The 14th Annual Waste Testing & Quality Assurance Symposium

PROCEEDINGS

WTQA '98

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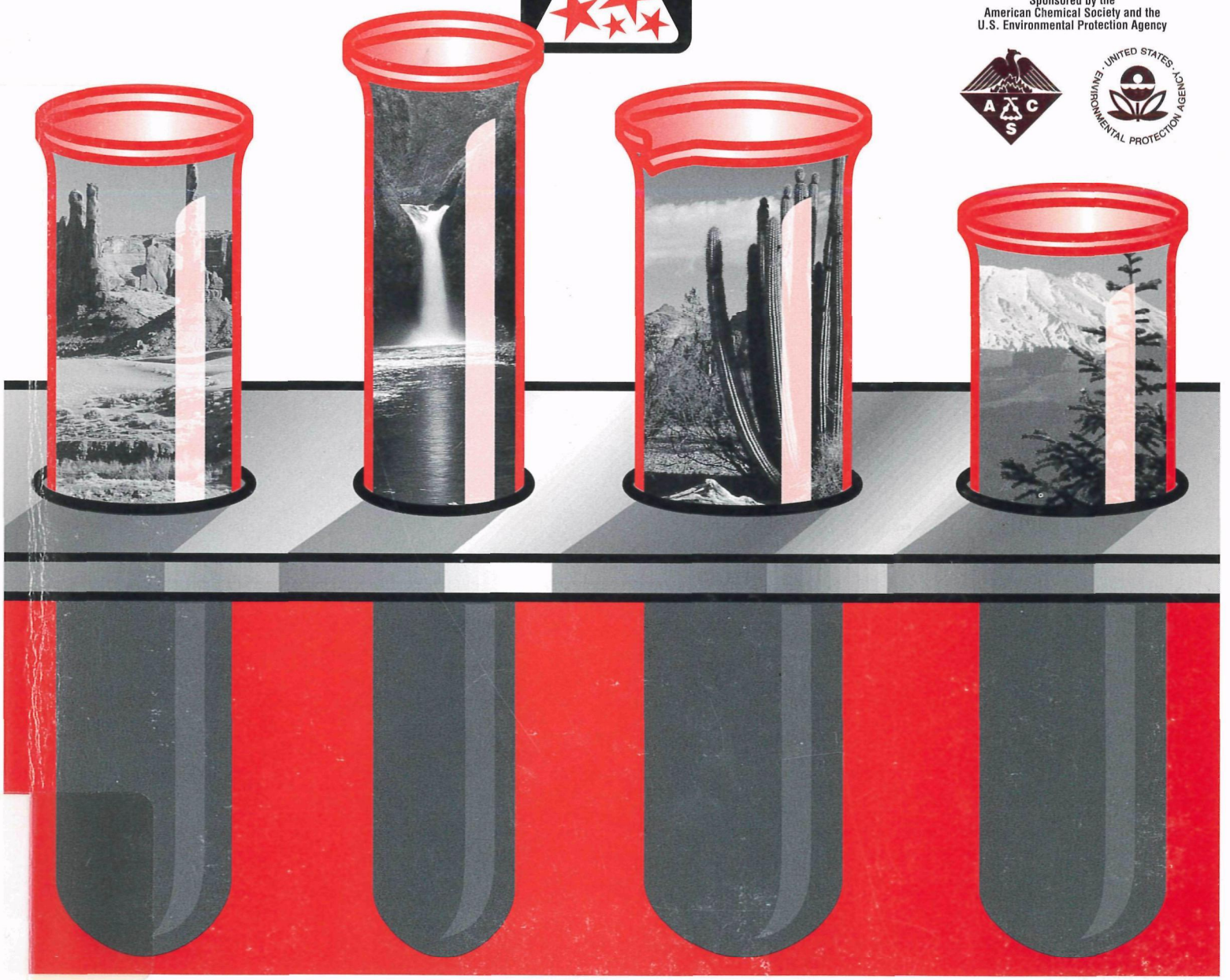

July 13-15, 1998 ■ Crystal Gateway Marriott ■ Arlington, VA

Proceedings

The Fourteenth Annual

Waste Testing & Quality Assurance Symposium (WTQA '98)

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Crystal Gateway Marriott
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HIGHLIGHTS

14th Annual Waste Testing & Quality Assurance Symposium (WTQA '98) Using A Performance-Based Measurement System (PBMS)

WTQA '98, cosponsored by the American Chemical Society (ACS) Division of Environmental Chemistry and the U.S. Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response (OSWER), will be held at the Crystal Gateway Marriott in Arlington, VA, July 13-15, 1998. This year's symposium continues the partnership between the regulated community and their supporting laboratories and state and federal regulators from the Research Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) programs.

Highlights

EPA is actively working to implement the President's program for "reinventing" government and reforming regulatory policy. As part of this endeavor, EPA has been trying to break down barriers to using new monitoring techniques. One barrier that OSWER is tackling is the requirement to use specific measurement methods or technologies in complying with Agency regulations. EPA's Environmental Monitoring Management Council (EMMC), members of the regulatory community, and Congress all agree that EPA needs to change the way it specifies monitoring requirements in regulations and permits. There is broad acceptance for use of a performance-based measurement system (PBMS). The EPA Office of Solid Waste and Emergency Response (OSWER) strongly supports this position and is committed to using this approach in both the RCRA and CERCLA monitoring programs. This year's plenary session speakers, including Fred Hanse, Deputy Administrator of EPA; Brad Campbell, Associate Director for Toxics & Environmental Protection; Steve Koorse, Hunton and Williams; Elizabeth Cotsworth, Acting Director, Office of Solid Waste; and Larry Keith, Waste Policy Institute, will focus their remarks on various aspects of PBMS.

PBMS Implementation Session

This session, organized by the International Association of Environmental Testing Laboratories Section of the American Council of Independent Laboratories (ACIL-IAETL), will include a presentation of EPA Program Office PBMS Implementation Plans, followed by speakers presenting the laboratory community, regulated community, and state regulatory agency perspectives on PBMS. The focus of the talks from the regulated community will be on the barriers they expect to face when trying to obtain the benefits of PBMS and what we all need to do to overcome the problems.

PBMS Methods Validation Session

Now that the EPA has moved towards implementing a PBMS approach to environmental monitoring, the regulated community needs to know how to validate methods under this new system. This session, also organized by ACIL-IAETL, will focus on how to tailor measurement system validation to the required data quality; how validation criteria should be specified in order that it not serve as a barrier to using alternative measurement technologies; and what is the minimum methods validation data set that one needs for the data obtained from the analysis to be of known and documented quality.

EPA's Environmental Monitoring Research Program

This session will focus on environmental monitoring methodology research supported under EPA's Science to Achieve Results (STAR) competitive, extramural grant program. The program has funded a number of research projects whose goal it is to develop unique or novel techniques for monitoring pollutants in the environment. Methodology to monitor air, water, soil and other media will be presented. The session will review the results from projects funded in prior years, and discuss the objectives and approaches to be undertaken in research studies that received funding this past year.

Superfund Session

The keynote for this Superfund session will be "Times Are Changing." Planned highlights include (1) a description of the Superfund pipeline over time, emphasizing the near and longer term future and how that relates to analytical service need; (2) information on how Superfund is working with other EPA program offices to enhance our operation; (3) the trend to encouraging economic redevelopment at Superfund sites; (4) how Superfund is implementing a PBMS approach; (5) initiatives related to data quality and minimal Quality Systems; (6)

electronic data delivery and validation; (7) usefulness of the National Environmental Laboratory Accreditation Conference (NELAC) accreditation for Superfund analytical work; (8) future direction for the Contract Laboratory Program (CLP); (9) Contracts 2000, Performance-Based Contracting, and what this means to the laboratory community, and (10) laboratory perspective on working for Superfund (a panel discussion).

SYMPOSIUM-AT-A-GLANCE

Sunday, July 12

8:00 a.m. - 9:30 a.m.	Registration for Short Courses
9:00 a.m. - 12:00 noon	Short Course: Analytical Strategy for the RCRA Program
9:00 a.m. - 4:00 p.m.	Short Course: An Introduction to Practical Ethics for Environmental Laboratories
1:00 p.m. - 5:00 p.m.	Short Course: Clean Chemistry for Trace Elemental Analysis

Monday, July 13

7:00 a.m. - 4:00 p.m.	Registration Open
8:00 a.m. - 12:00 noon	SW-846 Workgroups (closed)
8:00 a.m. - 12:00 noon	Short Course: Quality Systems, PBMS and NELAC: Putting It All Together
11:00 a.m. - 12:00 noon	Trial Exam for Environmental Analytical Chemists
2:00 p.m. - 4:30 p.m.	Opening Plenary Session David Friedman, Office of Research and Development Gail Hansen, Office of Solid Waste Fred Hansen, Deputy Administrator of EPA Brad Campbell, Associate Director for Toxics & Environmental Protection Steve Koorse, Hunton & Williams Elizabeth Cotsworth, Acting Director, Office of Solid Waste Larry Keith, Waste Policy Institute
5:00 p.m. - 7:00 p.m.	Opening Reception

Tuesday, July 14

7:00 a.m. - 5:00 p.m.	Registration Open
8:15 a.m. - 12:00 noon	Organic I Session
8:15 a.m. - 12:00 noon	Inorganic Session
10:00 a.m. - 10:30 a.m.	Break
12:00 noon - 1:00 p.m.	Lunch Break
1:15 p.m. - 5:00 p.m.	Organic II Session
1:15 p.m. - 5:00 p.m.	Environmental Monitoring Research Session
3:00 p.m. - 3:30 p.m.	Break
7:00 p.m. 8:00 p.m.	Trial Exam for Environmental Analytical Chemists

Wednesday, July 15

7:00 a.m. - 5:00 p.m.	Registration Open
8:15 a.m. - 12:00 noon	PBMS Implementation Session
8:15 a.m. - 12:00 noon	QA Session
10:00 a.m. 10:30 a.m.	Break
12:00 noon - 1:00 p.m.	Lunch Break
1:15 p.m. - 5:00 p.m.	PBMS Validation Session
1:15 p.m. - 5:00 p.m.	General Session
3:00 p.m. - 3:30 p.m.	Break
7:00 p.m. - 8:00 p.m.	Trial Exam for Environmental Analytical Chemists

Thursday, July 16

9:00 a.m. - 12:00 noon	Short Course: Analytical Strategy for the RCRA Program
9:00 a.m. - 4:00 p.m.	Superfund Session

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ORGANIC

INORGANIC

INORGANIC (continued)

EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM SESSION

EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM SESSION (Continued)

QUALITY ASSURANCE

GENERAL

ORGANIC

OVERVIEW OF CURRENT STATUS OF RCRA ORGANIC METHODS PROGRAM

Barry Lesnik
US EPA, Office of Solid Waste, 401 M ST., SW, Washington, DC

NO ABSTRACT AVAILABLE

APPROPRIATE WAYS TO MODIFY EXISTING METHODS FOR NEW APPLICATIONS

Barry Lesnik
US EPA, Office of Solid Waste, 401 M ST., SW, Washington, DC

NO ABSTRACT AVAILABLE

QUESTIONABLE PRACTICES IN THE ORGANIC LABORATORY

Joseph F. Solsky
US Army Corps of Engineers (CENWO-HX-C), 12565 W Center Road, Omaha, NE 68144
Phone: (402) 592-9542, Fax: (402) 592-9595
e-mail: joseph.f.solsky@usace.army.mil

SW-846 is a collection of performance-based methods used by the US Army Corps of Engineers (USACE) for execution of environmental restoration projects. These methods provide guidance for the running of various organic and inorganic protocols that can be used for the analysis of samples from a variety of sample matrices. During recent laboratory audits conducted by the USACE, certain 'questionable practices' have been observed, especially in the organic analysis areas.

Most people have a relatively good idea of what constitutes a fraudulent activity today. The concepts of 'dry-labing,' 'peak shaving,' 'peak enhancing,' or 'time-traveling' are well understood. These practices clearly involve the deliberate direct manipulation and/or alteration of data, often to achieve or meet method QC criteria. However, there are a new group of 'questionable practices' now being observed that often involve the selective exclusion of data to achieve or meet method QC criteria.

This presentation will focus on several of these 'questionable practices'. Examples of some of these practices include the following: (1) One such practice involves the determination of initial calibration curves. Laboratories have been observed running eight or more standards for methods that state 'a minimum of five points should be used to establish the initial calibration curve.' Up to three points are then discarded, even from the middle of the curve, until the appropriate QC criteria can be met. No technical justification existed for the deletion of these points other than to meet the method QC criteria. (2) Another such practice involves the evaluation of the continuing calibration verification solution. Laboratories have been observed averaging the % difference or % drift across all target analytes even when several of the target analytes exceed the criteria by a significant amount such that the average still meets the criteria as stated in the method. (3) Another such practice involves the reporting of acceptance ranges for surrogates or laboratory control samples. Laboratories have been observed reporting a very tight range indicating that they have good method control. However, an examination of the actual control charts maintained by the laboratory shows a significantly wider range. (4) Another such practice involves the determination of the method detection limit (MDL). Laboratories have been observed running ten or more standards and then discarding points to achieve a lower MDL. No technical justification existed for the deletion of these points other than to achieve a lower MDL.

Should the above 'questionable practices' be considered as examples of fraudulent activities? Some of the laboratories have described these practices as 'the common approach used by everyone.' Yet when described to people within EPA, the clear response is that these approaches were never intended. The background history will be discussed as to how and why these practices have developed and what can be done to overcome them.

MODIFICATIONS TO SW-846 HPLC METHODS 8330 AND 8310

C.A. Weisberg, M.L. Ellickson
U.S. EPA, Region III, Office of Analytical Services and Quality Assurance,
839 Bestgate Road, Annapolis, MD 21401

Method 8000 of SW-846 allows for modification of the existing methodology, provided that the analyst has documented the ability to generate acceptable results by successfully performing an initial demonstration of proficiency with the altered conditions prior to sample analysis. Analysts may vary the extraction procedures and/or HPLC parameters (mobile phase composition, elution program, injection volume, etc) in order to improve sensitivity and chromatographic resolution, or to reduce interferences resulting in coelution with analytes of interest. The use of analytical columns different from those specified in the methods may require that different HPLC conditions and flow rates be used. Generally, the HPLC methods 8330 and 8310 have been found to perform acceptably as written. However, some method modifications need to be employed in order to improve analyte resolution, achieve desired quantitation limits and obtain definitive confirmation of the primary column results. Some of the modifications to Method 8330 and Method 8310 reported in this paper include: nitrogen blow-down to adequately concentrate the final acetonitrile extracts after the salting-out liquid-liquid extraction procedure or the solvent exchange procedures; reduced flow rates and gradient elution schemes for the C-18 primary columns; and, the use of an acetonitrile/water mobile phase for the cyano secondary column confirmations.

When reporting quantitated results for these analyses, it is more important to positively confirm the primary column results than it is to completely resolve all of the target compounds. The use of analytical columns different from those specified can produce coeluting pairs which may differ from those mentioned in the methods. This paper will also discuss the reporting of coeluting compounds as mixtures, and the use of confirmatory techniques (e.g. dissimilar secondary column analyses, spectral library matching, LC/MS, GC/MS and GC-ECD).

PCB SEPARATIONS USING 2 DIMENSIONAL GC FOR CONFIRMATION: USE OF A HEART-CUTTING SWITCHING VALVE

Dennis R. Gere and Allen Broske
Hewlett-Packard, 2850 Centerville Rd., Wilmington, DE 19808
Phone (302) 633-8162
email dennis_gere@hp.com
Russell Kinghorn
SGE International Pty. Ltd., 7 Argent Place Ringwood, Victoria 3134 Australia

Environmental gas chromatography analysis continues to be a difficult but necessary effort for the detection and identification of PCBs. One approach is the use of a very good separation column, which would resolve most if not all of the 140-150 key congeners from one another. Another approach uses a more user-friendly approach to the congener specific analysis of PCBs. This approach is not a new or novel approach, but a revisit of a variation of a general column-confirmation column method. The use of two different stationary phase columns (orthogonal) allows a geometric gain in separation power compared to the algebraic gain by making the column

longer or more efficient.

The approach we used involves a heart cutting switching valve, one injector and two detectors. Some discussion will be given concerning the choice of the stationary phases, the choice of carrier gas and especially the judicious combination of temperature programming rate and carrier linear velocity. Focus will be upon key critical PCB congeners as described by the European Union protocols, that is, congener specific detection and confirmation.

The configuration uses two columns and two detectors, with a valve between the two detectors and a second selective column before the second detector. In the initial analysis, the sample is nominally separated on a general-purpose column. As sets of unresolved PCBs elute, they are cut out of the first separation scheme and sent to the second more selective column. The front of the second column may be cooled cryogenically (we will also demonstrate what happens when the cooling of the second column is not used) to hold the analytes at the front of the second column until the analysis of the first column is complete. Then a second temperature program is begun to resolve previously unresolved pairs.

The first column is a 5 % phenyl phase and the second column we used was either a 35 % phenyl or a 50 % phenyl phase of intermediate polarity. Either column is useful, and a specific choice may be made depending upon the sensitivity level (the 35 % phenyl is a much lower bleed column) or whether additional selectivity is needed. There are a great many permutations of this approach possible, and we will outline what we did and what can be done if even greater resolution is required.

ESTIMATING THE TOTAL CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL AT SAMPLING LOCATIONS: FIELD TRIALS

Alan D. Hewitt
U.S. Army Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755-1290
(603) 646-4388
Martin H. Stutz
U.S. Army Environmental Center, Aberdeen Proving Ground, MD 21010-5401
(410) 612-6856

ABSTRACT
This report describes a method for estimating the total concentration of volatile organic compounds (VOCs) in soil relative to a site-specific 0.2-mg/kg working standard and presents the results from three separate field trials. This method was developed to provide a decision tool for field or laboratory personnel so they can implement the appropriate soil sample preparation procedure for the selected method of instrumental analysis. Coupling a rapid method for estimating the total VOC concentration with sample collection, handling, and preparation procedures that limit substrate dissaggregation and exposure complements efforts to achieve site-representative estimates for vadose zone contamination.

INTRODUCTION
Since the beginning of the Superfund and the Resource Conservation and Recovery Act (RCRA) programs, gas chromatography/mass spectrometry (GC/MS) (via Methods 8260 and 8240) has served as the major laboratory instrument for identifying and quantifying VOCs in soils[1] The principal reason for the selection of this analytical detection system is that it provides an unambiguous identification of analytes present. Unfortunately, this very desirable quality comes with the limitation that for quantification purposes the individual analytes must fall within a concentration range of 2 to 3 orders of magnitude. High analyte concentrations can degrade the performance of the MS detection system, which interrupts scheduled runs and may lead to expensive instrument repairs. Therefore, one of the challenges when using an MS is how to couple it with a sample collection, handling, and preparation protocol when analyte concentration can range over 7 orders of magnitude (percent levels to the current levels of instrumental detection, approximately 0.005 mg/kg). To cope with this concern, samples thought to be contaminated with VOCs at levels greater than 0.2 mg/kg are prepared by extraction (and perhaps further dilution) with methanol (MeOH), i.e., the high-level method. In contrast, samples thought to have concentrations less than 0.2 mg VOC/kg are analyzed directly, which is referred to as the low-level method. Many other commonly used laboratory instruments and their respective methods for VOC detection (e.g., Methods 8015 and

8021B) also benefit from using these two approaches to sample preparation.

A second challenge is that VOCs in soils fail to maintain their concentration integrity if they are not collected and handled with limited disruption and exposure and if preventive measures are not taken to limit biological degradation of aromatic compounds. Today it is generally recognized that the sample collection and handling guidance, provided in the past by Method 5030, often resulted in a greater than 90% loss of the VOCs from soil samples prior to laboratory analysis[2-6]. To minimize losses due to volatilization and biodegradation, new sample collection and analysis protocols were included in the third update of SW-846[1]: Method 5035, "Modified purge-and-trap and extraction for volatile organics in soil and waste samples," and Method 5021, "Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis."

The two most effective collection and handling protocols that can be used with these new methods for preventing the loss of VOCs are 1) the on-site, rapid transfer of discrete samples with a small coring tool to a vessel that hermetically seals and already contains the appropriate dispersion/extractant solution for the chosen method of analysis[7], or 2) obtaining and temporarily storing (two days at 4°C) a sample in an En Core™ (En Novative Technologies, Inc., 1241 Bellevue St., Green Bay, Wisc. 54302) sampler before transferring it into an appropriately prepared vessel[8]. In addition, it should be recognized that, if the sample is to be held for more than two days before analysis, then some form of chemical preservation may be necessary in addition to storage at 4°C. For example, acidification can be used for low-level sample preparation procedures when carbonates are not present[6].

Because there is often no a priori knowledge of the VOC concentrations at a given location, the data quality objectives for site characterization activities often require that samples be collected and prepared for both the lowand high-level analysis procedures. To avoid collecting and processing samples through both of these preparation procedures for every location, it has been suggested that a rapid screening analysis be performed to establish an estimate for the total VOC concentration[9] This screening indicates the levels of VOCs to expect, before the sample is prepared for analysis, and thus whether collocated sample(s) taken for laboratory analysis should be prepared using the low- or high- level procedures, or both. The method developed is based on the comparison of responses of a hand-held photoionization detector (PID) to a sample relative to a 0.2-mg VOC/kg site-specific working standard. Recognition of the potential effort and cost savings by using screening as a decision tool are two reasons why this method is being considered for inclusion in the fourth update of SW-846 (proposed Method 3815). This paper briefly outlines this screening method and presents the results from three case studies. Additional information concerning the development of this method for screening is available elsewhere[9]

SCREENING METHOD

Materials

The necessary equipment and reagents are as follows:

1) Modified VOA vials (40 or 44 mL), Teflon-lined septa with 5- to 6-mm hole punched through the middle and 3- x 3-cm squares of light-gauge aluminum foil for temporary covers (see Fig. 1).
2) Coring tool for the collection and transfer of discrete soil samples, e.g., disposable 10-mL plastic syringes with the Luer tip and rubber plunger cap removed, or an equivalent metal tube and plunger.
3) A portable photoionization detector (PID) analyzer with a 10.6-eV or greater electrode discharge tube, digital display, inlet flow rate greater than 200 mL/min, and sample inlet tube of 3 to 4 mm o.d. and at least 3 cm in length.
4) A 10-mL liquid syringe.
5) Reagent-grade water (i.e., water with no detectable VOCs), polypropylene glycol (PPG, or similarly low-vapor-pressure organic solvent), and principal VOC(s) of site interest.
6) A cylinder of calibration gas for the PID, e.g., 100 ppm isobutylene.

