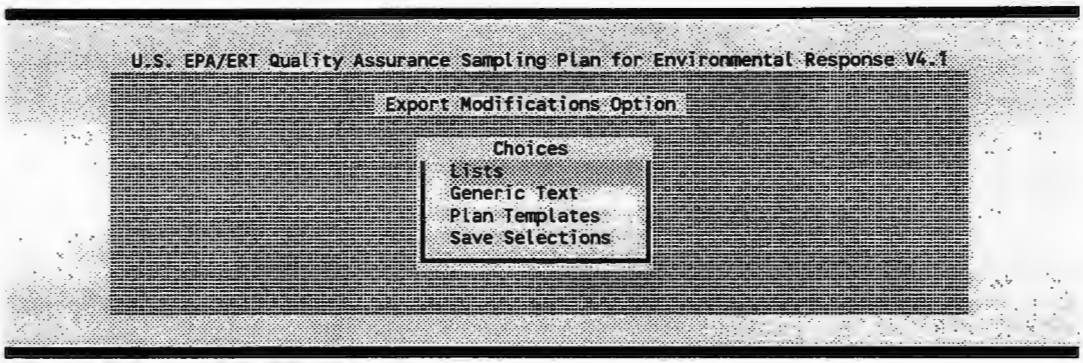

Figure 6. Export Modifications Option

Reindex - This utility recreates the indexes for the QASPER databases. This procedure is useful as an initial solution when data appear to be corrupted. For example, if the user knows that a picklist has five entries but sees only one, this option may be implemented. If the user is currently in a sampling plan and chooses this option, then the system files or the plan files may be reindexed.

Pack and Reindex - This option also recreates the indexes for the QASPER databases. In addition, it permanently removes any information that has been deleted.

System Configuration - Here the user may change monitor or printer types, and enter the command line for the word processing package that will be used during editing. This allows customizing of the QASPER software based on the user's hardware and software.

In addition to these features, status lines appear at the bottom of each screen throughout the QASPER program to assist users with input in any field. The status lines prompt the user for information required by QASPER. They also indicate available function keys.

An On-Line Help system is available any time the program is waiting for user input; however, not while reports are being generated, databases are being reindexed/recovered, or system files are being searched. Help may be accessed from anywhere in the program by pressing <F1>.

In addition, a User's Guide is provided with the software and technical support is available between the hours of 9:00 AM and 5:00 PM ET by calling: U.S. EPA/ERT Software Support, (800) 999-6990.

HARDWARE REQUIREMENTS

To run QASPER the following must be available:

- An IBM personal computer (PC) or 100% compatible system
- A hard drive with at least 2 megabytes (MB) of free space
- At least 640 kilobytes (K) of random access memory (RAM)
- A printer for hard-copy output

CONCLUSION

Using QASPER, Project Managers may save time, money, and resources by quickly developing sampling plans which address all of the elements required by current U.S. EPA guidance. Once familiar with QASPER, a user may generate a technically complete plan in approximately 90 minutes. When a base format is established, users may take advantage of QASPER's copy feature and generate plans in approximately 45 minutes.

Due to its minimal hardware requirements, QASPER may be incorporated into any site "tool-box" and may be used to generate sampling plans en route to or upon arrival at the site. These QA/QC Sampling Plans can be immediately utilized by knowledgeable field crews to collect representative samples and increase the probability of generating reliable data of known quality that will meet the intended use.

In addition, QASPER, Version 4.1, is highly flexible and may be adapted to a wide variety of regional or organizational situations. This allows organizations to customize or structure QASPER to provide QA/QC Sampling Plans in their own standard

appearance and with their own specific content. Standardized formats may be exported and transmitted to various regional and national locations.

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Office of Emergency and Remedial Response, U.S. EPA, *Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures*, Interim Final, EPA/540/G-90/004, April 1990.

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Monitoring VOC Losses in Soils Using Quantitation Reference Compounds and Response Pattern Analysis

Quantitation Reference Compounds (QRCs) can be used to monitor the behavior of target VOCs frequently found at Superfund sites. The QRCs are spiked into the sample matrix at the time of sampling and can monitor target VOC behavior in soils by response pattern similarities. Whatever the mechanism of VOC/soil interaction, be it surface sorption, inter- and intra-particle partitioning, biodegradation, etc., use of QRCs will accurately track the behavior and fate of certain VOC target compounds.

Spikes of target VOCs are spiked onto aliquots of soils of varying particle size distributions and total organic carbon contents. Phase I of the study spikes the QRCs onto the soil aliquots at the same time as the target VOCs, while Phase II spikes the QRCs at various lengths of time after the target VOC spike. The samples are then connected to a purge-and-trap GC/MS, and analyzed according to Method 8260. The absolute response of the target VOCs and the QRCs is plotted against the sample number, and the responses compared for pattern similarities.

The QRC responses paralleled the responses of certain target VOCs regardless of soil type or length of time target VOCs were held before addition of the QRC spike. The same target VOC/QRC pairs showing parallel response behavior were identified across the range of soil characteristics. Response factors were calculated from target VOC/QRC pairs exhibiting similar response patterns within a given soil type. These response factors were used in subsequent analyses using the same soil type to determine the percent recoveries of the target VOCs. These were compared to the percent recoveries using the current method without QRCs. Target compound recoveries ranged from 15-30% using the current method, while recoveries ranged from 93-105% using QRCs and response pattern similarities.

Target VOCs can be monitored for their behavior within a specific soil type by using QRCs as a compound capable of demonstrating similar behavior. This includes losses from sorptive mechanisms, biodegradation and losses arising from headspace partitioning prior to analysis and venting of the headspace when the sample container is opened.

There is a great amount of research designed to understand the behavior of VOCs in various matrices under various environmental conditions. Even the best VOC modeling systems available require many estimations or 'best guess' inputs to quantify VOC properties, movements, losses, etc. The properties of VOCs and their complex mobility pathways make piecing together the all of the information necessary to accurately describe the behavior of VOCs in soils very difficult. It is likely to be quite some time before this information can be tested and consolidated. In the meantime, using QRCs takes all of these variables into account as a 'summed' property, and demonstrates the capability to more accurately describe what VOCs existed in the sample at the time of sampling, not what is in the sample at the time of analysis.

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