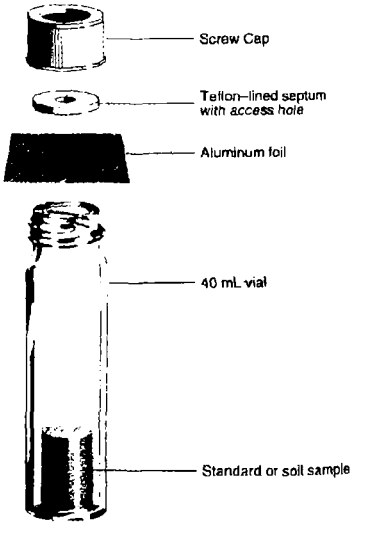

Figure 1. Modified VOA vials for rapid total VOC screening of soil samples.

Standards

A stock standard is prepared by transferring the VOC of interest into PPG. The stock standard concentration should be based on the density of the analyte of interest, so that a 1- to 3-µL volume transferred to a 40-mL VOA vial containing 10 mL of reagent water and 10 g of the site-specific soil matrix results in a 0.2-mg-VOC/kg working standard. For example,

Stock standard: 1.34 g/mL* x 2.0 µL/2.5 mL - 1.1 mg TCE/mL
Working standard: 1.1 mg TCE/mL x 1.8 µL/10 g soil = 0.2 mg TCE/kg
*Density of TCE

Immediately after spiking, these working standard vials are covered with a single sheet of aluminum foil that is held tightly in position with a septum with a hole punched in the middle and a screw cap (Fig. 1). The vial contents of the working standards should be thoroughly mixed by handshaking, then transported to the location of the sampling activity, stored out of direct sunlight, and allowed to equilibrate for 1 hr prior to use. Working standards should be prepared daily.

The PID response to the working standard should be at least 10x greater than its response to a blank (reagent water, contamination-free site-specific matrix, and appropriate volume of PPG). For analytes with high vapor pressures or low octanol water partition coefficients, or both, and soil matrices with low organic carbon contents, it may not be necessary to include the site-specific soil matrix in the working standards. This should be established on a site-by-site basis by comparing the means of triplicate working standards with and without the soil matrix. As a general rule, if the means differ by more than 20%, it is recommended that the soil matrix be included in the working standards.

Sample Collection and Analysis

Before field sampling, 10 mL of reagent water is added to the modified VOA vials. Once prepared, the VOA vials for screening samples should be transported to the sampling location and stored with the working standards until they are used. The native structure of the material being sampled for screening should be kept intact, thus experiencing as little disaggregration as possible during the collection and transfer process. This can often be accomplished with a coring tool designed to obtain a discrete sample. For example, a modified 10-mL syringe is a practical tool for obtaining up to a 10-g soil sample. If 10 g cannot be easily obtained in a single transfer, more than one corer can be used, or a couple of transfers with a single corer can be made. This coring device is transparent and comes with gradient markings so the volume/weight relationship for a given material can easily be established with a portable balance. The location of samples taken both for screening purposes and for laboratory analysis should be as close as possible to each other (generally within a 10-cm radius) and from the same stratum. Before preparing (or exposing) a fresh sampling surface, for instance, opening a split spoon or scraping away the top layer of a material, the cap and aluminum foil should be removed from the screening VOA vial. After retrieving a discrete sample, the core barrel should be inserted into the mouth of the screening VOA vial and the sample extruded. Once the sample has been extruded, the aluminum foil and cap should immediately be replaced on the vial. This collection and transfer process should take less than 10 seconds, and the sample weight only has to approximate 10 g (plus or minus 2 g).

Before a working standard or sample is analyzed, the VOA vial should be shaken by hand for 10 to 15 seconds. Cohesive materials, such as silts and clays, do not break apart rapidly upon shaking and may require more than 15 seconds for complete dispersion. The vial is then visually checked both for the complete dispersion of the sample matrix and for particles adhering to the aluminum foil cap liner (knock large particles off the aluminum foil if present). Then the inlet tube of the PID is pushed through the foil liner to a set position about 3 cm below the rim. A maximum response will be achieved within 2 to 3 seconds of punching through the foil liner. The maximum response for each sample screened and for the analysis of each working standard should be recorded.

Daily Operating Procedure for VOC Screening

The PID should be initially calibrated with a cylinder of standard gas (e.g., 100 ppm isobutylene) at the beginning of each day. This task can be performed before going to the sampling location. However, both the analysis of site-specific working standards and the screening of a sampling location should be performed under the same conditions, thereby normalizing meteorological influences on the performance of the PID. Site-specific working standards should be prepared daily and in sufficient quantity to satisfy the study's objectives. At a minimum, one working standard should be analyzed for every hour of site activity.

Collection of samples for VOC analysis should always be the first operation performed after a surface to be sampled has been exposed to the atmosphere. This includes samples both for screening and for laboratory analysis. To establish how to handle and prepare the discrete sample for laboratory analysis (low, high, or both procedures), a total VOC screening analysis should be performed at each sampling location. Therefore, before opening a split spoon, scraping a fresh surface on a pit wall, removing surface vegetation and the appropriate amount of top soil for a surface grid location, or removing the first several inches of some other type of waste material, the PID of choice should be operating. Furthermore, if a working standard is being utilized to verify performance of the PID for the sampling location, the analysis of a working standard should be completed before exposing a fresh sampling surface.

Once a fresh surface has been exposed, a sample should be quickly obtained, transferred to a screening VOA vial, dispersed, and analyzed. If the maximum response is greater than the working standard (or the running average), the sample or samples taken for laboratory analysis should be prepared using the high-level procedure (i.e., MeOH extraction). If the maximum response is below the working standard, the laboratory sample(s) should be prepared using a low-level procedure. The total elapsed time between exposing a fresh surface, screening a sample, and obtaining samples for laboratory analysis should be less than 2 minutes. As a precaution against false positive and false negative screening estimates relative to the decision point, locations where screening results are between 0.5 and 2x the working standard response should have samples prepared by both high- and low-level procedures.

Method Limitations

For this method of sample location screening to work, the VOC(s) of interest must be detectable by photoionization. If more than one analyte is of interest, and there are large discrepancies (greater than a factor of 2) in photoionization potentials, then the range around the decision point where samples are prepared by both high- and low-level procedures should be increased proportionally. That is, if the responses for the VOCs of interest differ by a factor of 3x, and the analyte with the highest response is used to make the working standard, then laboratory samples from locations where screening results are only 0.3x the working standard should be prepared by both procedures. However, this often will not be a problem for sites contaminated with common chlorinated and aromatic compounds because they have similar photoionization potentials. This approach may not be effective for sample matrices that are not readily dispersed in water (e.g., some clays and cementitious materials).

Table 1. Field screening measurements and sample preparation procedures.

No.	Screening (response)*		Sample Preparation Method
	Working Std	Sample	
Site 1			
S1-1	6.5	0.0	5021, LL**
S1-2	6.5	0.0	5021, LL
S1-3	---	0.4	5021, L
S1-4	---	790	5035, HL†
S1-5	---	480	5035, HL
S1-6	7.0	1400	5035, HL
S1-7	8.0	26	5035, HL
S1-8	---	2.2	5021, LL
S1-9	---	12	5035, HL
S1-10	6.3	4.4	5021, LL
Site 2			
S2-1	2.3,2.5	0.0	5035, LL††
S2-2	3.2	0.0	5035, LL
S2-3	4.2	0.0	5035, LL
S2-4	3.9	0.0	5035, LL
S2-5	---	0.0	5035, LL
S2-6	3.9	0.0	5035, LL
S2-7	---	0.0	5035, LL
S2-8	---	0.0	5035, LL
S2-9	3.8	0.0	5035, LL
S2-10	4.8	0.0	5035, LL
Site 3			
S3-1	5.6	0.0	5021, LL
S3-2	4.8	0.0	5021, LL
S3-3	5.3, 5.5, 5.2, 4.9	0.0	5021, LL

* PID field screening: Working Std--Results of analyzing a site-specific working standard 0.2 mg TCE/kg for Site 1 and 0.2 mg PCE/kg for Sites 2 and 3. Sample --Results from rapidly (<30 s) screening 10±2 g soil.

** 5021, LL--Sample placed in 22-mL VOA vial containing 10 mL water.

† 5035, HL--Sample placed in 40-mL VOA vial containing 5 mL MeOH.

†† 5035,LL--Sample placed in 40-mL VOA vial containing 5 mL water.

FIELD TRIALS

This method for rapidly estimating the total concentration of VOCs was tested during three different sampling activities performed under the supervision of personnel from EPA Region 1. At the sites visited, samples were obtained from near the surface with the aid of hand tools and from split-spoon core barrels. All samples, whether collected for on-site screening or for off-site analysis, were transferred using a

modified syringe. Samples collected for off-site analysis were placed into vials containing methanol or organic-free water, as appropriate for the intended method of sample preparation (Method 5035 or 5021) and analysis (Methods 8260, 8015, 8021), and analyzed within 48 hours.

The results of the screening analysis for both the working standards and samples are shown in Table 1, and the results of the laboratory analysis are shown in Table 2. During these field trials, the screening results were only used to decide whether to prepare samples by a low- or high-level procedure. With the possible exceptions of sampling locations S1-3 and S1-10, the samples were prepared appropriately for the intended method of analysis. That is, the analysis system was not exposed to an unexpectedly high analyte concentration. Indeed, this statement applies to all of the samples, since the concentrations were not much greater than 0.2 mg/kg for the individual analytes found in these two samples. Therefore, a scheduled run would not have been delayed nor would the detector have been damaged; however, there may have been individual analyte responses greater than the highest calibration standard.

Table 2. Laboratory results.

Site 1.

	HS/GC-PID/FID (mg/kg)							
No.	CDCE	TCE	Tol	PCE	EBen	p/m-Xyl	o-Xyl	Total
S1-1	---	---	---	<0.003*	---	---	---	<0.003
S1-2	---	---	---	<0.003	<0.003	<0.003	<0.009	
S1-3**	---	0.021	0.15	0.008	0.074	0.076	0.082	0.41
S1-4**	---	5.2	29	---	15	15	3.5	68
S1-5	---	---	---	140	---	---	---	140
S1-6	---	250	19	240	33	76	68	690
S1-7	---	---	---	7.4	---	---	---	7.4
S1-8	0.040	0.020	---	0.17	---	---	---	0.23
S1-9	---	---	---	1.0	---	---	---	1.0
S1-10	---	---	---	0.24	---	---	---	0.24

Site 2.

	PT/GC/MS† (mg/kg)		
No.	Trichlorofluoromethane	PCE	Total
S2-1	---	---	ND
S2-2	---	0.001	0.001
S2-3	---	0.001	0.001
S2-4	0.004	---	0.004
5	---	---	ND
6	---	---	ND
7	0.001	---	0.001
8	0.002	---	0.002
9	---	---	ND
10	---	---	ND

Site 3.

	HS/GC-PID/FID (mg/kg)	
No.	PCE	Total
1.	<0.003	<0.003
2.	---	ND
3.	---	ND

* <0.003--Peak identified but below quantation.
** Unidentified peaks present in chromatogram.
† Samples analyzed at EPA Region 1 Laboratory in Lexington, Mass.

In the case of sample S1-10, the recommendation that samples be processed through both procedures when sample screening results are within a factor of 2 to 0.5 of the working standards would have provided the necessary precaution. However, in the case of S1-3, where the screening results were well below 0.5x the working standard, this same logic would not have succeeded. Samples S1-3 and S1-4 were taken within 5 cm (vertical) of one another, and both the screening and laboratory results (Table 2) showed that this area had a large vertical gradient in VOC concentrations. In this case, a review of the data and perhaps the site history would alert the sample collectors to a potential problem and therefore the need to implement an additional precaution, so as not to overload the analytical system. Two potential solutions that would have worked at the site where samples S1-3 and S1-4 were taken are 1) to have taken screening samples on either side of (just above and below) the sample taken for laboratory analysis, 2) or alternatively, to have automatically prepared

samples by both low- and high-level procedures based on knowledge of where the source regions were on this site. Because of this experience, an additional recommendation is to use one of these two procedures (e.g., bracketing laboratory samples with screening samples or taking laboratory samples for both low- and high-level preparation procedures) when sampling near known or suspected source regions. Whenever samples are prepared by both a low- and high-level procedure, the sample prepared by the high-level method should be analyzed first. Furthermore, although not reported here, it has become evident that when a screening exceeds the scale of the PID, which is typically greater than 2000 ppm, further dilution of a sample processed by the high-level procedure is most likely warranted prior to analysis.

SUMMARY

The problems of underestimating the concentration of VOCs in samples taken from the vadose zone has facilitated the acceptance of new sample collection, handling, and preparation protocols (e.g., Methods 5035 and 5021). These changes not only present challenges to field sampling teams but to the laboratories responsible for sample analysis as well. For this reason both parties must be involved in the initial design of the sample collection plan and remain in contact throughout the project. To assist in deciding how samples should be prepared for instrumental analysis, a simple total VOC screening procedure has been developed. The main purpose of this screening method is to provide a decision tool during the sampling activity to help establish whether samples taken for laboratory analysis should be prepared by a low-level or a high-level procedure, or by both. This screening process is, however, not foolproof. Likewise, neither are any others that must contend with the possibility of a heterogeneous analyte distribution. For this reason, there are additional precautions that should be taken when using this method. One is for the case when screening results for samples are within a factor of 2 to 0.5 of the working standard results, another is for the case when sampling near known or suspected source regions, and the third is for when the PID's response to a screening sample is over range (greater than 2000 ppm). As demonstrated here, this screening procedure has the potential to greatly reduce the number of samples that would have to be collected and processed during a site investigation.

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FINAL EVALUATION OF METHOD 3546: A MICROWAVE-ASSISTED PROCESS (MAP™)* METHOD FOR THE EXTRACTION OF CONTAMINANTS UNDER CLOSED-VESSEL CONDITIONS

J.R. Jocelyn Paré and Jacqueline M. R. Bélanger
Microwave-Assisted Processes Division
Chung Chin and Richard Turle
Air Analysis and Quality Division, Environment Canada,
Environmental Technology Centre, Ottawa, ON, Canada K1A 0H3
Barry Lesnik
US EPA, Office of Solid Waste, Method Section, 401 M. St., SW, Washington, District of Columbia 20460, USA
Rodney Turpin and Raj Singhvi
US EPA, Emergencies Response Branch, 2890 Woodbridge Ave., Edison, New Jersey 08837-3679, USA

ABSTRACT

Microwave-assisted extraction (MAP™) has been the subject of enhanced interest from the environmental sector in the past year as a result of the need for methodologies that will improve sample preparation without compromising the quality of the data while being sustainable environmentally. Liquid-phase microwave-assisted extraction (MAP™) offers such advantages: it is a very fast extraction technique, it consumes less solvent and energy, and it is cost effective. A preliminary validation study involving closed-vessel apparatus and contaminants such as PAHs, PCDDs/PCDFs, chlorinated pesticides, and PCBs was performed. Excellent performance and precision were achieved for these analytes. In order to fully evaluate the method for the range of analytes an inter-laboratory study was performed. A round-robin study was performed with five laboratories and involved thermally labile RCRA target analytes such as phenols, phenoxyacids herbicides and organophosphorus pesticides. Three split samples were used along with a single standard operational procedure (SOP). All analyses were performed by a single laboratory in order to minimise the variability of the results due to the determinative procedure. Clean up was performed using standard procedures and analysis was done according to the appropriate SW-846 methods. The broad range of applicability, the reduced sample preparation time and the reduced amount of solvent used all contribute to reach sustainable environmental protection goals. Furthermore, the reduced operational costs associated with the protocol compared to conventional Soxhlet for example - are significant and will prove valuable in these times where the "greening" of the laboratory usually gives rise to higher operating costs. Further work involving open-vessels apparatus is under way.

INTRODUCTION

The microwave-assisted process (MAP) is a technology patented by Environment Canada[1-3] The most widely used applications to date make use of microwave energy to extract soluble materials from different matrices, mostly using organic solvents[4,5]. Microwave energy has been used in various ways to extract organic compounds from a variety of matrices[6]. For example, the technology has been applied to organochlorinated pesticides from sediments and PCBs from water[7], petroleum hydrocarbons from soil[8], and to herbicides from soils[9,10]. Lopez-Avila *et al.* used a MAP-approach to extract several groups of pollutants such as PAHs, PCBs, pesticides, phenols and base/neutral compounds in soils and sediments[11-13]. In all these studies, microwave-assisted extraction proved to be similar or more efficient than methods based upon the use of Soxhlet or ultrasound.

More recently, we reported on a preliminary validation of a draft method for inclusion into US EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)[14] Table 1 presents the types of compounds that have been subjected to that preliminary work.

The method reported herein makes use of partially microwave-transparent solvents (or a mixture of such solvents) contained into a closed vessel. Although not as elegant and efficient as methods using open-vessel microwave-transparent solvents, it provides the possibility of combining the benefits of heat (enhanced solubility and diffusivity) to the action of the microwaves on the matrix. Work is currently underway to validate open-vessel methods and the results will be reported elsewhere in due time along with the parameters to be controlled to effect even more efficient extraction procedures using MAP. This paper reports on the final evaluation of a closed-vessel microwave-assisted extraction procedure for environmental pollutants from soils and sediments that recently met with the US EPA approval and will be referred to as Method 3546 under SW-846. It is a procedure for extracting water insoluble or slightly water soluble organic compounds from soils, clays, sediments,

* MAP is a Trade-mark of Her majesty The Queen in Right of Canada as represented by the Minister of the Environment.

sludges, and other solid wastes. The method is applicable to the extraction of semi-volatile organic compounds, organo-phosphorus pesticides, organo-chlorine pesticides, chlorinated herbicides, phenoxy acid herbicides, substituted phenols, PCBs, and PCDDs/PCDFs which may then be analyzed by a variety of chromatographic procedures.

TABLE 1. List of target analytes used in preliminary validation package

Base Neutral and Acid	**PAH**	**Organo-chlorines**
Hexachloropentadiene	Acenapthylene	PCB-I
Dimethylphthalate	*d_{10}-Acenaphtene (surrogate)*	PCB-2
Diethylphthalate	Fluorene	Hexachlorobenzene
Di-*n*-butylphthalate	*d_{10}-Phenantrene (surrogate)*	Simazine
Butylbenzylphthalate	Phenanthrene	Atrazine
bis(2-Ethylhexyl)adipate	Anthracene	Lindane
bis(2-ethylhexyl)phthalate	Pyrene	PCB-3
	Benzo(a)anthracene	Alachlor
Pentachlorophenol	*d_{12}-Chrysene (surrogate)*	Heptachlor
	Chrysene	PCB-4
	Benzo(b)fluoranthene	Heptachlor epoxide
	Benzo(k)fluoranthene	PCB-5
	Benzo(a)pyrene	*gamma*-Chlordane
	d_{12}-Perylene (surrogate)	*alpha*-Chlordane
	Indeno(123-cd)pyrene	*trans*-Nonachlor
	Dibenzo(ah)anthracene	PCB-6
	Benzo(ghi)perylene	Endrin
		PCB-7
	d_{14}-Terphenyl (int. std)	Methoxychlor
		PCB-8

This method has been validated for solid matrices containing 50 to 10,000 µg/kg of semi-volatile organic compounds, 250 to 2,500 µg/kg of organo-phosphorus pesticides, 10 to 5,000 µg/kg of organo-chlorine pesticides and chlorinated herbicides, 50 to 2,500 µg/kg of substituted phenols, 100 to 5,000 µg/kg of phenoxy acid herbicides, 1 to 5,000 µg/kg of PCBs, and 10 to 6000 ng/kg of PCDDs/PCDFs.

EXPERIMENTAL

The experimental procedures for the preliminary validation work has been presented elsewhere, hence all the text presented herein refers exclusively to the inter-laboratory work and is relevant to Method 3546 as approved.

This method is applicable to solid samples only with small particle sizes. If practical, soil/sediment samples may be air-dried and ground to a fine powder prior to extraction. Alternatively, if worker safety or the loss of analytes during drying is a concern, soil/sediment samples may be mixed with anhydrous sodium sulfate or pelletised diatomaceous earth. The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity required for the analysis, but 2 - 20 g of material are usually necessary and can be accommodated by this extraction procedure.

Safety

The use of solvents combined with the operational parameters associated with this method will raise temperatures and pressures in the extraction vessels to values that can be a safety concern in the laboratory. Only equipment designed for laboratory use and manufactured under legitimate rights should be used to ensure that proper safety devices are built into the apparatus. Common sense laboratory practices can be employed to minimize this concern. For example, the following sections describe some additional steps that should be taken.

The extraction vessels are at elevated temperatures and pressure after the extraction stage. Allow the vessels to cool before opening (the use of a water bath is recommended for this purpose) and always monitor the temperature and pressure by re-connecting the control vessel to the apparatus prior to opening the vessels.

During the heating step, some solvent vapors may escape through the vessel liner/seal cover. Follow the

manufacturer's directions regarding the vessel assembly and instrument set up to prevent release of solvent vapors to the laboratory atmosphere. The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. If so equipped, follow the manufacturer's directions regarding replacement of extraction vessel seals when frequent vapor leaks are detected.

Extraction
Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composite samples. Discard any foreign objects (sticks, leaves, rocks, *etc.*). Air dry the sample at room temperature for 48 hours in a glass tray or on hexane-rinsed aluminum foil. Alternatively, mix the sample with an equal volume of anhydrous sodium sulfate or pelletised diatomaceous earth until a free-flowing powder is obtained.

If multiphase waste samples are used, then they must be prepared by the phase separation method in Chapter Two of SW-846 before extraction. Dry sediment/soil and dry waste samples amenable to grinding. Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Disassemble grinder between samples, according to manufacturer's instructions, and decontaminate with soap and water, followed by acetone and hexane rinses.

Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The analyst may add anhydrous sodium sulfate, pelletised diatomaceous earth, sand, or other clean, dry reagents to the sample to make it more amenable to grinding.

Grind a sufficient weight of the dried sample to yield the sample weight needed for the determinative method (usually 10 - 30 g). Grind the sample until it passes through a 10-mesh sieve. Prepare a method blank using an aliquot of a clean solid matrix such as quartz sand of the approximate weight of the samples. Add the surrogates listed in the determinative method to each sample and method blank. Add the surrogates and the matrix spike compounds appropriate for the project to the two additional aliquots of the sample selected for spiking.

A volume of about 30 mL of the appropriate solvent system is added to the vessel and sealed. The extraction vessel containing the sample and solvent system is heated to the extraction temperature and extracted for 10 minutes. The solvent systems used for this procedure vary with the analytes of interest and are listed below. The mixture is allowed to cool. The vessel is opened and the contents are filtered. The solid material is rinsed and the various solvent fractions are combined. The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed.

Six vessels were always placed in the microwave oven at any one time to standardise conditions. After extraction, the sample carousel was removed from the microwave and cooled in a water bath. To ensure that it was safe to proceed with the filtration step the control vessel was returned to the microwave oven and the temperature was monitored before opening. Solvent loss was checked randomly in some instances and found to be below 1%.

Interferences
Refer to Method 3500 of SW-846. If necessary, Florisil and/or sulfur cleanup procedures may be employed. In such cases, proceed with Method 3620 and/or Method 3660 of SW846.

Apparatus and Supplies
CEM Corporation (Matthews, NC) MAP™ solvent extraction systems equipped with appropriate microwave-transparent extraction vessels should be transparent to microwave energy and capable of withstanding the temperature and pressure requirements (200°C and 200 psi) for this procedure. Models MES-1000 or MSP-1000 have been used for the present work.

Solvents Systems and Reagents
All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

Organo-chlorine pesticides, organo-phosphorus pesticides, semi-volatile organics may be extracted with acetone/hexane (1:1, v/v) or acetone/methylene chloride (1:1, v/v).

PAHs, PCBs, dioxins, and furans may be extracted with acetone/hexane (1:1, v/v), or acetone/methylene chloride (1:1, v/v), or hexane.

Phenoxy acid herbicides and phenols may be extracted with acetone/hexane (1:1, v/v) and the phosphate buffer solution.

Reagent grade chemicals shall be used in all tests. Organic-free reagent water should be used. Sodium sulfate (granular anhydrous), Na_2SO_4 and pelletised diatomaceous earth can be used as desiccant. They should be purified by heating at 400°C for 4 hours in a shallow tray, or by extraction with methylene chloride. If the latter approach is used, then a reagent blank should be prepared to demonstrate that the drying agent is free of interferences.

Phosphate buffer solution - for use in extraction of phenols and phenoxyacid herbicides. Prepare a 0.1 M phosphate buffer solution by adding 1.2 g reagent grade sodium phosphate into a 250-mL beaker, add 100 mL of reagent water and thoroughly mix. Adjust the solution pH to 2 with the addition of reagent grade phosphoric acid

Quality Control
Chapter One and Method 8000 of SW-846 should be followed for specific Quality Control procedures and Method 3500 should be followed for sample preparation quality control procedures. Surrogate standards should be added to samples when listed in the appropriate determinative method.

RESULTS AND DISCUSSION
Reference 14 presents a large body of information and specific data on a number of analytes. It provides the basis for a major portion of the performance work associated with this procedure. References 12 and 15 are reports of similar, more specific studies. References 16 to 18 deal specifically with phenols. Representative data sets are presented in Tables 2 to 6. They are not exhaustive and are reported here as they are new data. Other data can be found in the references cited herein including references 19 and 20.

Chlorinated pesticides: Single-laboratory accuracy data were obtained for chlorinated pesticides using natural soils, glass-fiber, and sand matrices. Concentrations of each target analyte ranged between 0.5 to 10 µg/g. Four real-world split samples contaminated with pesticides and creosotes were also used (obtained from US EPA ERT, Edison, NJ). The latter were extracted by an independent laboratory using standard Soxhlet procedures and results compared to those obtained with this procedure. Extracts were analyzed by the appropriate method. Method blanks and five spiked replicates were included. Work was also carried out to assess the level of degradation of thermally labile pesticides and it was found that no significant degradation takes place under the procedure described herein. The data are reported in detail in Reference 4. Data summary tables are included in Method 8081.

TABLE 2. Single-laboratory organochlorine pesticides analysis data from a real contaminated soil

Compounds	Average (ppb)	Std. Dev.	RSD (%)	n	REAC value (ppb)
DDE+Dieldrin	3380	340	10.06	3	7100
Endrin	21500	2290	10.66	3	22000
*DDD	40000	5750	14.38	3	45000
*DDT	62670	8430	13.45	3	62000
*Methoxychlor	16500	1980	12.03	3	16000
α-Chlordane	730	100	13.37	3	750
γ-Chlordane	720	90	12.47	3	910

*(dilution 1:5); Soil samples obtained from US EPA Emergency Response Center archive bank through their contract laboratory REAC (Edison, NJ). The standard Soxhlet extraction procedures were performed by REAC three years earlier; this long storage period is believed to account for the low DDE+Dieldrin recovery data in the present study. DDE+Dieldrin is the sum of the compounds since they were not resolved by chromatography.

Semivolatile organics: Single-laboratory accuracy data were obtained for semivolatile organics using natural soils, glass-fiber, and sand samples. Concentrations of each target analyte was about 0.5 µg/g. Extracts were analyzed by the appropriate method. Method blanks and five spike replicates were included. The data are reported in detail in Reference 14. Data summary tables are included in Method 8270.

PAHs: Single-laboratory accuracy data were obtained for PAHs using five reference materials comprising marine sediments (HS-3, HS-4, and HS-5, all from the National Research Council of Canada), lake sediments (SRM-1491, from the National Institute of Science and Technology), and a natural soil contaminated with creosote (SRS103-100, from Fisher Scientific, Fairlawn, NJ). Natural soils, glass-fiber, and sand samples were also used in spiked matrices work. Concentrations varied between 0.1 and 2000 µg/g. One real-world split sample contaminated with creosote and pesticides was also used (obtained from US EPA ERT, Edison, NJ). The latter was extracted by one laboratory using standard Soxhlet procedures and results compared to those obtained with this procedure. Extracts were analyzed by the appropriate method. Method blanks, spikes and five spiked replicates were included. Surrogates were used in real-world split sample. The data are reported in detail in Reference 14. Data summary tables are included in Method 8270.

PCBs: Single-laboratory accuracy data were obtained for PCBs using three reference materials EC-1, EC-2, EC-3 (from Environment Canada). Natural soils, glass-fibre, and sand samples were also used in spiked matrices work. Concentrations varied between 0.2 and 10 µg/g (total PCBs). Extracts were analyzed by the appropriate method. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in Reference 14. Data summary tables are included in Method 8082.

TABLE 3. Single-laboratory PCB recoveries data from certified Great Lake sediment materials

Sediment	Aroclor (ppb)	Std Dev.	RSD (%)	n	Certified value (ppb)
EC-1	1850	0.07	3.78	3	2000 ± 54
EC-2	1430	0.09	6.60	4	1160 ± 70
EC-3	670	0.02	3.12	3	660 ± 54

Sample size = 2 g extracted into a final volume of 4 mL; EC-2 and EC-3 certified values were provisional values only, at the time the work was conducted. The data presented herein were part of the validation data package used to confirm the certified values. Real samples were also tested when fortified with mixtures of native Aroclor (1242, 1254, and 1260) to a 600 ppb level. Recoveries were in the 88% range with a reproducibility of 2% RSD.

Chlorinated herbicides (phenoxyacid herbicides): Multi-laboratory accuracy data were obtained for chlorinated herbicides spiked at 100 ng/g in one soil type. A certified spiked material was used (obtained from ERA, Arvada, CO). Extracts were analyzed by Method 8151. Method blanks and three replicates from five laboratories were included. Data summary tables are included in Method 815 1.

Phenols: Single-laboratory accuracy data were obtained for phenols using a number of spiked natural soils and a number of real-world split soils. Concentrations varied between 0.2 and 10 µg/g. Extracts were analyzed by the appropriate method. The data are reported in detail in References 14 to 18. Data summary tables are included in Method 8041. Multi-laboratory accuracy data were obtained for phenols spiked at 250 µg/kg in one soil type. A certified spiked material was used (obtained from ERA, Arvada, CO). Extracts were analyzed by Method 8041. Method blanks and three replicates from five laboratories were included. Data summary tables are included in Method 8041.

TABLE 4. Multiple-laboratory phenoxyacid herbicides recoveries from certified spiked material

Compounds	**Average (µg/kg)**	**Recovery (%)**	**RSD**
2,4-D	81	81	13.0
2,4-DB	122	122	15.1
2,4,5-T	74	74	11.8
2,4,5-TP (Silvex)	68	68	17.9
Dicamba	50	50	17.6
Dichlorprop	87	87	20.7
Dinoseb	118	118	29.4

Material spiked at 100 µg/kg. Number of participating laboratories = 4. N = 3

TABLE 5. Multiple-laboratory phenols recoveries from certified spiked material

Compounds	Average (µg/kg)	Recovery (%)	RSD
2,4-D	81	81	13.0
2,4-DB	122	122	15.1
2,4,5-T	74	74	11.8
2,4,5-TP (Silvex)	68	68	17.9
Dicamba	50	50	17.6
Dichlorprop	87	87	20.7
Dinoseb	118	118	29.4

Material spiked at 250 µg/kg. Number of participating laboratories = 4. N = 3

Organophosphorus pesticides and chlorinated herbicides: Multi-laboratory accuracy data were obtained for organophosphorus pesticides spiked at 250 µg/kg in one soil type. A certified spiked material was used (obtained from ERA, Arvada, CO). Extracts were analyzed by Method 8141. Method blanks and three replicates from five laboratories were included. Data summary tables are included in Method 8151.

TABLE 6. Multiple-laboratory organophosphorus pesticides recoveries from certified spiked material

Compounds	Average (µg/kg)	Recovery (%)	RSD
Bolstar (Sulprofos)	74	30	8.0
Chlorpyrifos	70	28	7.7
Demeton O & S	nq	nq	nq
Diazinon	111	44	3.8
Dichlorvos	nq	nq	nq
Dimethoate	143	57	14.1
Disulfoton	nq	nq	nq
EPN	107	43	12.9
Ethoprop (Prophos)	198	79	6.8
Fensulfothion	207	83	7.5
Parathion ethyl	159	63	12.3
Parathion methyl	146	58	10.6
Phorate	117	47	13.5
Ronnel (Frenchlorphos)	145	58	5.0
Sulfotepp	nq	nq	nq
TEPP (Tetraethylpyrophosphate)	nq	nq	nq
Tetrachlorvinphos (Stirifos)	158	63	3.5
Tokuthion (Prothiofos)	153	61	5.5

Material spiked at 250 µg/kg. nq = not quantified. Number of participating laboratories = 4. N = 3.

Dioxins and furans: Single-laboratory accuracy data were obtained for dioxins and furans using two reference materials (DX-1 from Environment Canada and SRM-1944 from NIST). Concentrations varied between 0.01 and 6 µg/kg. Extracts were analyzed by the appropriate method. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in References 19 and 20. Data summary tables are included in Method 8280.

SUMMARY

A variety of simulated samples as well as real matrix materials have been analysed to evaluate and validate a well-defined microwave-assisted extraction process. Recoveries in all cases were satisfactory, problems encountered usually are in the actual instrumental analysis due to the complex nature of the matrix. Relatively low recoveries are all caused by volatility losses of the particular compounds during sample workup, and not due to the extraction process. Studies carried out using thermally labile organochlorine pesticides and organo-phosphorus pesticides showed that the use of microwaves, under the operational conditions presented herein, did not cause any significant degradation, if any, despite the relatively rigorous conditions prescribed in the proposed method. Commercially available extractors, such as those used herein, can process up to 12 samples in less than 1 hour while taking up much less space, solvent and energy than the currently used Soxhlet extractor. The rapid sample turn around time is a yet another advantage over traditional Soxhlet techniques. We will report elsewhere on other approaches related to more precise control over extraction conditions and that will

ensure even shorter extraction times as well as higher extraction efficiencies.

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PHENOXYACID HERBICIDE SCREENING

Mark L. Bruce, Kathleen L. Richards and Raymond M. Risden
Quanterra Inc., 4101 Shuffel Dr. NW, North Canton, OH 44720
brucem@quanterra.com

Abstract
EPA SW-846 Methods 8150 and 8151 have been traditionally used for phenoxy acid herbicide analyses. These methods require the use of hazardous derivatization reagents and a highly flammable solvent. The sample preparation process is very long, complex, labor intensive and time consuming. Immunoassay, as used in EPA SW-846 Method 4015, uses aqueous based chemistry with minimal solvent volume and much simpler and faster sample preparation.

Quanterra has demonstrated that EPA SW-846 Method 4015 (2,4-D) can be extended to include 2,4,5-T and silvex by using both the 2,4-D and silvex kits from Strategic Diagnostics Inc. It is useful for screening both water and soil samples for phenoxyacid herbicides. Non-detect samples from the immunoassay (IA) screen are reported as nondetect at the applicable reporting limit. Samples which have responses greater than the threshold (i.e. positive response) are confirmed by the traditional methods. The overall false negative rates of 0.5% for waters and 1.0% for soils were well below the EPA Office of Solid Waste criteria of 5% at the reporting limits listed below. The false positive rates were 12.5% and 11.5% for waters and soils respectively. Water reporting limits were 2 µg/L, 10 µg/L and 10 µg/L for 2,4-D, silvex and 2,4,5-T respectively. Soil reporting limits were 1 mg/kg, 1.5 mg/kg and 1.5 mg/kg respectively.

Switching to IA improves laboratory safety, reduces organic solvent usage and disposal, improves turn-around-time and reduces analytical costs.

Introduction
Many herbicide analysis requests target three main analytes of interest: 2,4-D, 2,4,5-T and silvex (2,4,5-TP). Also, >95% of these samples are reported as "non-detect" for these analytes. Thus, it would be very useful to screen samples submitted for the. analysis of these herbicides. Only those samples with herbicides above the reporting limit would be subjected to quantitation by the more exhaustive traditional analysis methods. Immunoassay is capable of providing the screening information with an aqueous chemistry based method that is simpler, faster, safer and less expensive.

Currently Immunoassay Method 4015 is only applicable to 2,4-D. However, this validation study demonstrates that it is possible to extend the method by including a Strategic Diagnostics Incorporated (SDI) analysis kit developed specifically for silvex by Ohmicron. Both the 2,4-D and silvex immunoassay kits have cross reactivity for 2,4,5-T because of structural similarities. This cross reactivity enables the combined use of the two kits to effectively screen for all three compounds, The cross reactivity is shown below expressed as least detectable dose (LDD).

Table 1. Cross Reactivity

Compound	2,4-D Assay LDD (µg/L)	Silvex Assay LDD (µg/L)
2,4-D	0.70	100
2,4,5-T	3.0	1.0
Silvex	170	1.4

The Ohmicron (now part of SDI) 2,4-D kit has been validated following Office of Solid Waste (OSW) guidelines. It was approved by the OSW Organics workgroup and incorporated into Method 4015. Method 4015 was part of the Update III package for SW-846 promulgated in mid 1997. Ohmicron had established threshold test levels of 10 µg/L in water and 150 µg/kg in soil with their magnetic particle based assay kit. The sensitivity difference between the two matrices is mostly due the large dilution of the methanol soil extract needed to reduce antibody exposure to methanol.

The Ohmicron Silvex kit was validated similarly to the 2,4-D kit but the results were not submitted to the OSW workgroup. The silvex kit has comparable sensitivity to the 2,4-D kit. Ohmicron has documented that the silvex assay responds similarly to 2,4,5-T (i.e. cross reactivity).

Immunoassay Method Summary
The immunoassay form applied in these two kits is enzyme linked immunosorbent assay (ELISA). Information is available from SDI product literature and the EPA - Las Vegas (web site http://www.epa.gov/crdlvweb/asb/immuchem/forum.htm) describing IA basics.

For these SDI kits a subaliquot (250 µL) of aqueous sample is combined with 250 µL of enzyme conjugate solution. One portion of the conjugate molecule resembles the analyte of interest. Antibody which is bound to small magnetic particles is added to this analyte/conjugate mixture. The analyte and conjugate compete for antibody binding sites. The higher the analyte concentration the less conjugate is bound to the antibody. The lower the analyte concentration the more conjugate is bound to the antibody.

A magnet is used to retain the antibody particles and the analytes and conjugates that have bound to the antibodies. All other analytes, conjugates and matrix components are washed away. A color development reagent is added to the antibodies. This reagent reacts with another portion of the conjugate molecule and develops color proportional to the amount of bound conjugate present. Thus, the color (i.e. absorbance measured on the filter photometer) is highest (~1) for blanks and clean samples and the least absorbance is produced for high concentration standards and samples. This inverse relationship between analyte concentration and absorbance response has caused some confusion.

Thus, when using this IA format for threshold testing the results scenarios are:

a) if sample absorbance > threshold standard absorbance then analyte concentration is < threshold (e.g. non detect at 10 µg/L), b) if sample absorbance ≤ threshold standard absorbance then analyte concentration is ≥ threshold (e.g. positive analyte ≥ 10 µg/L)

Since the color response will always have some variability associated with both the threshold standard and the sample, it is customary to prepare the threshold standard at a concentration slightly below the reported test threshold. This "low bias" on the standard favors the assay toward producing false positives in order to reduce the false negative rate. The following 10 µg/L report threshold example illustrates:

Table 2. Example Assay Batch

Assay	Absorbance	Comment
threshold standard #1 (7 µg/L)	0.8	
threshold standard #2 (7 µg/L)	0.88	use the avg std response 0.84 for cutoff
LCS (10 µg/L)	0.6	pass
sample #1	0.97	ND <10
sample #2	0.92	ND <10
sample #3	1.02	ND <10
sample #4	0.86	ND <10
sample #5	0.4	positive >10
sample #6	0.55	positive >10
sample #7	0.7	positive >10*
NIS of ND sample #1(>10 µg/L)	0.57	pass
MS of ND sample #2(>10 µg/L)	0.86	fail - false negative**

* sample #7 may be a false positive at the test threshold since it falls between the. threshold standard and the LCS. In other words it may have herbicide present at 8 µg/L. It would be sent for 8150 confirmation.

** This MS illustrates a documented false negative which would trigger corrective action.

The threshold standard (7 µg/L) is intentionally lower than the reported test threshold (10 µpg/L) to reduce the false negative rate due to normal statistical variability and minor preparation losses and matrix interferences.

Quanterra intended to improve the sensitivity of the soil assay by reducing or eliminating the need for the large dilution used to reduce the impact of methanol on the antibodies. Evaporating the methanol from a small aliquot of sample extract, followed by reconstitution in water was effective at removing the methanol. However, this process also concentrated the interferences in the soil matrices and raised the level of non-specific antibody binding. Unfortunately, this raised the false positive rate to an unacceptable level. Thus, this preparation modification was not used in the validation study.

The silvex kit has not been "validated" for 2,4,5-T but the SDI cross reactivity data suggest that the silvex antibodies work similarly for 2,4,5-T threshold testing. 2,4,5-T was investigated along with 2,4-D and silvex for which the IA kits were designed. In fact, 2,4,5-T was detected by both the 2,4-D and silvex IA kits during the validation study. At least one kit produced an acceptable 2,4,5-T response for each sample included in the study.

This validation study builds on top of the existing studies and knowledge discussed above. Quanterra has demonstrated that the two IA herbicide kits are appropriate to screen out water and soil samples that have no detectable levels of 2,4-D, 2,4,5-T or silvex at the applicable reporting limits. This is not intended to replace Method 8151 for quantitation but to focus its use where it is most applicable. Since the extended IA method is not intended for quantitation and much validation work has already been completed for the IA kits very little additional direct comparison between IA and GC data is necessary to establish that the IA method is capable of screening out non-detect samples. We intended to utilize matrix spikes of well characterized matrices, matrix spikes of real samples (ND for herbicides by 8150/51) and a few real samples with herbicides that have been previously analyzed by 8150/51. Hereafter, herbicides that entered the sample by environmental transport mechanisms and have undergone aging and weathering are referred to as *native* herbicides, Unfortunately, the native herbicide samples that were available at the time of the validation study could not be used as intended because the analyte concentrations were much lower than the final test thresholds. To compensate, many of these samples were fortified with known amounts of each herbicide and included in the study as matrix spiked samples.

Validation Goal

The main goal was to demonstrate that the IA method responds to herbicide levels known to be at or above the IA reporting limit (threshold) for each analyte. Since samples with *native* herbicides above the final test thresholds were not available, the number of matrix spiked samples was significantly increased over the original validation plan. Water matrix spiked samples were increased from 6 to 18. Soil matrix spiked samples were increased from 7 to 12. Also, using matrix spikes allowed us to more accurately document performance at the critical area near the reporting limit. It was not necessary to analyze the matrix spiked samples with 8150/51 since the herbicide concentrations were already known. The matrix spiked soil samples were stored at 4°C at least overnight and usually for several days between spiking and extraction in order to age them and more closely mimic *native* analytes.

Validation Protocol

Matrix spiked samples were prepared using techniques previously employed for SW-846 methods development work. Separate spike solutions containing known amounts of each of the three target analytes were prepared at appropriate concentrations in acetone. These high concentration standards were further diluted in reagent water. Water samples were spiked with these aqueous solutions, homogenized by shaking and immediately assayed. Soil samples were spiked, acetone solvent evaporated at room temperature and tumbled overnight in a rotary mixer. The spiked soil samples were stored at least overnight at 4°C and usually for several days prior to extraction in order to "age" the samples and thus more closely mimic *native* soil samples. Obviously this process does not duplicate the extensive weathering which can occur in real environmental samples, but the combined use of short term "aging" and fuller's earth that is known to be difficult to extract should simulate many *difficult* samples. Each of the following sample-analyte combinations in Tables 3 & 4 was assayed at least once. Replicate analyses indicated in ().

Analytical Procedure Summaries

Water preparation

Allow particulates in water sample to settle, filter (0.45 µm PTFE) if sample is cloudy with suspended solids, aliquot 250 µL of sample into plastic assay tube. Aqueous matrix spike solution added as appropriate. TCLP buffers and samples were spiked as appropriate in a small vial. A 25 µL aliquot was transferred to the assay tube and 225 µL of diluent was added.

Soil preparation

Weigh 10 g of soil sample into 50 mL plastic centrifuge tube. Add acetone matrix spike solution as appropriate. Allow solvent to evaporate. Add 2-3 ball bearings. Tumble overnight (note: some wet clay samples formed large clumps during tumbling and were not tumbled when matrix spiking was required for additional analyses). After "aging", add 30 mL of extraction solvent (75% methanol, 23% reagent water, 2% acetic acid). Recap centrifuge tube, rotate onto side and mechanically shake at about 200 cycles/minute for 30 minutes. Stand centrifuge tubes up and allow soil to settle for 1 hour and/or centrifuge for 3-5 minutes. Filter (0.45 µm PTFE) a few milliliters of extract. Transfer 5 µL of extract into plastic assay tube and add 245 µL of diluent.

Table 3. Water Sample List and Matrix Spike Levels

Sample	No spike	Analyte					
		2,4-D µg/L		silvex µg/L		2,4,5-T µg/L	
		high	low	high	low	high	low
ground water	(10)	10	2(4)	10	5	10(27)	5
industrial waste water	(4)	10	2	10	5	10	5
TCLP buffer #1	(13)	100		100 (2)		100 (27)	
TCLP buffer #2		100 (7)		100 (7)			
TCLP Buffer #1 samples †							
X3		100		100			
02		100		100			
43		100		100			
01		100		100			
ZX		100		100			
Water samples †							
HN	(6)	10	2	10	5	10	5
HV	(7)	10	2	10	5	10	5
QK	(5)	10	2	10	5	10	5
5G	(4)	10	2	10	5	10	5
DA	(5)	10	2	10	5	10	5
W2	(6)	10	2 (8)	10	5	10	5
4JL	(5)	10	2	10	5	10	5
Performance Evaluations							
Wisc. PE	(3)						
WS038 PE	(3)						
Additional water samples screened for false positives †							
8H							
AH	(4)						
HK	(4)						
WC							
5V							
65							
6							
K1							
K2							
W3							
W6							
W7							
WA							
JW							
K0							

† Samples previously analyzed by 8150 but no herbicides detected.

Immunoassay

Allow all IA reagents (particularly the enzyme conjugate and antibodies) to warm to room temperature. Add sample or standard aliquot (250 µL final volume). Add 250 µL of enzyme conjugate. Add 500 µL of suspended antibody coupled magnetic particles and vortex mix for 1-2 seconds. Incubate at room temperature for 30 minutes. Apply magnetic rack base for 2 minutes to separate magnetic particles from bulk fluid in tubes. Pour out tube contents while the magnetic particles are retained at the bottom of the tubes. Rinse the antibodies twice with wash solution. Remove magnetic rack base. Add 500 µL of color development reagent and incubate for 20 minutes. Add 500 µL of sulfuric acid stop solution and read absorbance at 450 nm.

The assay tubes were arranged in a 3 X 10 layout in the SDI magnetic rack. Often two batches of 30 assays were performed simultaneously in the rack which holds a maximum of 60 tubes. A typical 30 tube layout is shown below. It was quite common in the early batches of the validation study to assay standards prepared by both SDI

and Quanterra® (QES) as a means of verifying the standards prepared in-house.

Table 4. Soil Sample List and Matrix Spike Levels

Sample	No spike	Analyte					
		2,4-D µg/kg		silvex µg/kg		2,4,5-T µg/kg	
		high	low	high	low	high	low
sandy soil	(5)	1.0	0.3 (2)	1.5		1.5 (2)	
loam soil	(4)	1.0	0.3 (2)	1.5		1.5 (2)	
fuller's earth* (dry)	(4)	1.0	0.3 (2)	1.5		1.5 (2)	
fuller's earth* (50% moisture)	(3)	1.0	0.3	1.5		1.5	
Soil -samples †							
03		1.0	0.3	1.5		1.5	
04		1.0	0.3	1.5		1.5	
2N		1.0	0.3	1.5		1.5	
36		1.0	0.3	1.5		1.5	
20		1.0	0.3	1.5		1.5	
20	(4)	1.0	0.3	1.5(8)		1.5 (8)	
22	(4)	1.0	0.3	1.5		1.5 (8)	
25		1.0	0.3	1.5		1.5	
1V		1.0		1.5		1.5	

* Fuller's earth is an absorptive clay known to *challenge* the efficiency of solid extraction procedures.
† Samples previously analyzed by 8150 but no herbicides detected above (or near) spike concentrations.

Raw Response Data

The average difference in response between duplicate SDI and QES standards was 4%. The response difference between silvex and 2,4,5-T was small (average 12.5%) and 2,4,5-T consistently produced less response. Thus, 2,4,5-T was used as the threshold compound for all silvex kit assays in order to reduce the false negative rate, particularly for 2,4,5-T containing samples. The test threshold standards were prepared at 70% of threshold concentration (0.7 x expected reporting level) in order to reduce false negatives for water matrices. Threshold standards were prepared at 50% of the threshold concentration for the soil assays.

Table 5. Example IA Batch Layout for 2,4-D kit assays - 10 µg/L Reporting Level and matrix spikes

	A	B	C	D	E	F	G	H	I	J
1	QES "10" std	GW	GW+ ***D***	TCL P	TCLP + ***D***	WW	WW + ***D***	W1	W1+ ***D***	SDI "10" std
2	W2	W2+ ***D***	W3	W3+ ***D***	QES LCS at 10 RL	SDI LCS at 10 RL	W4	W4+ ***D***	W5	W5+ ***D***
3	SDI "10" std	W6	W6+ ***D***	W7	W7+ ***D***	Wisc PE	Wisc PE	WS038 PE	WS038 PE	QES "10" std

Key:
QES "10" std = 7 µg/L 2,4-D standard prepared by Quanterra
SDI "10" std = 7 µg/L 2,4-D stock standard prepared by SDI
QES LCS at 10 RL = 10 µg/L 2,4-D standard prepared by Quanterra
SDI LCS at 10 RL = 10 µg/L 2,4-D stock standard prepared by SDI
D = 2,4-D spiked sample (10 µg/L)
GW = Ground water
TCLP = TCLP buffer #1 [10 X dilution]
WW = Industrial waste water
W1, W2, W3, W4, W5, W6, W7 = real water samples without *native* herbicides
PE = Performance evaluation samples from Wisconsin and EPA WS038 programs.

Results and Discussion

The key questions when evaluating the reliability of this screening method are:
1) If an analyte is present in a sample at a concentration greater than or equal to the threshold (i.e. reporting

limit), what are the chances of the assay generating a false negative response?

2) If no analyte is present in a sample at or above the threshold concentration, what are the chances of the assay generating a false positive response?

Table 6. Threshold Standards

Threshold Level (reporting limit)	Compound	actual standard concentration
	water samples	
2.0 µg/L	2,4-D	1.4 µg/L 2,4-D
10. µg/L	silvex or 2,4,5-T	7.0 µg/L 2,4,5-T
	soil samples	
1.0 mg/kg	2,4-D	3.3 µg/L 2,4-D
1.5 mg/kg	silvex or 2,4,5-T	5.0 µg/L. 2,4,5-T

False negatives are undesirable since they would report a sample as "clean" with regard to the target herbicides when it was not and potentially increase environmental health risks. False positives are undesirable since they would needlessly "trigger" a batch of traditional 8151 analyses which would increase organic solvent usage, analyst exposure to hazardous reagents, turn-around time and cost.

Since the same number of replicates were not run for each sample it is not appropriate to simply divide the number of false negatives or positives by the total number of assays. The false negative or positive rate was determined for each sample - analyte combination or unspiked sample. These individual rates were then averaged to determine the overall false negative and positive rates. LCS results were not included in these calculations because they do not contain real sample matrix. The false negative rate must meet the normal Office of Solid Waste criteria, ≤5%. The false positive rate was expected to be ≤10%.

The matrix spike results from samples producing consistent false positive responses were not included when calculating the false negative rates for either water or soil samples.

Water Samples

Production threshold levels of 2 µg/L for 2,4-D and 10 µg/L for silvex and 2,4,5-T were selected after evaluating the initial water sample data. Table 7 summarizes the percentage of false positives and false negatives for each sample - analyte combination.

The overall false negative rate of 0.5% for water samples was excellent. Sample W2 had one false negative among 8 replicates at the 2 µg/L threshold for 2,4-D for a false negative rate of 12.5% for this sample - analyte combination. The ground water (GW) and TCLP buffer #1 produced many false negatives for 2,4,5-T when assayed with the silvex kit at the 10 µg/L (GW) and 100 µg/L (TCLP) levels. Keeping the spike levels and analyte the same but switching to the 2,4-D kit significantly improved the assay reliability. The false negative rates dropped to 16.7% and 5.9% for these two matrices respectively. Since 2,4,5-T is not a normal TCLP analyte these false negatives have little practical impact on assays of TCLP samples, although this does indicate that 2,4,5-T may be more susceptible to false negatives than the other two analytes. The ground water false negative rate was reduced by assaying for 2,4,5-T with the 2,4-D kit as noted above. This indicates that either immunoassay kit will respond to 2,4,5-T and that at least one kit is likely to produce a positive response at the 10 µg/L threshold when 2,4,5-T is present.

The false positive rate was determined by dividing the total number of "non-detect" samples included in the study into the number of samples that produced false positives for a false positive rate of 12.5%. Replicate assays were performed on two of the samples that produced false positives. This confirmed that a matrix interference existed which produced the false positive. One of the false positive sample responses was near the response of the threshold standard and probably would not produce a false positive in all instances if replicate assays were performed. It appears that false positives are primarily generated by matrix interferences. Thus, positive matrix interferences are likely to be site specific and the false positives that do occur in actual production use of the IA kits should be clustered together in a limited number of sample lots. This means that most of the sample lots assayed are expected to be free of false positives.

Table 7. False Negative and False Positive Rate Calculations for Water Samples

Matrix or sample	No spike % false positives	2,4-D % false negatives	Silvex % false negatives	2,4,5-T % false negatives
ground water	0	0	0	3/18 = 16.7
waste water	0	0	0	0
TCLP buffer #1	0	0	0	1/17 = 5.9
TCLP buffer #2	0	0	0	
X3	0	0	0	
02	0	0	0	
43	0	0	0	
01	0	0	0	
ZX	0	0	0	
HN	0	0	0	0
HV	0	0	0	0
QK	0	0	0	0
5G	0	0	0	0
DA	0	0	0	0
W2	0	1/8 = 12.5	0	0
JL	0	0	0	0
Wisc PE		0	0	
WS038 PE		0	0	
Matrix or sample	No spike % false positives	2,4-D % false negatives	Silvex % false negatives	2,4,5-T % false negatives
8H	0			
AH	100			
HK	100			
WC	0			
5V	0			
63	0			
65	0			
6	0			
K1	0			
K2	0			
W3	0			
W6	0			
W7	100			
WA	0			
JW	0			
K0	100			
Average rates	12.5%	0.7%	0%	2.3%
		overall false negative rate 0.5%		

Soil samples

Attempts to improve the sensitivity of the soil method were unsuccessful. Initial information from SDI indicated that the 50X extract dilution included in the SDI soil preparation method was designed to remove the deleterious effect that methanol has on the immunoassay. We intended to remove the methanol interference by evaporating a small aliquot of the extract to dryness then redisolving the analytes in diluent solution or water. Analyte recovery appeared acceptable and there was no visible methanol residue, but there was still some small positive interference which probably would have prevented reliable assays at the 30 µg/kg target threshold. Real soil extracts showed very large positive interferences when 250 µL of extract were concentrated for the assay. Thus, it was necessary to restrict to soil preparation to the original SDI/Ohmicron soil prep method. This was accomplished by diluting 5 µL of extract with 245 µL of diluent. When this 50X dilution was combined with higher analyte spike levels the interference problems were reduced to an acceptable level.

The following preparation method was used for most soils: 10 g soil + 30 mL extract solvent, shake for 30 minutes, settle or centrifuge, filter, 5 µL of extract + 245 µL diluent. Thus, the final concentration of analytes

presented to the assay were 150X more dilute than in the original soil sample. Quantities of some samples were limited so the preparation amounts were scaled back to 5 g soil and 15 mL of extraction solvent. The assay threshold standard concentrations reflected the dilution built into the sample prep. Most spike levels were 1.0 mg/kg for 2,4-D and 1.5 mg/kg for silvex and 2,4,5-T. Some low level (0.03 and 0.3 mg/kg) work was attempted, but the false positive rate was unacceptably high.

The concentration of the test threshold standard concentration was also reduced from 70% to 50% of threshold for soil assays. This decreased the false negative rate without unacceptably raising the false positive rate. Table 8 below shows 3 soil - analyte combinations had false negative results for silvex or 2,4,5-T when spiked initially at 1.5 mg/kg. Replicate sample aliquots were spiked, extracted and assayed. No additional false negative results were produced. Thus, the overall false negative rate was 1.0%, which is excellent. False positive results were reported for two samples at the 1.0 mg/kg 2,4-D or 1.5 mg/kg silvex/2,4,5-T assay levels. The overall false positive rate for soil samples was 11.5%. It is expected that false positives will be primarily caused by specific constituents in the soil samples and are thus more likely to be related to specific sites rather than be evenly distributed through all sample lots.

Table 8. False Negative and False Positive Rate Calculations for Soil Samples

Matrix or sample	No spike % false positives	2,4-D % false negatives	Silvex % false negatives	2,4,5-T % false negatives
ground water	0	0	0	0
loam soil	0	0	0	0
fullers earth dry	0	0	0	0
fullers earth wet	0	0	0	0
03	50	0	0	0
04	0	0	0	0
2N	0	0	0	0
36	0	0	0	0
2E	100			
20	0	0	1/8 = 12.5	1/8 = 12.5
22	0	0	0	1/8 = 12.5
25	0	0	0	0
1V	0	0	0	0
Average rates	11.5%	0%	1.0%	2.1%
		average false negative rate = 1.0%		

The soil extraction procedure did not appear to suffer any serious extraction efficiency problems despite its simplicity and short time frame. Even though the IA results were not quantitative, the low false negative rate indicates that analyte recovery was > 50% and many recoveries were > 70%. Previous Quanterra work with wet fullers earth with nonpolar analytes and solvents, showed very low (<20%) analyte recovery for hydrocarbons. Good extraction efficiency of the phenoxy acid herbicides with the simple shake extraction used with these IA kits was probably due to the following reasons: 1) The polar extraction solvent (methanol / water / acetic acid) readily permeated the wet clay matrix. 2) The polar solvent molecules could effectively displace polar analyte molecules from the polar sorption sites on the matrix. 3) The polar analytes were readily soluble in the polar extraction solvent.

Conclusion

The validation study results are summarized in Table 9 below. The false negative rates easily meet the normal EPA Office of Solid Waste criteria of ≤5%. The. false positive rates although slightly higher than the target 10%, are still acceptable. The water reporting limits are in the low part-per-billion range and meet the validation plan minimum objectives. In particular, analyses from TCLP buffers and samples demonstrated excellent performance for 2,4-D and silvex at levels well below the regulatory limits. The soil reporting limits although higher than originally expected should still be useful for many types of herbicide samples.

Table 9. Summary of Performance Results and Reporting Limits

Matrix	2,4-D	Silvex	2,4,5-T	False Negative	False Positive
water	2 µg/L	10 µg/L	10 µg/L	0.5%	12.5%
soil	1 mg/kg	1.5 mg/kg	1.5 mg/kg	1.0%	11.5%

Acknowledgments
The authors would like to thank Allen Debus from US EPA, Region 5, Craig Kostyshyn and Timothy Lawruk from Strategic Diagnostics and Susie Dempster, Carolynne Roach, Chris Lee and Richard Burrows from Quanterra Inc.

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3. SW-846 Method 4015 - Screening for 2,4-Dichlorophenoxyacetic Acid by Immunoassay.

FIELD DEMONSTRATION OF A PORTABLE IMMUNOSENSOR FOR EXPLOSIVES DETECTION

Anne W. Kusterbeck[1], Paul T. Charles[1], Paul R. Gauger[2] and Charles Patterson[1]
[1]Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC 20375
phone: 202 404-6042, fax: 202 404-8897
akusterbeck@cbmse.nrl.navy.mil
[2]GeoCenters, Inc., 1801 Rockville Pike, Suite 405, Rockville, MD 20852-1633

Environmental biosensors are being developed at the Naval Research Laboratory for detection of the explosives TNT and RDX in groundwater and monitoring of cleanup progress for these compounds at remediation sites. Based on a displacement immunoassay, the portable sensor, known as the FAST 200, has been engineered by Research International (Woodinville, WA) to quantitate water samples with no sample preparation or reagent addition. Analysis is complete within five minutes. The sensor, along with a fiber optic biosensor, recently was extensively tested in field trials at several U.S. EPA Superfund sites to validate sensor performance. Results of these studies and application of the technology will be described.

ENVIRONMENTAL APPLICATIONS OF A FIBER OPTIC BIOSENSOR

Lisa C. Shriver-Lake[1], Irina B. Bakaltcheva[2], and Saskia van Bergen[3]
[1]Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC 20375
phone: (202) 404-6045, fax: (202) 404-8897
email: lcs@cbmse.nrl.navy.mil
[2]GeoCenters, Inc., 1801 Rockville Pike, Suite 405, Rockville, MD 20852-1633
[3]George Mason University, 4400 University Drive, Fairfax, VA 22030-4444

Detection and remediation monitoring of the explosives TNT and RDX on-site requires a sensitive and preferably portable method. The fiber optic biosensor is based on a competitive fluoroimmunoassay being performed on the core of an optical fiber probe. A portable version of the sensor was engineered by Research International (Woodinville, WA) and is known as the Analyte 2000. With this sensor, four optical probes can be monitored simultaneously and relatively Adirty@ samples can be employed. Analysis takes 16 minutes for the four probes. This sensor, along with the FAST 2000, was extensively evaluated at three on-site trials to validate sensor performance. Results of these studies and other applications for the fiber optic biosensor will be described.

DEVELOPMENT AND VALIDATION OF AN IMPROVED IMMUNOASSAY FOR SCREENING SOIL FOR POLYNUCLEAR AROMATIC HYDROCARBONS

Titan S. Fan and Brian A. Skoczenski
Beacon Analytical Systems, Inc., 4 Washington Ave., Scarborough, ME 04074

Polynuclear aromatic hydrocarbons (PAHs) are a group of fused ring compounds most typically found as combustion by-products. Over the past 4 - 5 years a number of immunoassay kit manufacturers have developed and commercialized soil screening method for PAHs. Briefly, there methods involve a rapid extraction of soils by shaking with methanol followed by analysis of the filtered sample extract using competitive enzyme immunoassay. We have developed an improved method for screening of PAHs in soil samples. The new method utilizes a modified sample extraction step that results in improved extraction efficiency compared to earlier methods. In addition, the specificity of the antibody used in the method allows for a better estimate of the total PAHs present. Immunogen design and antibody specificity will be described in detail. Results of concordance study with a gas chromatographic method will be presented.

A NEW DIOXIN/FURAN IMMUNOASSAY WITH LOW PICOGRAM SENSITIVITY AND SPECIFICITY APPROPRIATE FOR TEQ MEASUREMENT: APPLICATIONS DEVELOPMENT

Robert O. Harrison
CAPE Technologies, L.LC, 3 Adams St., South Portland, ME 04106
Robert E. Carlson
ECOCHEM Research, Inc., 1107 Hazeltine Blvd, Chaska, MN 55318

Since 1990 the commercial development of immunoassay kits his opened a new market in environmental analysis. The US EPA has approved more than 10 immunoassay screening methods under the 4000 series of Field Screening Methods within SW-846. These tests are now widely used in assessment and remediation of hazardous waste sites.

This recent success has not included the development of a useful immunoassay method for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The development and application of immunoassays for PCDD/Fs pose unique challenges not found in immunoassays for other analytes. First, the sensitivity requirements of PCDD/F analysis are typically in the ppt range rather than the high ppb to mid ppm range of the existing 4000 series screening methods. Second, if the test is to provide useful data, the EIA response must correlate to the relative toxicity of the 17 most toxic PCDD/F congeners. No previous immunoassay has demonstrated the necessary combination of sensitivity and specificity required for measurement of toxic equivalency (TEQ) at ppt levels. No immunoassay specific sample preparation methods have been developed because of the obvious lack of commercial potential demonstrated by all previous PCDD/F immunoassays

A new enzyme immunoassay (EIA) for PCDD/Fs has been developed using novel chemistry. The sensitivity of this test is approximately 4 pg of 2378-TCDD, which is more than an order of magnitude better than previous PCDD/F immunoassays. Based on typical sample size, this sensitivity is sufficient to measure low ppt TEQ levels in solid samples or 0.1 ng/m^3 TEQ in stack gases using only a small fraction of the prepared sample extract. This sensitivity allows detection of 2378-TCDD in a 10 µL sample aliquot at the same concentration as the lowest calibration solutions typically used for HRGC/HRMS based PCDD/F methods such as EPA Methods 1613, 8290, and 23. These sensitivity comparisons indicate that the EIA is capable of screening samples prior to HRGC/HRMS analysis without consuming an unacceptably large proportion of the sample.

The dioxin/furan congener cross-reaction profile of this EIA is suitable for TEQ measurement. The test is most sensitive to the three most toxic congeners, 2378-TCDD, 12378-PnCDD, and 23478-PnCDF EIA specificity data plus HRGC/HRMS data from previously analyzed samples have been utilized in a simple, additive response model to predict the EIA response for each sample. The resulting correlation between predicted EIA response and TEQ validates the concept of TEQ screening by EIA for a variety of samples.

A muliti-laboratory collaborative effort is now in progress for evaluation of kit performance and development of sample preparation methods. Results for fly ash and soil validate the additive response model for TEQ measurement by EIA. These results also validate the use of the kit for screening fully cleaned samples. Extension of this validation to partially cleaned samples is in progress, with positive initial results for fly ash and soil. Work on immunoassay specific sample preparation methods, including rapid extraction of soil and fly ash, is also in progress. The ultimate goal of this coli program is to develop sample preparation protocols which will maximize throughput and cost-effectiveness of immunoassay based PCDD/F screening.

DEVELOPMENT AND VALIDATION OF AN IMMUNOASSAY FOR SCREENING SOIL FOR POLYCHLORINATED BIPHENYLS

Titan S. Fan and Brian A. Skoczenski
Beacon Analytical Systems, Inc., 4 Washington Ave., Scarborough, ME 04074

Polychlorinated Biphenyls (PCBs) were commonly used in electrical applications due to their properties of high thermal transfer and low conductivity. Since being identified as toxic substances their use has been banned in the US. Due to the once widespread use and their stability in the environment a large number of sites are contaminated with PCB residues. A number of immunoassay kit manufacturers have developed and commercialized soil screening methods for PCBs. Briefly, these methods involve a rapid extraction of soils by shaking with methanol followed by analysis of the filtered sample extract using competitive enzyme immunoassay. We have developed an improved method for screening of PCBs in soil samples. The new method utilizes a modified sample extraction step that results in improved extraction efficiency compared to earlier methods. The immunoassays performed on the sample extract and yields qualitative results at 1, 5, 10 or 50 ppm. The test can be used for measuring Aroclors 1016, 1242, 1248, 1254 and 1260. Results of a concordance study with a gas chromatographic method will be presented.

GASOLINE RANGE AROMATIC/ALIPHATIC ANALYSIS USING PATTERN RECOGNITION

Steven E. Bonde
Petro Star Inc., 201 Arctic Slope Ave., Suite 200, Anchorage, Alaska 99518-3030

Finding an analytical technique for the analysis of aromatic and aliphatic compounds in the gasoline range of hydrocarbons is of great interest to not only the laboratory but also the regulated community. In many states, including Alaska, great pressure to apply risk based cleanup standards is driving the need to separate "high risk compounds" from a given matrix in an economical manner with high confidence. False positives can mean an unneeded costly cleanup, while false negatives can mean non-compliance and possible fines if found. Analysis of aromatic and aliphatic compounds in the gasoline range has been accomplished using pattern recognition algorithms based on PCB matching criteria. Using existing methodologies for the analysis of gasoline range hydrocarbons in multimedia samples by GC-FID-PID this algorithm has been developed using widely available software to recognize and quantify aromatic hydrocarbons in a given sample. Soil, sediment, and water samples were analyzed using standard Alaska Department of Environmental Conservation methodology (AK101/EPA8021) and the results of pattern matching showed a significantly reduced number of false positives for the aromatic portion of the analysis.

BIOREMEDIATION ASSESSMENT USING CONSERVED INTERNAL BIOMARKERS

P. Caleavecchio, E.N. Drake, G.C. VanGaalen and A. Felix
Corporate Research Laboratories, Exxon Research and Engineering Company,
Rt. 22 East, Annandale, New Jersey 08801
(908) 730-2308

ABSTRACT

The lack of homogeneity of field samples is often a primary concern in the analytical assessment of hydrocarbon bioremediation treatment efficacy. One approach to handling the sampling variability is to take a statistically significant number of samples to adequately represent the distribution of the contaminant. This approach is limited in that small biodegradation changes often cannot be seen within the inherent sampling variability. An additional drawback of this approach is the high cost of analyzing sufficiently large numbers of samples to draw conclusions.

An alternative approach, which can minimize the effects of sampling variability, is to use naturally occurring molecules, which resist biodegradation as conserved internal "biomarkers". There are a number of marker classes commonly found in petroleum products, which can be analyzed by GC/MS, these include hopanes, steranes and isoprenoids. These markers can be used as the basis for relative comparisons of target analytes before and after treatment. The ratios of two or more markers can also be used as a fingerprint to help identify the petroleum product source.

This poster demonstrates the application of biomarker normalized GC/MS data to evaluate the biodegradation of petroleum products from well-mixed refinery sludge waste. A comparison is shown tracking the treatment progress using absolute target analyte quantities and relative amounts normalized to biomarkers. The results show that the biomarker normalized data provided a good basis for determining the percent biodegradation of total oil as well as the molecular components, similar to the results obtained using absolute quantities.

The conclusions of the above study indicate that although significant amounts of 2, 3, 4 and 5 ring polynuclear aromatic hydrocarbons (PAHs) were removed during treatment the biomarkers used to normalize the data were conserved, resisting significant biodegradation. The implication of this work is that the use of biomarkers can be effective in situations that are less homogeneous to assess biodegradation of petroleum constituents from products with similar sources.

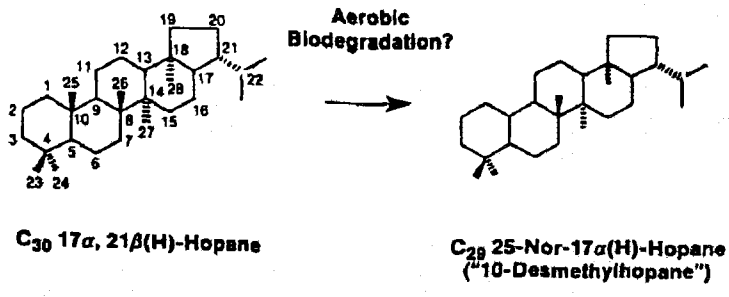
INTRODUCTION

The objective of the following study was to remediate a refinery process sewer sludge, through aerobic biodegradation, using composting to accelerate this process. Composting is a modification of the "biopile" process, which includes the addition of biodegradable ammendments (straw, wood chips, manure, etc.) to help aerate and supply energy for microbial growth. The laboratory scale evaluation was conducted in three-liter insulated glass beakers designed to minimize the loss of heat generated by the compost.

To minimize the effects of sludge heterogeneity on analytical results, a number of steps were taken which included mixing the sample well. An additional approach was to use naturally occurring "biomarker" molecules, which resist biodegradation, as internal standards. The latter approach was taken considering that future field applications would probably have much higher sampling variability due to the difficulty in homogenizing large volumes of compost.

The sludge used in these tests had significant amounts of two biomarkers typically found in petroleum products, C_{30} 17*a*, 21*B*(H)-Hopane ("hopane") and C_{29} 25-Nor-17*a*(H)-Hopane ("norhopane"). The above molecules are related by a mechanism proposed by Peters and Moldowan that suggests the origin of norhopane through the biological demethylation of hopane (see figure 1). Both biomarkers were found by selective ion (SIM) GC/MS at *m/z* 191, norhopane also has a characteristic peak at *m/z* 177.

The progress of the composting experiments were tracked by periodic sampling during the period of peak biological activity as indicated by naturally occurring elevated temperatures within the cells. The analytical tests performed on the extracted hydrocarbon included Total Petroleum Hydrocarbon (TPH, modified New Jersey method OQA-QAM-025-10/91) and GC/MS analysis for priority pollutant (PP) polynuclear aromatic hydrocarbons (PAHs). The TPH data was quantified by total ion GC/MS response using an external calibration of free oil



Proposed origin of 25-norhopanes by bacterial demethylation of 17α (H)-hopanes. The methyl group attached to the C-10 position in the C_{30} 17α (H)-hopane (left) is removed to produce the C_{29} 25-norhopane (right).

Figure 1. Proposed origin of norphopane from hopane

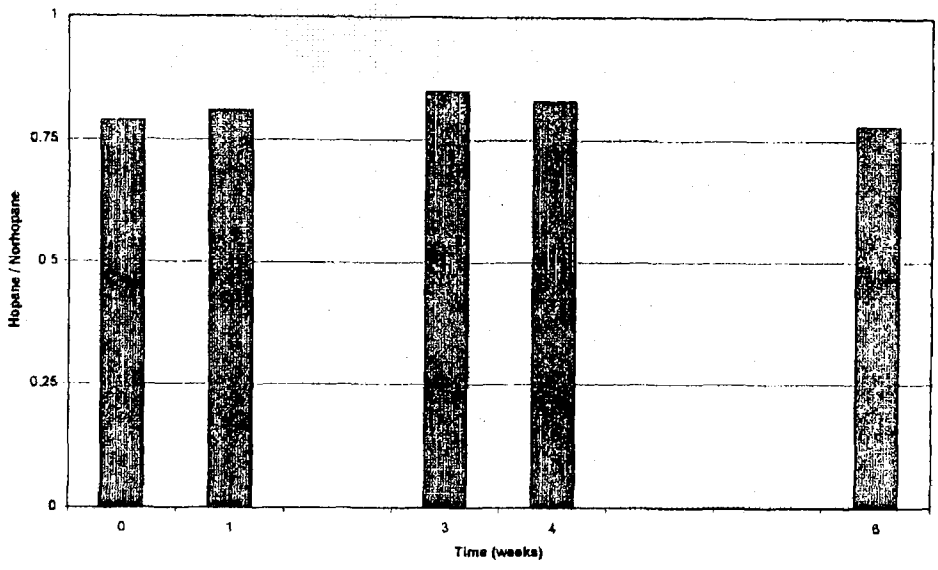


Figure 2. Biomarker ratio of hopane/norhopane

collected from the sludge. The PAHs were quantified using internal standards spiked into the extracts as prescribed in EPA SW846 method 8270.

The "biomarker normalized" data was obtained by dividing the GC/MS response of the analyte by that of hopane. The degradation measured relative to hopane was then compared to the "absolute" values obtained using the traditional approach described in the above paragraph. The conservation of hopane throughout the test, was monitored by comparing its GC/MS response relative to that of norhopane.

SUMMARY

The results show that rapid degradation of both TPH and PAHs occurred over the six-week period of the composting experiments, using both the absolute measurement and the hopane normalized approach. During this period there was no indication to suggest that significant hopane degradation occurred as shown by little change in the ratio of hopane to norhopane (see figure 2). Also qualitative examination of the biomarker's ion chromatograms at *m/z* 191 and 177 show little change before and after treatment (see figures 3 and 4). In contrast, the total ion chromatogram of the extracted hydrocarbon shows significant removal of the oil during treatment (see figure 5).

The TPH removal during treatment is shown in figure 6, which compares the absolute measurement to the hopane normalized results. These results show somewhat higher degradation estimates relative to hopane, ranging from 4% higher after one week to 30% higher after 6 weeks of treatment. The comparison of a selection of the more abundant 3, 4 and 5 ring PP PAHs using the absolute and hopane-normalized approaches is shown in figures 7 and 8 respectively. This comparison shows good agreement for phenanthrene and pyrene measurements using both approaches, with a somewhat lower estimate for the hopane normalized benzo(a)pyrene degradation (~ 30% lower). The lower concentration of benzo(a)pyrene (1 ppm) compared to

phenanthrene (27 ppm) and pyrene (15 ppm) may have attributed to the variability seen in its degradation measurements.

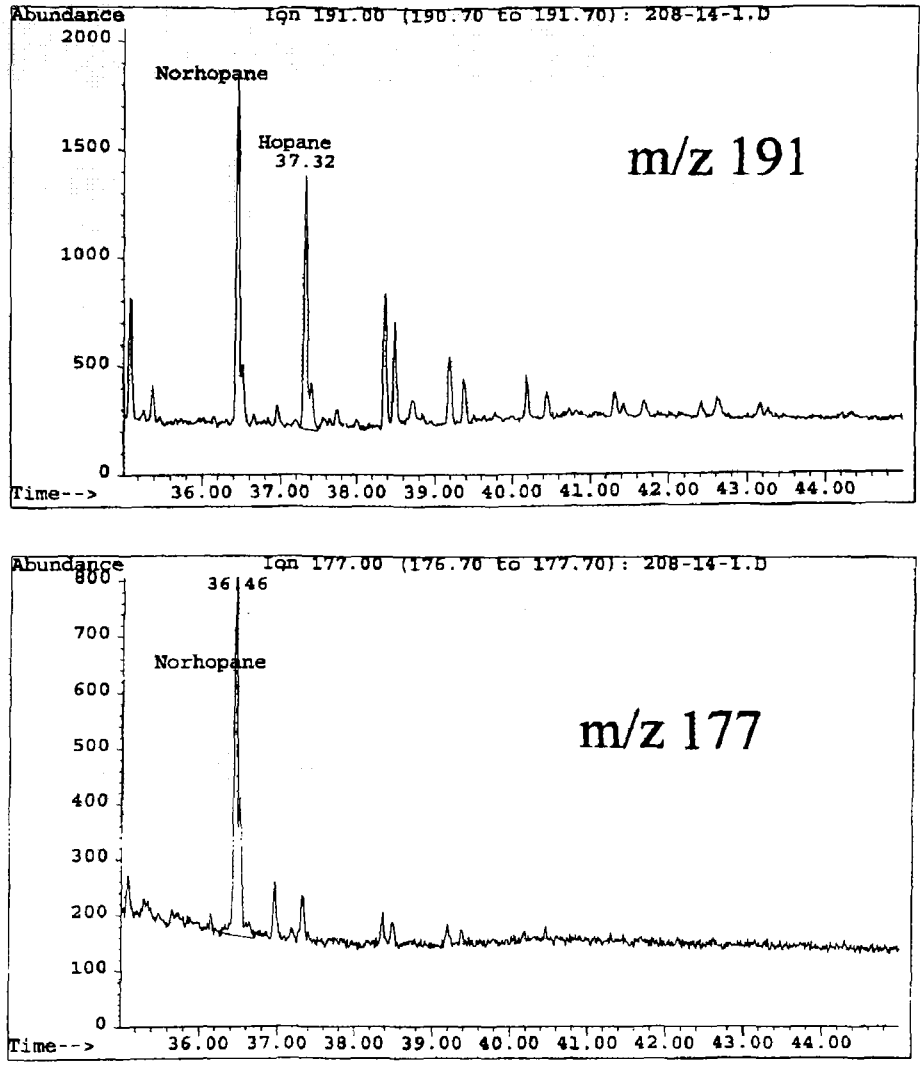


Figure 3. Before treatment ion chromatograms with hopane and norhopane

The degradation of the C1, C2 and C3 alkylated homologs of phenanthrene and anthracene are shown in figures 9, 10 and 11 respectively. This comparison shows very close agreement between the absolute and hopane normalized approaches (less than 10% difference) over the duration of the composting experiments.

CONCLUSIONS

This work demonstrates a practical application using selective ion GC/MS to characterize the biodegradation of petroleum contaminants relative to naturally occurring biomarkers. The hopane and norhopane biomarkers used in the above composting experiments showed no sign of significant biodegradation over the tests duration, while 2, 3, 4 and 5 ring PAHs as well as TPH showed rapid biodegradation. A comparison of biodegradation measurements using conventional quantification and biomarker normalized approaches showed good agreement for the most abundant analytes with somewhat higher variability for those in low concentrations.

The biomarker approach was easy to use and is independent of many sources of analytical and sampling variability associated with absolute measurements of analytes. Although this was a controlled experiment using a relatively homogeneous sludge, many pilot and field applications often deal with a wide range of contaminant distribution, resulting in sampling variability which is difficult to handle. The large numbers of samples needed to measure statistically significant changes can be avoided using biomarkers since analyte responses are normalized to stable (naturally occurring) internal standards.

An additional benefit of biomarkers is in site characterization of petroleum spills where ratios of two or more biomarkers can be used as a fingerprint to help identify the source of the contaminant. The degree of weathering and natural attenuation in various areas of a spill can also be assessed using this approach.

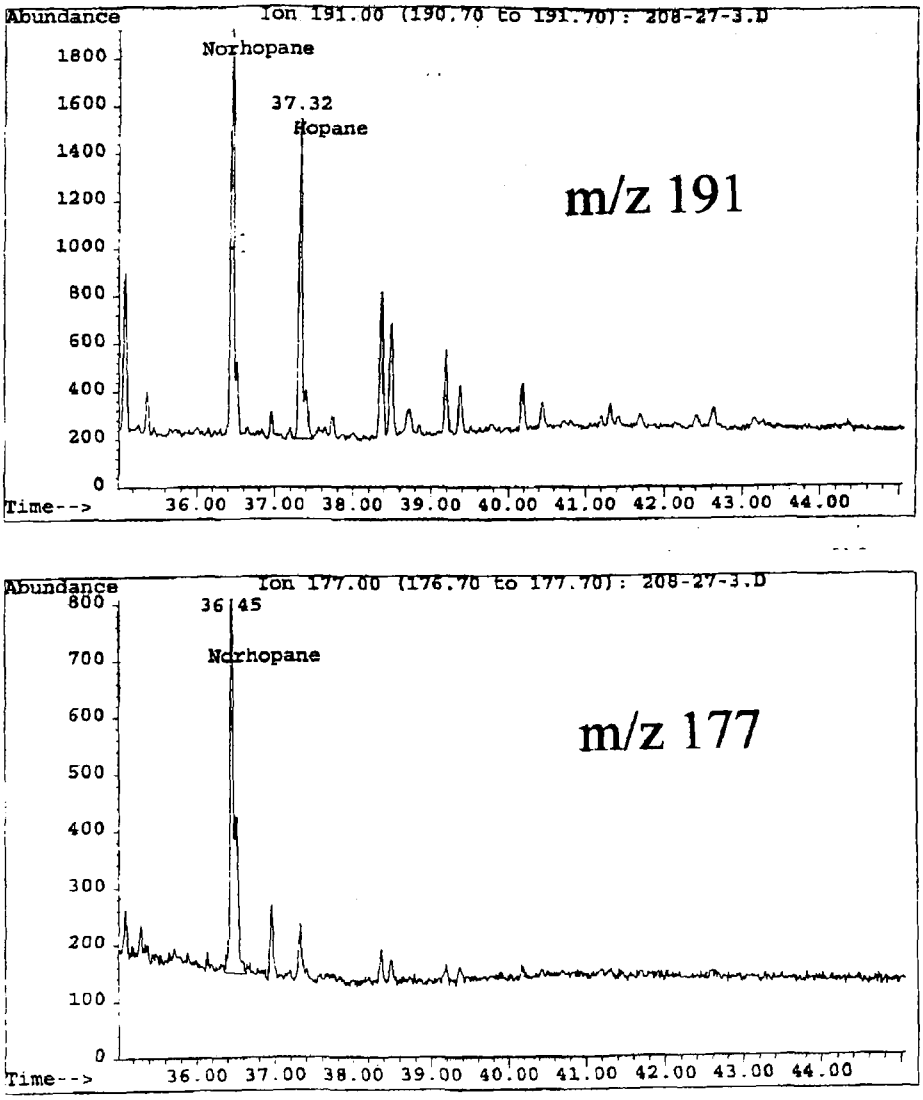


Figure 4. After treatment ion chrmatograms with hopane and norhopane

ACKNOWLEDGMENTS

Dr. Roger C. Prince for his insights into the application of biomarkers to oil spills.

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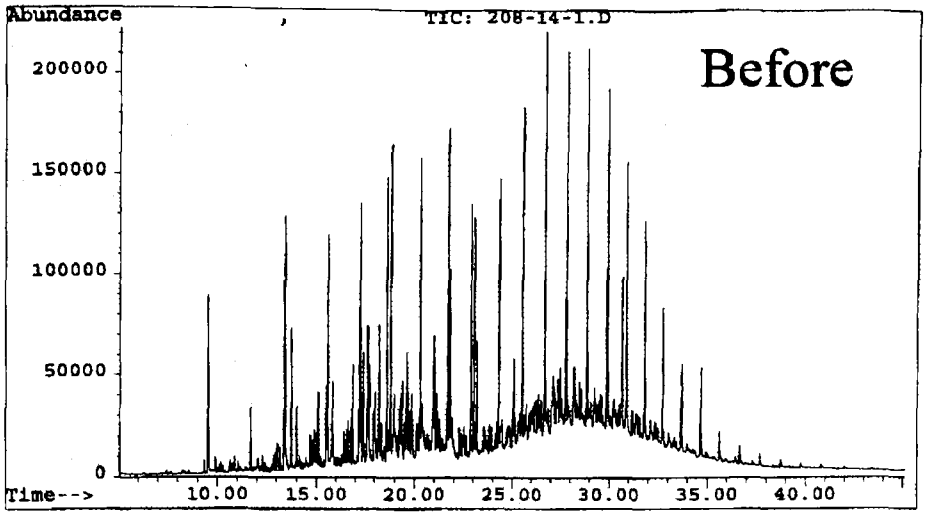

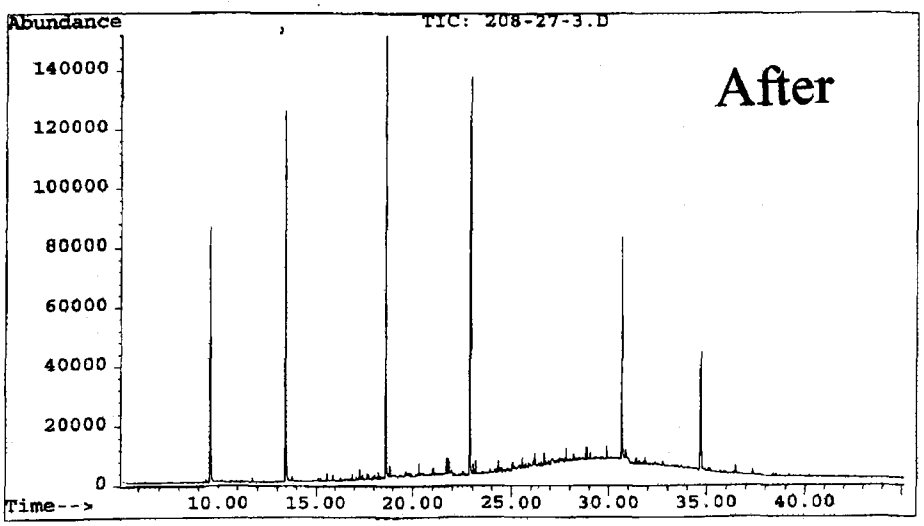

Figure 5. Before and after treament total ion chromatograms

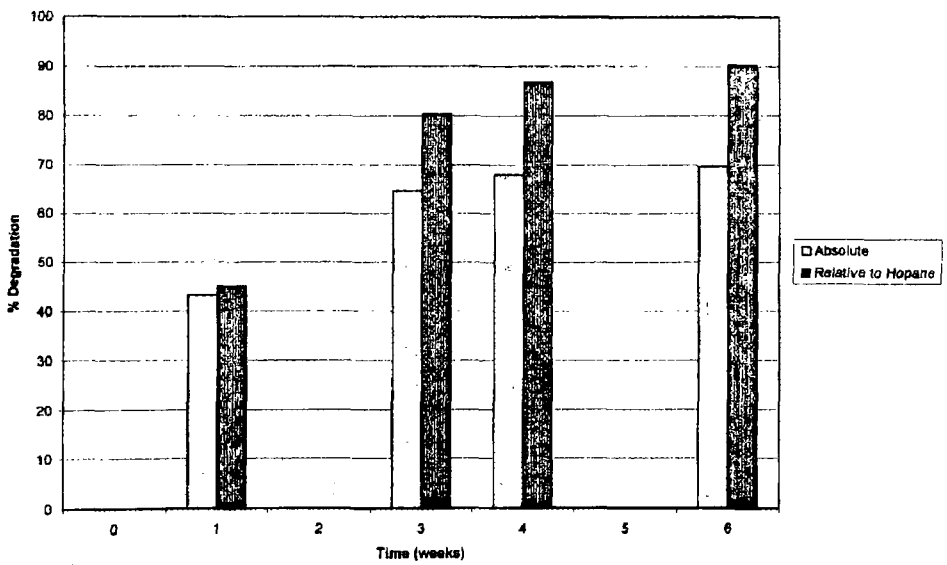

Figure 6. Comparison of absolute and relative TPH (GC) degradation

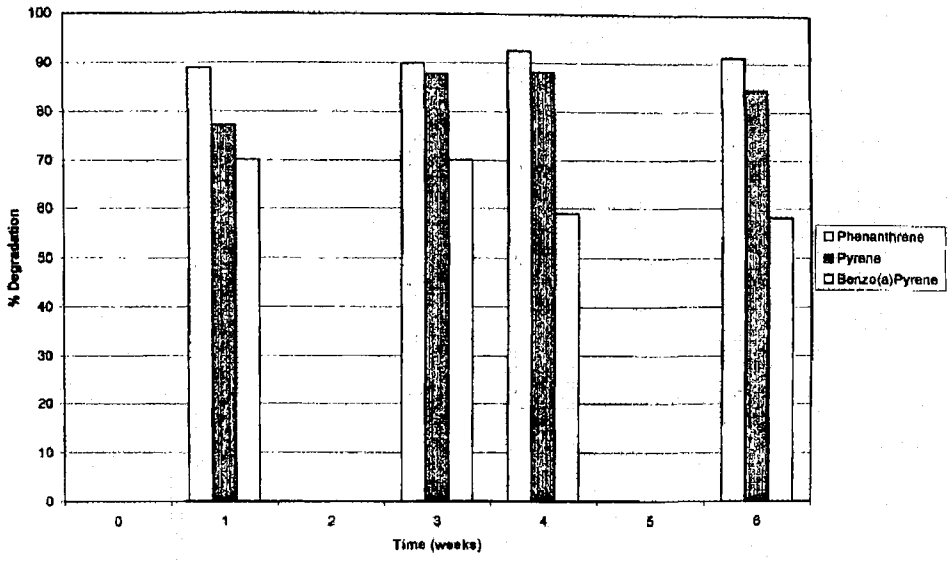

Figure 7. Degradation of 3, 4 and 5 ring PAHs absolute values

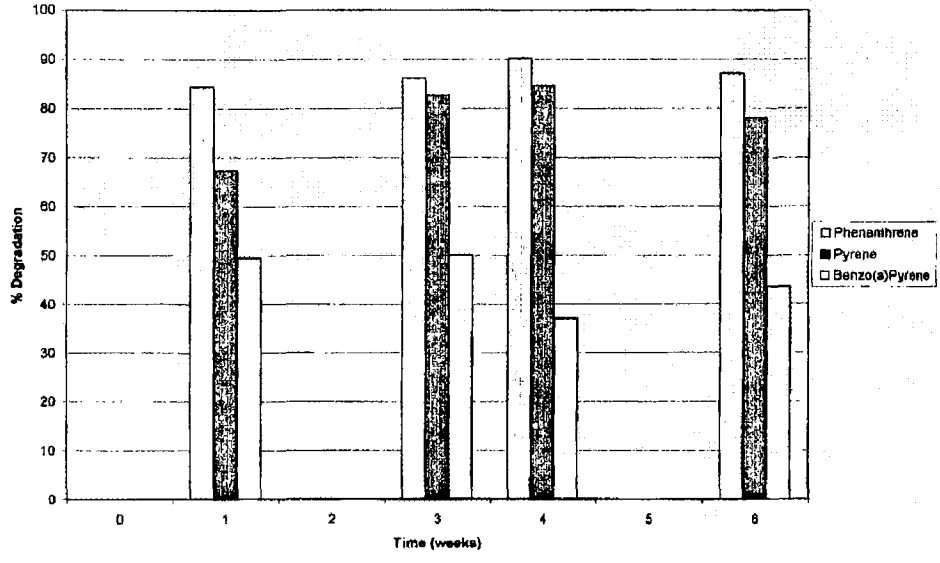

Figure 8. Degradation of 3, 4 and 5 ring PAHs relative to hopane

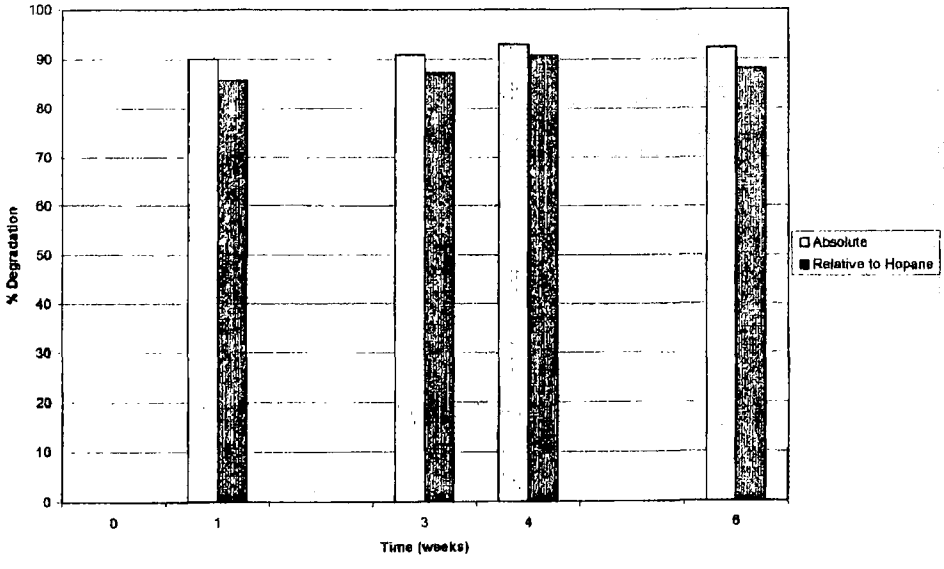

Figure 9. Comparison of absolute and relative C1-phenanthrene / anthracene degradation

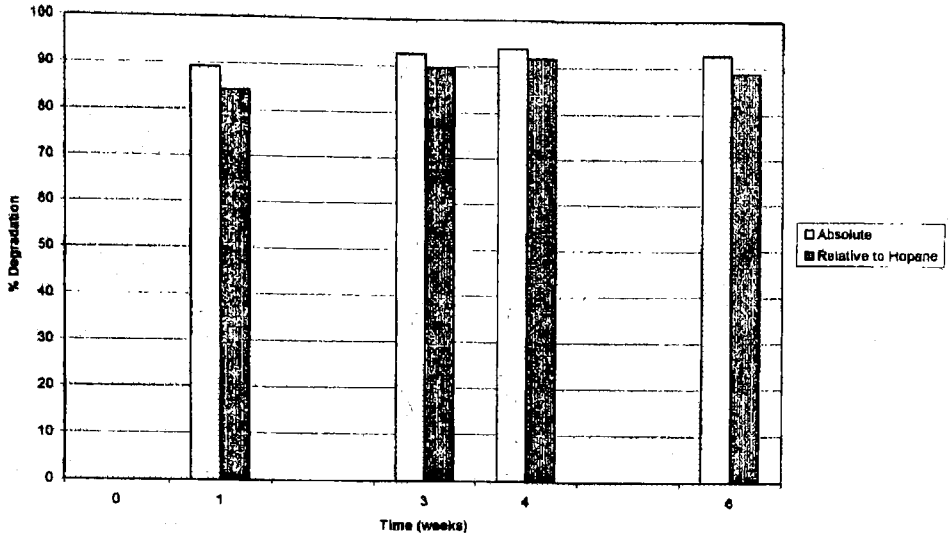

Figure 10. Comparison of absolute and relative C2-phenanthrenes / anthracenes degradation

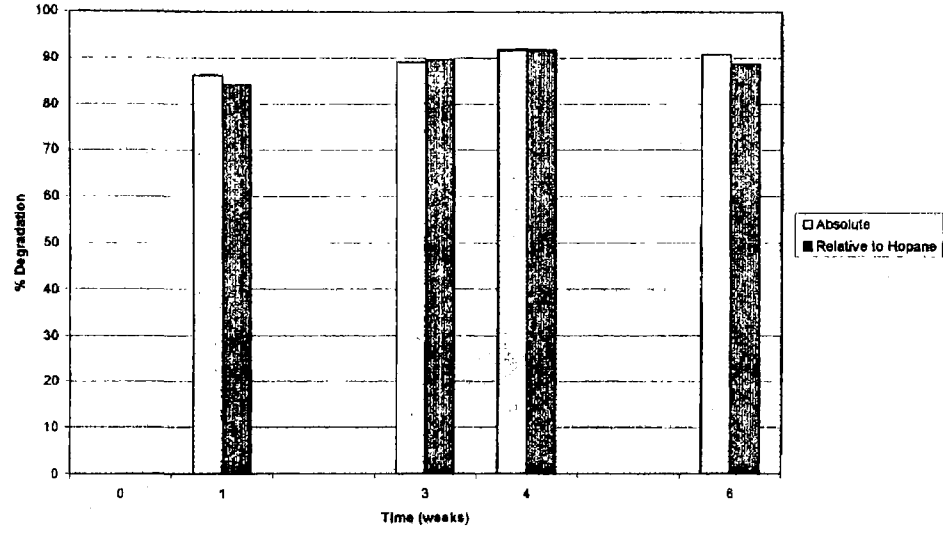

Figure 11. Comparison of asolute and relative C3-phenanthrenes / anthracenes degradation

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METHOD 8270 FOR MULTICOMPONENT ANALYTE ANALYSIS

Elaine A. LeMoine and Herman Hoberecht
The Perkin Elmer Corporation, 761 Main Avenue, Norwalk, Connecticut 06859

ABSTRACT

The identification and quantitation of multicomponent analytes (yielding more than one chromatographic peak) can be an analytical and productivity challenge. Multicomponent analytes such as Aroclors, Toxaphene, and technical Chlordane tentatively identified by another method may be confirmed using SW846 method 8270. Alternate confirmation of a tentative identification may be made using an electron capture detector (ECD) method such as 8081 or 8082 with a second column. For instruments with sufficient sensitivity, the mass spectrometer and ECD can be used in parallel for a simultaneous tentative identification and quantification. This paper will investigate the utility of a new mass spectrometer system for the quantitative identification of a mixture of multicomponent analytes. The method will be evaluated for detection limits, linearity, accuracy, and precision. The GC-MS method will be compared with the dual column method for analytical capability, productivity, and compliance.

INTRODUCTION

While the ability to positively identify sample analytes can be accomplished with the use of two columns, it is not necessarily the most desirable of options. In many cases the confirmational column alone is not sufficient and additional clean-up procedures need to be performed to eliminate co-eluting analytes. The additional equipment and analysis time required places productivity burdens on a laboratory. Gas Chromatography/Mass Spectrometry is widely used because its selectivity enables positive identification without additional sample processing. Along with the ability to make qualitative determinations, GC/MS is an invaluable tool for providing quantitative results. Mass Spec methods however, are generally considered less sensitive than conventional detector methods, although sensitive enough for most applications. The analysis of multicomponent analytes, such as Toxaphene and the Aroclors is more of a challange. EPA Method 8270C states, "In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits."[1] The development of more sensitive quadrupole mass spectrometry technology along with innovative sample introduction techniques, allow for the quantitation of many of these analytes at levels previously not achievable. The data to follow illustrates the ability of quadrupole mass spectrometry to quantitate multicomponent analytes at these lower levels. The ability to accurately identify and quantitate using GC/MS can eliminate the need for additional confirmatory analyses and reduce the amount of sample preparation required.

EXPERIMENT DESCRIPTION

Identical standards were analyzed using two sets of experimental conditions. A 50 µL Large Volume Injection was used in both cases. One set of standards was analyzed using the GC/MS Full Scan mode (FS-50) and the second using the Selected Ion Recording mode (SIR-50). Table 1 lists the chromatographic conditions used for both experiments, while Tables 2 and 3 list the Mass Spec conditions used for each set. The results are evaluated with respect to the accepted standard analytical techniques.

Perkin-Elmer AutoSystem XL	
Column:	PE-5MS 30 to x 0.25 mm; 0.25 µm film thickness
Pre-Column:	1 m x 0.32 mm deactivated fused silica
Oven Temperature Program:	55°C for 5 min., 45°C/min. to 160°C; 6°C/min to 320°C
Programable Pneumatic Control (PPC):	Helium 1.0 mL/min.
Programable Split/Splitless (PSS) Injector:	55°C for 4 min.; ballistic to 250°C; Solvent Purge Mode
Injection Volume:	50 µL

Table 1. Chromatographic Conditions

	FS-50
Perkin-Elmer TurboMass Mass Spectrometer	
Mass Scan Range:	50 - 350 m/z
Scan Speed:	2.0 scans/sec
Filament Delay:	5 min.
Ion Source Temperature:	150 °C
Transfer Line Temperature:	250 °C
Ionization Mode:	EI

Table 2. Full Scan Mass Spectrometer Conditions

	SIR-50
Perkin-Elmer TurboMass Mass Spectrometer	
Selected Scan Masses:	159, 231, 233 m/z
Scan Speed:	2.0 scans/sec.
Filament Delay:	5 min.
Ion Source Temperature:	150°C
Transfer Line Temperature:	250°C
Ionization Mode:	EI

Table 3. Selected Ion Recording (SIR) Mass Spectrometer Conditions

RESULTS

Toxaphene standards at 0.10 ng/µL, 0.20 ng/µL, 0.50 ng/µL, 1.00 ng/µL, and 5.00 ng/µL concentrations were

analyzed using both methods. The chromatograms shown in Figure 1 were obtained using the SIR mode. All the calibration standards clearly exhibit the characteristic Toxaphene pattern.

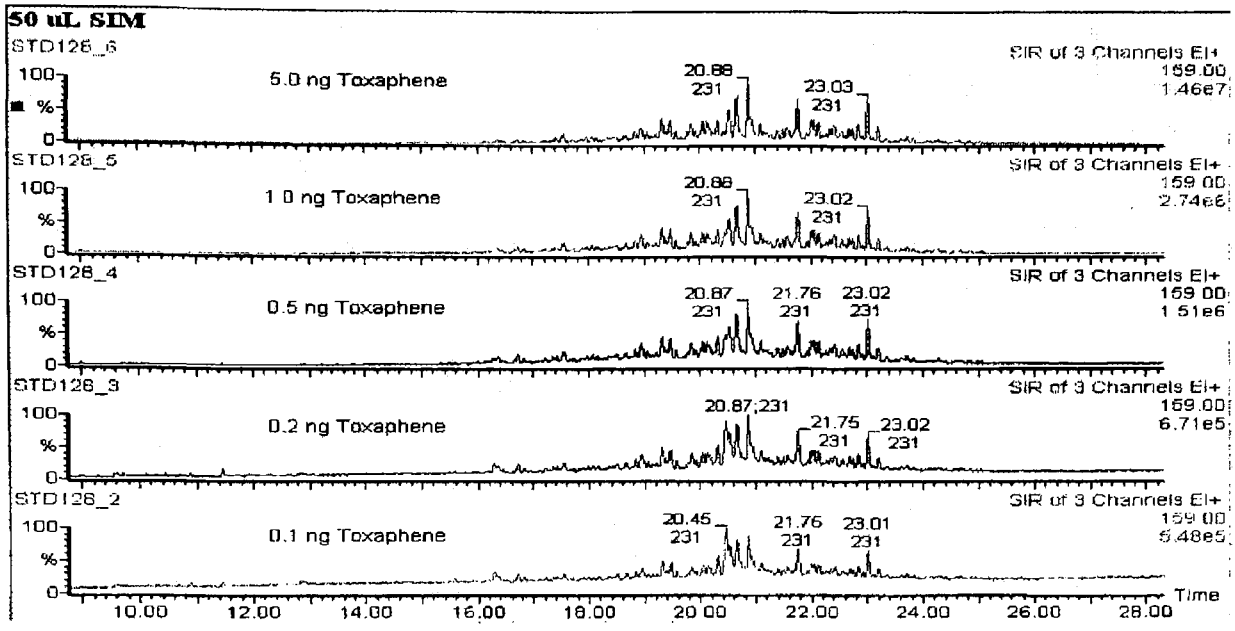
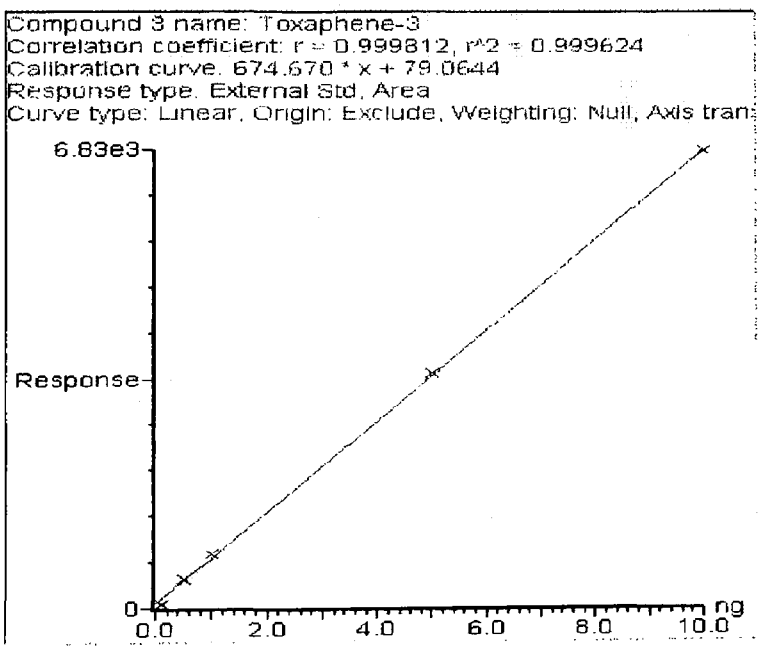


Figure 1. Calibration Standards show recognizable pattern for all levels.

Full Scan Mode

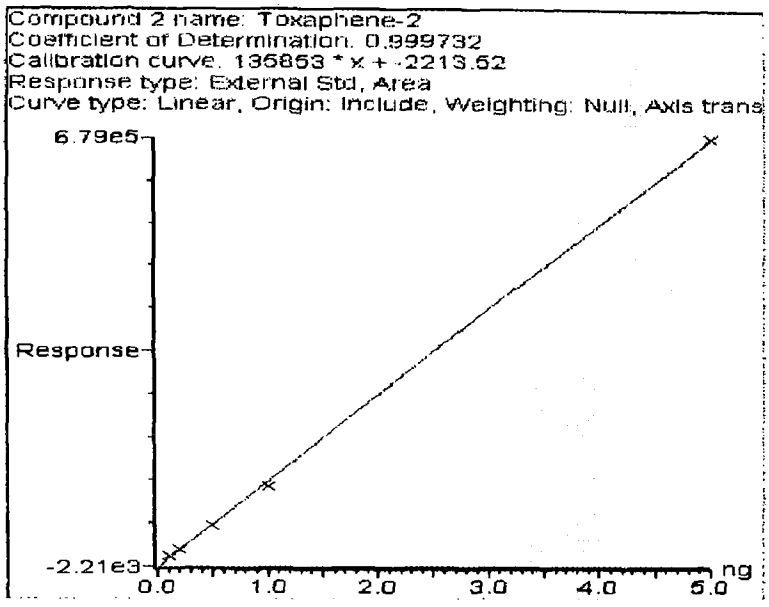


Four chromatographic peaks were selected and determined as representative of the multicomponent analyte Toxaphene. Calibration Factors (CF) were calculated based on the integrated peak areas and the known standard concentrations. From these results, the Relative Standard Deviation (RSD) for each multilevel concentration range was determined. These results were averaged providing a final Toxaphene RSD. Correlation coefficients were calculated in a similar fashion and are illustrated in Figures 2 and 3.

The results of all the calibration data and acceptance criteria are listed in Tables 4 and 5. Both experimental results easily comply with method performance specifications.

Figure 2. Toxaphene peak #3 Calibration Curve.

SIR Mode



The Method Detection Limits (MDLs) listed in Table 6 are the result of seven (7) replicate injections of a 0.10 ng/µL standard using the standard deviation and the t-statistic. Integrated peaks representative of the entire calibration range can be seen in Figure 4. The bottom chromatogram was obtained from a 0.05 ng/µL standard which is below the lowest calibration standard of 0.10 ng/µL. The peaks are readily discernible above the noise and can be easily integrated.

Figure 3. Toxaphene peak #2 Calibration Curve.

Full Scan-50

Calibration Peaks	**RSD**		**Correlation Coefficient**	
	Actual	Acceptance Limit	Actual	Acceptance Limit
Peak #2	11.0		0.99934	
Peak #3	13.6		0.99949	
Peak #4	12.6		0.99962	
	8.4		0.99948	
Toxaphene (Average of 4 peaks)	**11.4**	**15.0**	**0.9995**	**0.99**

Table 4. Comparison with Calibration Acceptance Criteria using Full Scan mode.

SIR-50

Calibration Peaks	**RSD**		**Correlation Coefficient**	
	Actual	Acceptance Limit	Actual	Acceptance Limit
Peak #1	10.4		0.99936	
Peak #2	8.2		0.99973	
Peak #3	10.8		0.99967	
Peak #4	7.5		0.99934	
Toxaphene (Average of 4 peaks)	**9.2**	**15.0**	**0.9995**	**0.99**

Table 5. Comparison with Calibration Acceptance Criteria using Selected Ion mode.

Calibration Peaks	**Calculated Analytical Detection Limits**	
	FS-50	**SIR-50**
	(ng/µL)	(ng/µL)
Peak #1	0.073	0.065
Peak #2	0.089	0.009
Peak #3	0.105	0.021
Peak #4	0.035	0.014
Toxaphene (Average)	**0.07**	**0.02**

Table 6. Calculated Detection Limits

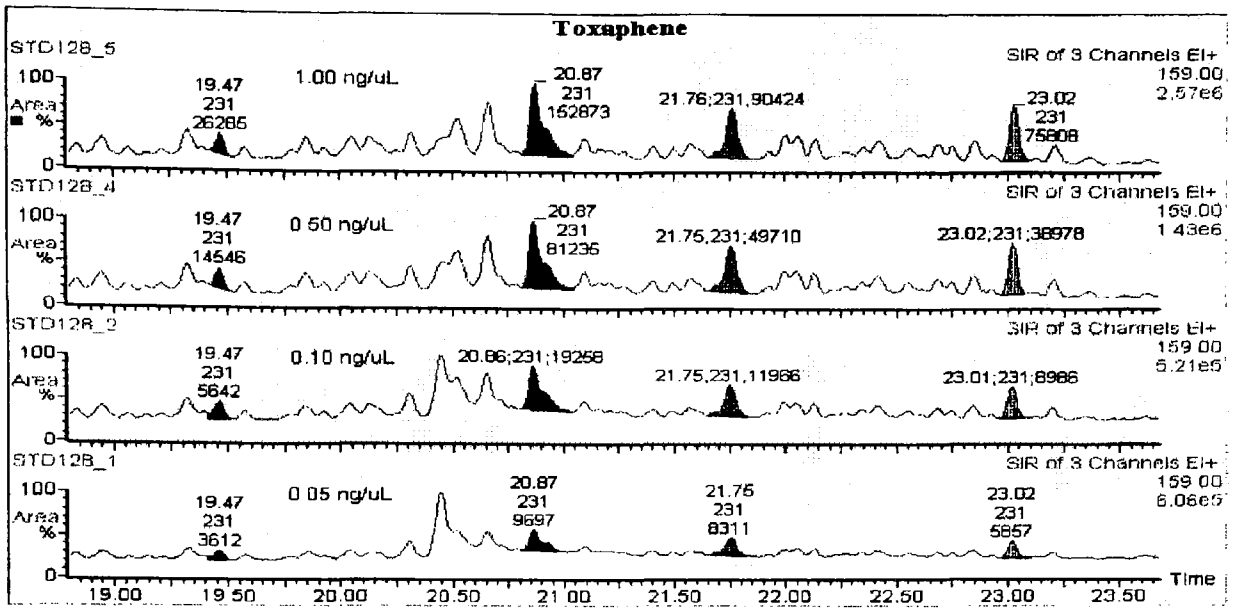


Figure 4. Integrated Toxaphene Peaks

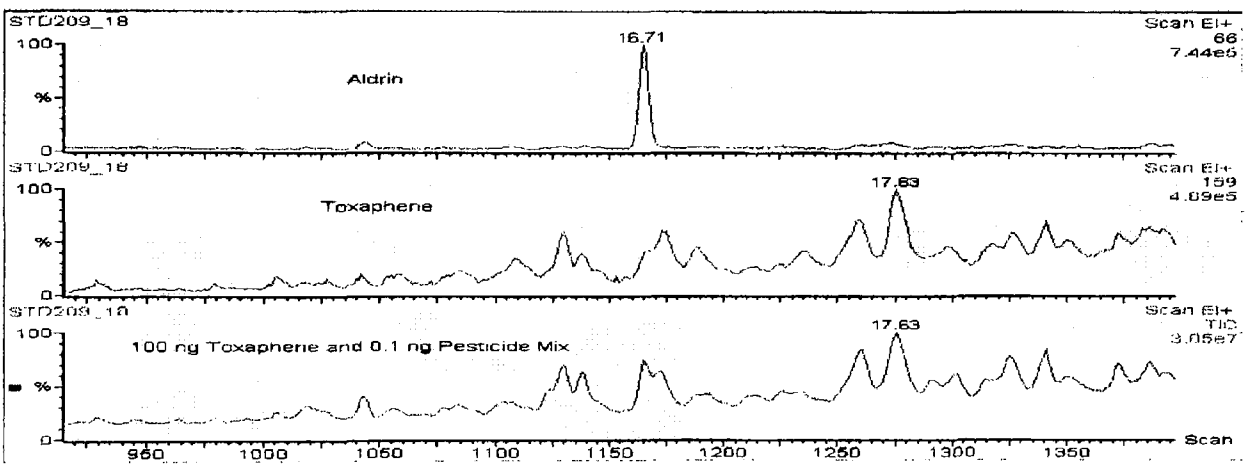


Figure 5. Aldrin and Toxaphene Extracted Ions

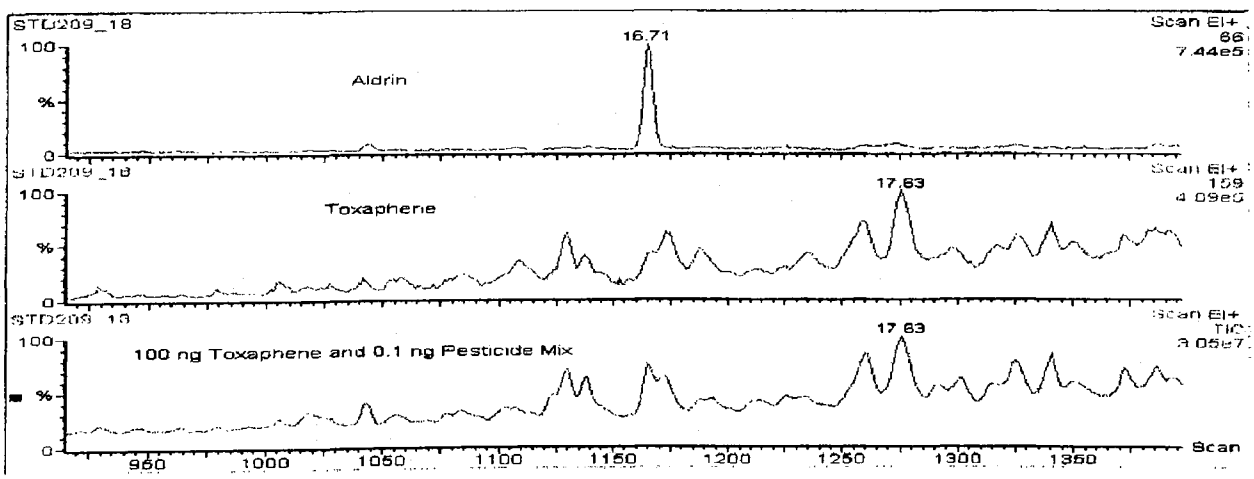


Figure 6. Library Searchable Spectra

What sets the Mass Spectrometer apart from other forms of detectors is the ability to selectively-identify individual masses. Figure 5 shows the Total Ion Chromatogram (TIC) of a mixture of 100 ng/µL Toxaphene and 0.10 ng/µL Pesticide Mix. The Extracted Ion (EI) mass 159 is Toxaphene, and the Extracted Ion (EI) mass 66 is Aldrin which was confirmed by a NIST library search as seen in Figure 6. Aldrin is easily identified and integrated without additional preparatory procedures.

The Contract Laboratory Program (CLP) lists 0.2 ng/µL as the quantitation limit for Aroclor 1221 using an Electron Capture Detector. Figure 7 shows Aroclor 1221 well above the noise level at the 0.20 ng/µL quantitation level, using GC/MS in the SIR mode and large volume injection.

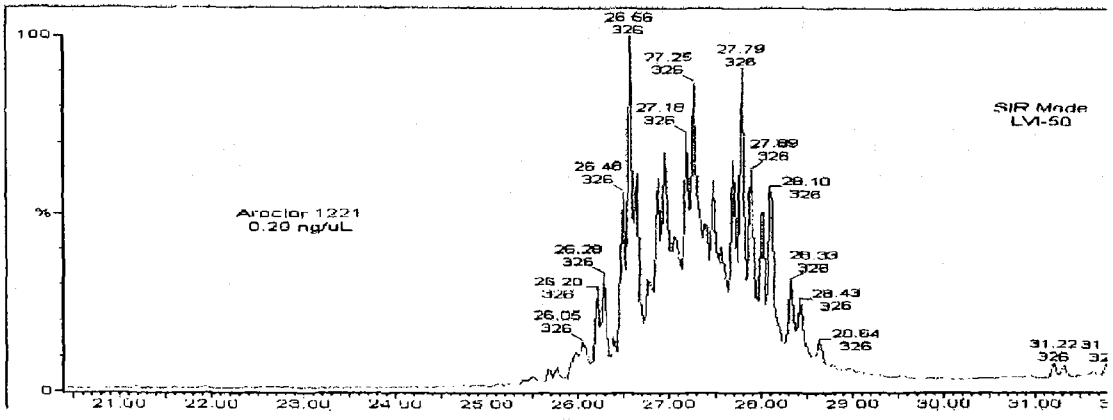


Figure 7. Quantitation Limit Pattern Recognition

SUMMARY

The ability of GC/MS to selectively identify a component based on an extracted ion chromatogram from a mixture of compounds not only assures a positive identification, but also saves time by eliminating additional cleanup and analyses. Recent technological advances in quadrupole Mass Spectrometry have increased the instrument's sensitivity. The use of Selected Ion Recording provides further sensitivity enhancements. In addition to the detector and it's mode of operation, the use of large volume injection with a programmable inlet system allow for introduction of larger sample volumes. The combination of these elements enhances the sensitivity of a GC/MS system so multicomponent analytes can be *identified and quantified* in an efficient and prOductive manner.

References

1. "Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)," in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods,* SW-846, Third Edition, U.S. Government Printing Office, Springfield, VA (1996).

BENZIDINE? REALLY?

Roy-Keith Smith
Analytical Services, Inc., 110 Technology Parkway, Norcross, GA 30092
(770) 734-4200, Fax (770) 734-4201

ASI has been performing sample analysis using GC-MS Method 8270, with a variety of sample preparations from SW-846 for many years. In 1995 soil samples were received from a manufacturing site for analysis. The samples were part of a general site survey of the manufacturers facility to determine what may need remediation efforts in the future. ASI performed the requested analyses, and found and reported benzidine in several of the samples at levels approaching 1000 mg/kg. Unfortunately the data reports were simply filed by the manufacturer.

In late 1997, the manufacturing site became under consideration for sale to another company. As part of the

pre-sale investigation of the site, past analytical records were examined and the benzidine results came to light. As there had never been any benzidine used or stored on the site and the manufacturing processes involved no chemical syntheses, there were some questions about the validity of the reported results.

The raw data generated during the sample analyses was examined in detail. The initial calibration was acceptable, as were the daily calibration verifications and tunes. The system performance criteria were being met. The initial calibration was used for quantitation, with retention times and user generated library spectra being updated on a daily basis. Examination of the raw chromatograms (Figure 1) from the samples revealed a hump-o-gram. Random MS scans from the hump suggested a petroleum-based background interference. Although the benzidine hits were buried in the hump-o-gram, rather than being isolated well defined peaks, the candidates matched up perfectly with the retention time and daily generated mass spectrum of the benzidine standard.

The client had not requested a library search for TIC with the original analysis. By happenstance during the data review, a library search of the questioned peak was performed. Quite surprisingly the search generated a match for dibenzothiophene, rather than the expected benzidine. Spectra of both compounds were pulled from the database for examination.

It is rather startling how similar the mass spectra of benzidine and dibenzothiophene appear in a fast visual comparison (Figures 2 and 3). Both have a dominant peak at m/z 184 and an assortment of low intensity smaller m/z signals. The two compounds have the same unit mass molecular weight (184), the only difference in the molecular formulas being the two amino groups in benzidine and the sulfur in dibenzothiophene, $C_{12}H_8(NH_2)_2$ *vs.* $C_{12}H_8S$. By coincidence the mass of the two amino groups (32) is the same as the sulfur (32).

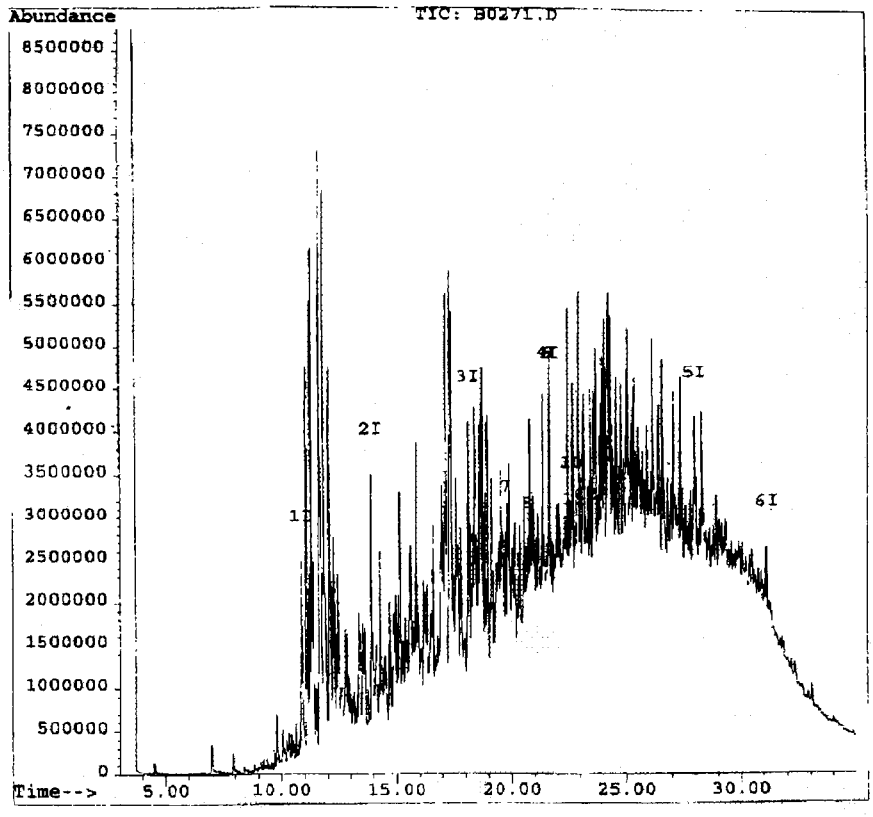
Detailed peak mass matching and relative abundance comparisons of select peaks reveal definitive mass spectral variances between the compounds that allows conclusive identification of either analyte. First off, both compounds have a M + I isotopic peak, however only dibenzothiophene has a very prominent M + 2 signal due to the sulfur. The fragmentation patterns of the molecular ions of the two compounds are nowhere near alike. Both compounds can loose a hydrogen to give M-1 signals, however only benzidine will continue to lose hydrogens giving the M-2 and M-3 peaks. Benzidine can also lose a $-NH_2$ group to generate the M-16 peak at m/z 168 or a NH_3 group, forming a benzyne at m/z 167 (M-17). Dibenzothiophene has no fragmentation pathway to generate either m/z 167 or 168. Extrusion of sulfur from dibenzothiophene gives rise to a prominent peak at m/z 152 (M-32).

The stability of the molecular ion of benzidine is probably enhanced through ring-expansion of one of the aromatic rings to include a nitrogen in a seven-membered aromatic ring (aza-tropyllium ion). Concerted ejection of a CNH_4 unit (M-30) from this ring generates m/z 154. A similar ring expansion, followed by concerted ejection of SCH from dibenzothiophene forms m/z 139 (M-45) as a significant signal that is quite undistinguished in the benzidine spectrum. Other important differences are indicated in Figures 2 and 3, and include m/z 65 and 77 in the benzidine spectrum, while Dibenzothiophene exhibits 69 and 79.

Although the distinguishing features of the two spectra are easy to overlook by eye, it was obvious that the computer spectral matching algorithm was having no such problem, and further investigation focused upon the user generated spectra. This is displayed in Figure 4, along with the spectra from one of the challenged identifications. What was in the sample matched up almost perfectly with what was stored as a spectrum of benzidine from the standard. Using the identification criteria listed above to examine the library spectra led to the inescapable conclusion that the standard used for initial and continuing calibration was dibenzothiophene rather than benzidine.

The retention time of dibenzothiophene is slightly less than that of benzidine, however not so much as to be really startling. Benzidine itself exhibits shifts in absolute and relative retention times as columns are changed in the GC-MS. As it is our habit to replace columns with recalibration, the slight shift in retention time from one initial calibration to the next was unexceptional. The quick visual examination of the mass spectra that accompanied the recalibration failed to detect any differences.

Dibenzothiophene is a naturally occurring substance commonly found in high sulfur crude oils. Discussions with the client revealed that the samples with "benzidine" all came from the soil underneath a storage area where several barrels of high sulfur Venezuelan fuel oil #6 had been placed. The high sulfur levels had made the oil



unacceptable for use in the boilers at the facility. The GC-MS chromatograms contained hydrocarbon humpograms along with the "benzidine" and other sulfur-containing aromatics. As all the evidence was now consistent, the reports were re-issued deleting the benzidine hit.

The investigation was expanded to include examination of the calibration spectra both prior to and after these particular samples were analyzed. It was found that the problem began several months prior to October, 1995 surprisingly in the middle of a supplier's lot number. The problem continued after October, 1995, through the next lot number of benzidine standard purchased from the supplier. It was not until Summer, 1996 and a further lot number change that the spectra reverted back to the correct benzidine mass spectrum.

Figure 1. Chromatogram of sample

ASI contacted the supplier of the benzidine standard and presented them with the above evidence. The supplier was not making any spectral checks upon purchased stock standards as part of their QA program. Only the technically outdated melting point determination was being verified, and it was not being performed as a mixed melting point. There were no ampules of the particular lot numbers available for examination, however the supplier offered to reimburse the cost of the standards.

We went back through every sample analyzed during the year that the incorrect standard had been used. Fortunately we found that no other samples had been reported with hits for benzidine, thus there were no false positives. We are still in the process of doing a manual search of the tape archives for any false negative benzidine hits in these samples. None have been found to date.

How could we have caught the error and prevent it's happening again in the future? The corrective actions we have instituted are to: 1) inject new GC-MS standards under old calibrations prior to changing out the column and re-calibrating; 2) use second source standards to check each new calibration; and 3) closely examine the mass spectrum of each new benzidine standard that is purchased.

The lesson learned? Don't trust anyone's claims or documentation of purity or authenticity. Their acceptance standards may well be different than your own.

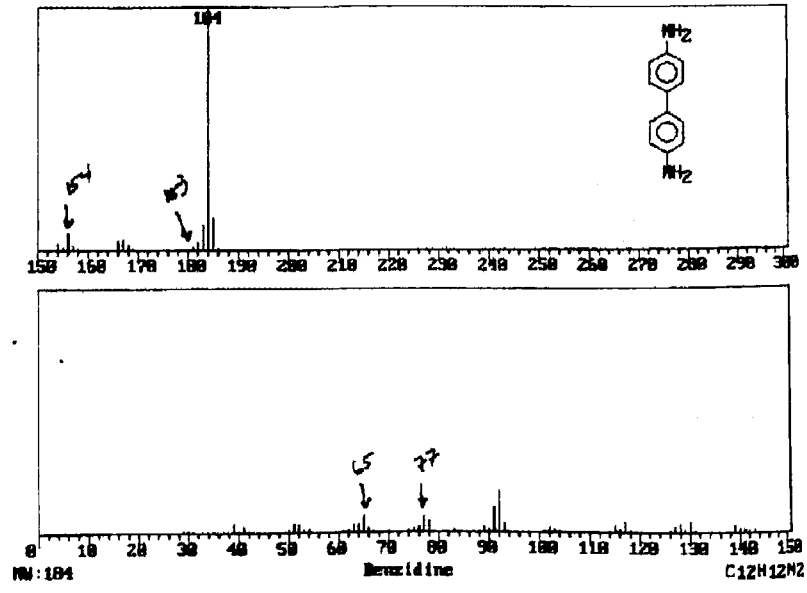


Figure 2. Mass spectrum of benzidine from Wiley-NIST library

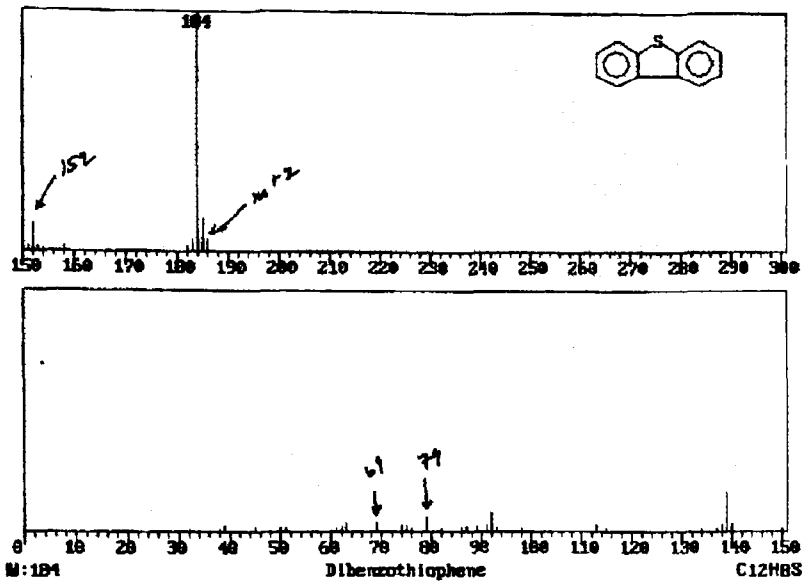


Figure 3. Mass spectrum of dibenzothiphene from Wiley-NIST library

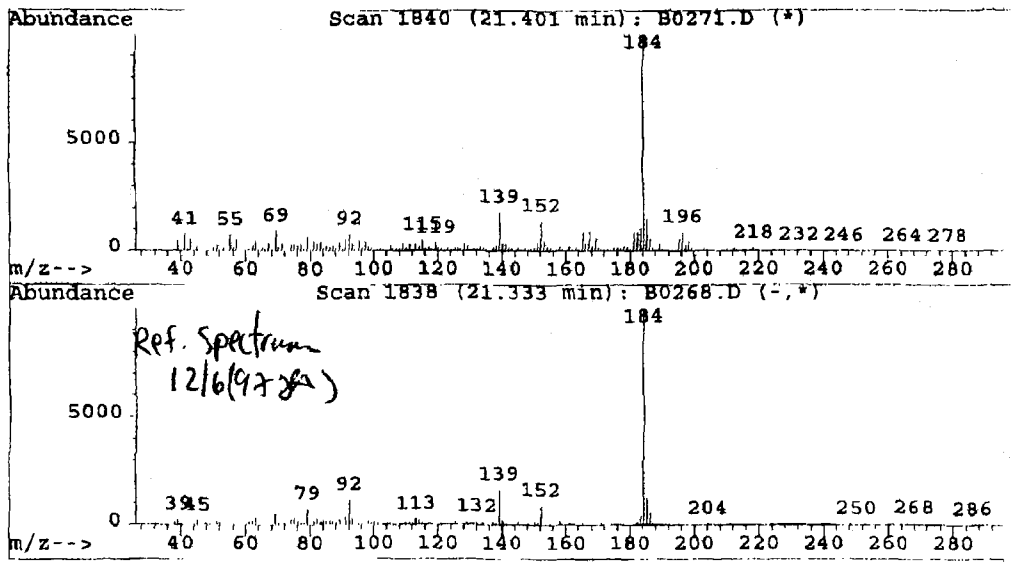


Figure 4. Mass spectra from sample and lab generated library

COMPARISON OF VOLATILE ORGANIC COMPOUND RESULTS BETWEEN METHOD 5030 AND METHOD 5035 ON A LARGE MULTI-STATE HYDROCARBON INVESTIGATION

Rock J. Vitale, Ruth Forman, and Lester Dupes
Environmental Standards, Inc., 1140 Valley Forge Road, Valley Forge, Pennsylvania 19482

ABSTRACT

With the promulgation of SW-846 Update III during June of 1997, elimination of Method 5030 and implementation of Method 5035 have created significant challenges for the regulatory and laboratory communities (US EPA, 1997). Based on historical data, the results for volatile organics in certain sample types using the previously approved direct heated purge technologies were observed to be biased low (Hewitt, 1994). The loss of volatile organics was not observed to be the determinative process of Method 5030 but of the sampling, preservation, and preparatory aspects of the methodology (Hewitt, 1997, Siegrist, 1992). The promulgation of Method 5035 requires training of field samplers and a decision-tree approach to collecting and analyzing samples.

As recent as the first quarter 1998, for previously initiated on-going projects, various regulatory agencies have been issuing directives to either implement Method 5035 or continue with Method 5030 (US EPA, 1997). In order to understand the implications of implementing Method 5035 after several years of using "traditional" soil sampling methods and analysis by Method 5030 on a large multi-state hydrocarbon investigation, a 4-week study was performed to ascertain the differences in field activities, documentation issues, and analytical results.

A description of the comparative study, inclusive of observations between the traditional Method 5030 and the three Method 5035 options (e.g., Encore®, sodium bisulfate, and methanol), will be presented. In addition, some of the lessons learned from the study will be discussed.

INTRODUCTION

A two-phased study was performed to determine the comparability between investigative samples collected and analyzed by the "traditional" sampling/analytical method (SW-846 Method 5030) and investigative samples collected and analyzed by the recently promulgated sampling/analytical method (SW-846 Method 5035). Soil samples included in this study were collected from four states with different soil types and contaminant concentrations. The soil samples were analyzed for a list of 18 volatile compounds by gas chromatography/mass spectroscopy (SW-846 Method 8260A).

STUDY DESIGN

The study included the collection of soil samples in two phases. The first phase of sampling was conducted at select locations in Ohio, West Virginia, Pennsylvania, and Maryland from January 27 through February 11, 1998. Soil samples were collected at 56 sample locations. Nine field duplicates were collected during this phase. A trip blank (one sodium bisulfate and one deionized water) was collected for each day of sample collection. Based on previous analyses and remedial activities, samples collected during phase one were expected to either be "clean" or require low-level analysis. Accordingly, methanol samples were not collected for this phase. Specifically, for the first phase of sampling, samples were collected utilizing three techniques as follows:

- The traditional method of sample collection (in a 125 ml wide-mouthed glass jar);
- Utilizing a plastic syringe and placing five grams of soil into a 40 ml glass vial pre-preserved (by the laboratory) with sodium bisulfate; and
- Utilizing an Encore® sampler (the Encore® analyses for both phases were performed with the modifications recommended by the International Association of Environmental Testing Laboratories [IAETL]).

The second phase of sampling was performed the week of March 2, 1998. Samples were collected at 33 select locations (including two field duplicates) in West Virginia. The selection criteria for sample locations collected for the second phase of the project were based upon available historical sample concentration data. The sample locations were selected to include samples that contained low, medium, and high concentrations of volatile compounds (based on the traditional sample collection historical data).

Trip blanks (one sodium bisulfate, one deionized water, and one methanol) were collected for each day of sample collection. For the second phase of sampling, samples were collected utilizing four techniques as follows:

- The traditional method of sample collection (in a 125 ml wide-mouthed glass jar;
- Utilizing a plastic syringe and placing five grams of soil into a 40 ml glass vial pre-preserved (by the laboratory) with sodium bisulfate;
- Utilizing an Encore® sampler (the Encore® analyses for both phases were performed with the modifications recommended by the IAETL); and
- Placing five grams of soil into a vial containing methanol.

All samples were packed in coolers at 4°C under Chain-of-Custody and shipped via overnight courier to a reputable commercial environmental laboratory. All samples were analyzed within a holding time of 14 days of samples collection. In addition, each sample type (i.e., traditional, Encore® sodium bisulfate and methanol)

collected at a given sample location was analyzed within 24 hours of the other sample types. In order to minimize possible confounding effects of analytical holding times, all sample types at a given location were analyzed within the sample 24-hour time period.

DATA REVIEW

Reduced data package deliverables were prepared by the laboratory for all samples. The reduced data package deliverables included a summary of the reported analytical results for all field samples (including samples, field duplicate samples and trip blanks), the associated method blank results, the associated laboratory control sample recoveries, and the surrogate recoveries. The analytical data for both phases were reviewed for completeness of the data package deliverables, compliance with the SW-846 Methods 5035 and 8260A, and usability of the reported analytical results (Clark and Vitale, 1996). Although important for comparability, compliance with methodologies often provides little information on data quality (Blye and Vitale, 1995).

The initial and continuing calibration criteria for Method 8260A were met for all study samples. With the exception of one compound in one laboratory control sample (LCS), the LCS recoveries were within study-specified limits (75-125%). The recoveries for one or more of the three volatile surrogate compounds were outside the limits specified (varying limits for each surrogate with limits between 70-121%) for many (38) of the study samples. Because the "true value" accuracy was not important for this study, the surrogate recoveries are not expected to affect the operational definition for comparing techniques on respective sample aliquots, which was most relevant in a comparative study. Analysis of the study trip blanks and laboratory method blanks did not reveal the presence of target analytes, with the exception of methylene chloride and acetone. The positive sample results for these two compounds were rejected from further consideration.

Eleven field duplicate samples were collected for the study; approximately one field duplicate sample was collected per day of sample collection. Field duplicates provide valuable information on precision and sample representativeness when evaluated properly (Zeiner, 1994). Acceptable precision (<50% RPD, as defined for this project) was noted between six field duplicate pairs. High RPDs (>50% RPD) were noted for five of the duplicate pairs. Such sample variability appears to have complicated a meaningful comparison of techniques as separate sample aliquots were collected and analyzed for each of the study sampling techniques.

SUMMARY OF RESULTS

A summary of the reported analytical results is provided on Table 1. All results are reported on a dry-weight basis. Variations between sample-specific quantitation limits were evident due to the sample collection volume, the percent moisture of the sample, and the sample-specific dilutions performed. The sample collection volume at a given sample location is different for each sample type due to the manner in which the sample was collected. The quantitation limits for samples preserved with methanol were raised by the laboratory due to the medium-level sample preparation.

Fourteen of the sodium bisulfate samples were not analyzed due to the observed concentrations of non-target compounds in these samples (samples containing sodium bisulfate cannot be analyzed using medium-level protocol). The corresponding traditional and Encore® samples at these sample locations were analyzed at a medium-level due to the same reason. In addition, six of the sodium bisulfate samples could not be analyzed due to observed sodium bisulfate effervescence.

In total, 79 Encore® samples, 79 traditional samples, 62 sodium bisulfate preserved samples, and 23 methanol-preserved samples were collected for the volatile pilot study. Of the 79 sample locations examined, positive results were reported in 33 of the sample locations. Positive results were reported for four aromatic compounds (benzene, toluene, ethylbenzene, and total xylenes); two ketones (4-methyl-2-pentanone and 2-butanone); and four chlorinated aliphatic hydrocarbons (1,1-dichloroethene, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, and tetrachloroethene).

TABLE 1. SUMMARY OF ANALYTICAL RESULTS

Sample Number	Encore™	Traditional	Sodium Bisulfate	Methanol
SAMPLE 1				
total xylenes	6U	6U	6	N/A
SAMPLE 2				
benzene	6U	6U	6	N/A
ethylbenzene	6U	6U	12	N/A
total xylenes	6U	15	14	N/A
SAMPLE 3				
toluene	6U	5U	8	N/A
2-butanone	95U	110	110U	N/A
SAMPLE 4				
toluene	6U	6U	7	N/A
SAMPLE 5				
toluene	6U	7U	12	N/A
SAMPLE 6				
tetrachloroethene	6U	6U	23	N/A
toluene	6U	6U	23	N/A
ethylbenzene	6U	6U	15	N/A
total xylenes	6U	6U	260	N/A
SAMPLE 7 (DUPLICATE OF SAMPLE 6)				
tetrachloroethene	5U	6U	13	N/A
toluene	5U	6U	9	N/A
total xylenes	5U	6U	7	N/A
SAMPLE 8				
total xylenes	36	140J	45	N/A
SAMPLE 9 (DUPLICATE OF SAMPLE 8)		0	0	
total xylenes	610	440U	N/A	N/A
SAMPLE 10		0	0	
total xylenes	760	130U	N/A	N/A
SAMPLE 11				
1,1-dichloroethene	200J	320U	N/A	N/A
1,1,1-trichloroethane	2200	570	N/A	N/A
toluene	1200	110J	N/A	N/A
ethylbenzene	210J	320U	N/A	N/A
total xylenes	930	160J	N/A	N/A
SAMPLE 12				
1,1,2,2-tetrachloroethane	310	330U	N/A	N/A
ethylbenzene	200J	280J	N/A	N/A
total xylenes	1200	2100	N/A	N/A
SAMPLE 13				
toluene	5U	6U	6	N/A
SAMPLE 14 (DUPLICATE OF SAMPLE 13)				
1,1,2,2-tetrachlorethane	6U	6U	16	N/A
SAMPLE 15				
4-methyl-2-pentanone	31,000	9700	N/A	N/A
SAMPLE 16				
4-methyl-2-pentanone	13,000	8400	N/A	N/A
SAMPLE 17				
toluene	1000	1600	15	N/A
ethylbenzene	6200	12,000	16	N/A
total xylenes	30,000	63,000	53	N/A
SAMPLE 18				
4-methyl-2-pentanone	2700U	6500U	1,300	N/A
ethylbenzene	2000	1400	790	N/A
total xylenes	20,000	18,000	240	N/A

TABLE 1. (Cont.)

Sample Number	Encore™	Traditional	Sodium Bisulfate	Methanol
SAMPLE 19				
toluene	63	34	61	N/A
ethylbenzene	20	11	31	N/A
total xylenes	160	59	280	N/A
SAMPLE 20				
tetrachloroethene	6300	5000	2900	N/A
toluene	5U	6U	14	N/A
ethylbenzene	5U	6U	9	N/A
total xylenes	11	6U	24	N/A
SAMPLE 21				
toluene	7U	6U	7	N/A
2-butanone	130U	120U	120	N/A
SAMPLE 22				
1,1-dichloroethene	5U	6U	16	530U
toluene	5U	6U	6U	100J
SAMPLE 23				
benzene	250J	220J	N/A	670
tetrachloroethene	901	300U	N/A	200J
toluene	1300	1100	N/A	3300
ethylbenzene	470	550	N/A	870
total xylenes	4600	5500	N/A	8400
SAMPLE 24 (DUPLICATE OF SAMPLE 23)				
benzene	250J	220J	N/A	400J
tetrachloroethene	80J	300U	N/A	200J
toluene	1200	1500	N/A	1900
ethylbenzene	570	430	N/A	740
total xylenes	5600	4500	N/A	7200
SAMPLE 25				
benzene	5U	6U	45	570U
toluene	5U	6U	90	570U
ethylbenzene	5U	6U	26	570U
total xylenes	5U	6U	130	300J
SAMPLE 26				
ethylbenzene	600	230J	N/A	1200
total xylenes	370	110J	N/A	930
SAMPLE 27				
benzene	6U	6U	12	610U
ethylbenzene	6U	15	7U	610U
SAMPLE 28				
benzene	2000	6U	N/A	650U
toluene	7400	6U	N/A	200J
ethylbenzene	1500	6U	N/A	650U
total xylenes	14,000	6U	N/A	600J
SAMPLE 29 (DUPLICATE OF SAMPLE 28)				
benzene	6U	7J	6U	540U
toluene	6U	30	6U	100J
total xylenes	6U	4600	23	780
SAMPLE 30				0
ethylbenzene	120J	120U	N/A	340U
total xylenes	60J	320U	N/A	80J
SAMPLE 31				
benzene	5U	13J	6U	260U
ethylbenzene	5U	23J	6U	60J
total xylenes	5U	33	7	670

TABLE 1. (Cont.)

Sample Number	Encore™	Traditional	Sodium Bisulfate	Methanol
SAMPLE 32				
toluene	210J	280U	N/A	470U
ethylbenzene	540	280U	N/A	470U
total xylenes	3300	280U	N/A	550
SAMPLE 33				
benzene	6U	6U	8	610U
toluene	6U	6U	14	610U
total xylenes	6U	6U	8	610U

Notes: U - Not detected at or above the associated numerical value
N/A Not analyzed
J - Estimated value; result less than the quantitation limit
E Estimated value; result exceeded the calibration range and not reanalyzed

COST ANALYSIS

For the reputable commercial laboratory that was utilized for this study, the cost of analysis of all four sample collection types is identical, and there are not any cost implications for analyzing a volatile soil sample by any of the four sample collection methods. The cost of sample bottleware preparation is different between the four sample collection types. The cost for traditional sample collection bottleware is built into the contract with the laboratory. The cost for the Encore® sampler is roughly $10.00 per sampler. Three Encore® samplers are filled at each sample location at a total of <$30.00 per sample location. The cost for a methanol-preserved vial (two vials are sampled at a given location when the methanol preserved sample is not collected in tandem with a sodium bisulfate preserved sample; otherwise, only one vial is submitted) is <$35.00 per sample or <$60.00 per sample location. The cost for a sodium bisulfate preserved vial is approximately $50.00 per sample. Two sodium bisulfate preserved vials are collected per sample location at a cost of approximately $100.00 per sample location.

The labor costs for the collection of the various sample types can vary and exact costs could not be precisely calculated based on information available. The Encore® sampler and the traditional method of sample collection were found to be the quickest and easiest sample types to collect. The sodium bisulfate samples were found to take the longest time to collect and provided the most difficulty in the field.

FIELD OBSERVATIONS

Sodium Bisulfate and Methanol Sampling Techniques

The sodium bisulfate and methanol techniques are very similar and are reviewed here jointly. These methods were by far the most cumbersome of the selected sampling techniques. The necessity of using an analytical balance under imperfect field conditions proved frustrating. The balance readings would fluctuate wildly with the slightest amount of wind or movement of the sample preparation surface. In addition, unless the sample preparation surface was perfectly horizontal, the scale could not calibrate nor zero out. Furthermore, calibration of syringes with soil matrix was time consuming in comparison to the traditional and Encore® methods. Using razor knives to cut syringe tips evenly required practice and care. Finally, preservative solution was prone to spillage unless great care was taken while placing the soil in the vials.

The methanol technique has an additional drawback. When shipping samples via popular air couriers, samples must be packaged according to IATA regulations. The regulations regarding shipping of flammable compounds are very strict and may result in lost or delayed delivery if the sample containers are not properly packaged. In addition, the appropriate paperwork and package labeling must be completed in a precise manner, or the shipment will be delayed or returned to the sender. From a field sampling perspective of the methods used during the pilot study, these were by far the most time consuming and frustrating.

Encore® Sampling Technique

The Encore™ sampling system was very straightforward in its approach and implementation, although some minor problems were encountered during the pilot study. Problems were encountered when trying to place loose and/or wet soils into the Encore® sampler. Soils of this type had to be manipulated into the Encore® with another sampling device (such as a spatula). The only other sample collection issue involved improper seating of the cap on the plunger. However, by pushing down on a hard surface with the T-handle, the cap could be seated properly. Overall, the Encore® system appeared to be easy to use even under adverse field conditions.

Traditional Sampling Technique

This sampling method is well-known to most field technicians and has been employed under a wide variety of field conditions. It was apparent during the field study that this technique was easily implemented and rivaled the Encore® sampling technique for ease of use. However, from a field perspective, some clays, silts and other tightly compacted soils are difficult to place into a sample container so that no head space is allowed. Breaking up soils to place into sample containers may result in loss of volatiles, thereby lowering detectable concentrations. However, from a field perspective, this technique has been historically easily implemented.

CONCLUSIONS

The following observations can be made from the overall study. With the exception of the first bullet item, the conclusions presented below should not be interpreted to be applied to other sites, soil types, and concentrations of analytes. These are general conclusions regarding this particular data set; there may not be an equivalent trend noted in other data sets. Our findings suggest that inherent difficulties associated with analyzing soil samples makes definitive states regarding data comparability difficult. Furthermore, the number of positive data points and the disparity observed for half of the collected field duplicates makes statistical trend analysis problematic at best.

- At sample locations where methanol-preserved samples were collected and where the concentration of target analytes was within range of the medium-level analysis, the concentration of target analytes of the methanol-preserved sample type was greater than the concentration of the analytes in the other sample types at the same sample location. This is consistent with other studies appearing in peer-reviewed literature.

- At sample locations where methanol-preserved samples were not collected and where the concentration of target analytes was within range of the medium-level analysis, the concentration of the aromatic analytes appeared to be greater in the traditional sample collection type than the other sample collection types at the same location.

- At sample locations where methanol-preserved samples were not collected and where the concentration of analytes was within range of the medium-level analysis, the concentration of the non-aromatic target compounds appeared to be greater in the Encore sample collection type than the other sample collection types at the same location.

- At sample locations where methanol-preserved samples were not collected and where the concentration of target analytes was not within range of the medium-level analysis, the concentration of the analytes appeared to be greater in the sodium bisulfate sample collection type than the other sample collection types at the same location.

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INORGANIC

SW-846 INORGANIC METHODS UPDATE

Oliver Fordham
U.S. EPA, Office of Solid Waste, 401 M. St., SW, Washington, DC

NO ABSTRACT AVAILABLE

DIRECT MERCURY ANALYSIS: FIELD AND LABORATORY APPLICATIONS

Helen M. Boylan, H.M. "Skip" Kingston, and Robert C. Richter
Duquesne University, Department of Chemistry & Biochemistry, Pittsburgh, PA 15282-1503

ABSTRACT
EPA Method 7473 is designed for the determination of total mercury in solid and aqueous samples. This method is based on the instrumental methodology of the Direct Mercury Analyzer-80 (DMA-80) (Milestone, Inc.) in which sample preparation and analysis are essentially integrated into a single analytical step. The method's unique capability for direct analysis allows for application in either laboratory or field settings. Method 7473 has been validated by analysis of various Standard Reference Materials (SRMs) in both the laboratory and in the field. This validation data has been presented[1] Results from Method 7473 have also been confirmed by independent analysis using traditional methods. Method 7473 has been used on-site in conjunction with mercury remediation. Real-time analysis using this technique has provided an accurate and cost-effective risk assessment of mercury contaminated sites.

INTRODUCTION
There are several analytical techniques that may be applied for the determination of mercury in solid waste. Existing EPA methods for the analysis of mercury include inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Method 6010B), cold vapor atomic absorption spectroscopy (CV-AAS) (Method 7471A), and anodic stripping voltammetry (ASV). Regardless of the method used, sample preparation is required. "Soils, sludges, sediments, and other solid wastes require digestion prior to analysis"[2]. Method 7473 has an advantage over traditional mercury analysis because it eliminates the need for a discrete sample preparation step. Direct analysis is performed by integration of thermal decomposition, amalgamation, and atomic absorption spectroscopy. While the fundamental theory for this type of analysis has been available in the literature, the DMA-80 is the firs instrumental implementation of these integrated concepts.

A schematic of the DMA-80 is shown in Figure 1. The sample is automatically inserted into the quartz deomposition tube, where it is first dried and then thermally decomposed. The gaseous decomposition products are carried by a flow of oxygen to the catalytic core, which is maintained at a temperature of 750 °C to ensure complete thermal decomposition. The oxygen flow continues to carry the gases to the gold amalgamator, where mercury is selectively trapped. Continuous oxygen flow removes any remaining decomposition products. The amalgamator is subsequently heated, releasing the mercury vapor to the absorbance cuvettes where peak height is measured at 253.7 nm as a function of ng of mercury.

Calibration for Method 7473 can be performed in two ways. One method is by the traditional analysis of aqueous standards. The ability for direct analysis also allows for unique calibration using solid standards with a certified mercury content. Method 7473 provides the option to perform calibration using solid samples, "An alternative calibration using standard reference materials may be used..."[3] This option is beneficial, especially for on-site analysis, when transport and storage of aqueous standards may be problematic.

Subsequent to validation of Method 7473 in both laboratory and field settings, the method was applied to the laboratory analysis of a series of contaminated soils. Duplicate soil samples were sent to a commercial laboratory for independent analysis. Only those soils with a mercury content less than 10 mg/kg were analyzed directly due to the extreme sensitivity of the instrument. Soils above 10 mg/kg were leached using EPA Method 3051A prior to analysis. Mercury content in these soils ranged from 1-700 mg/kg. Regardless of the mercury content, results using Method 7473 agree with results using the traditional cold vapor Method 7471A and show

greater precision. Average RSDs for Methods 7473 and 7471A were less than 10% and 15%, respectively.

In collaboration with a local engineering firm, Method 7473 has been used on-site to evaluate the remediation efforts of a large national utility company. A site near Gettysburg, Pennsylvania, was first evaluated. A sample was taken from each wall and the floor of the 124 ft^3 excavated area. It was determined that remediation efforts were successful, as the mercury content in all samples was below the action level of 20 mg/kg. These results have been confirmed by independent commercial laboratory analysis.

A second on-site evaluation was performed in Hocking County, Ohio. Real-time results were used to direct the extent of excavation. The original scope of work based exclusively on the site characterization was an excavation area of 750 ft^3 Use of Method 7473 on-site produced real-time information as to the level of remediation required and allowed remediatiors to reduce the planned excavation area by more than half to 250 ft^3. Real-time Method 7473 results indicated that the reduced excavation was adequate in all areas except one. Further excavation in that location was thus performed, providing a more accurate remediation and eliminating the need for a return trip to the site. Approximately $9,000 in savings resulted from the reduced amount of soil remediated and elimination of a return trip.

SUMMARY

A method for the direct determination of total mercury in both laboratory and field environments has been established. Method 7473 has been validated by analysis of SRMs as well as by independent analysis. Data indicates that Method 7473 can achieve lab-quality results in a field setting. use of Method 7473 in the field can lead to more accurate and cost-effective risk assessment of mercury contaminated sites. The next step will be to investigate compatibility of Method 7473 with speciation technology.

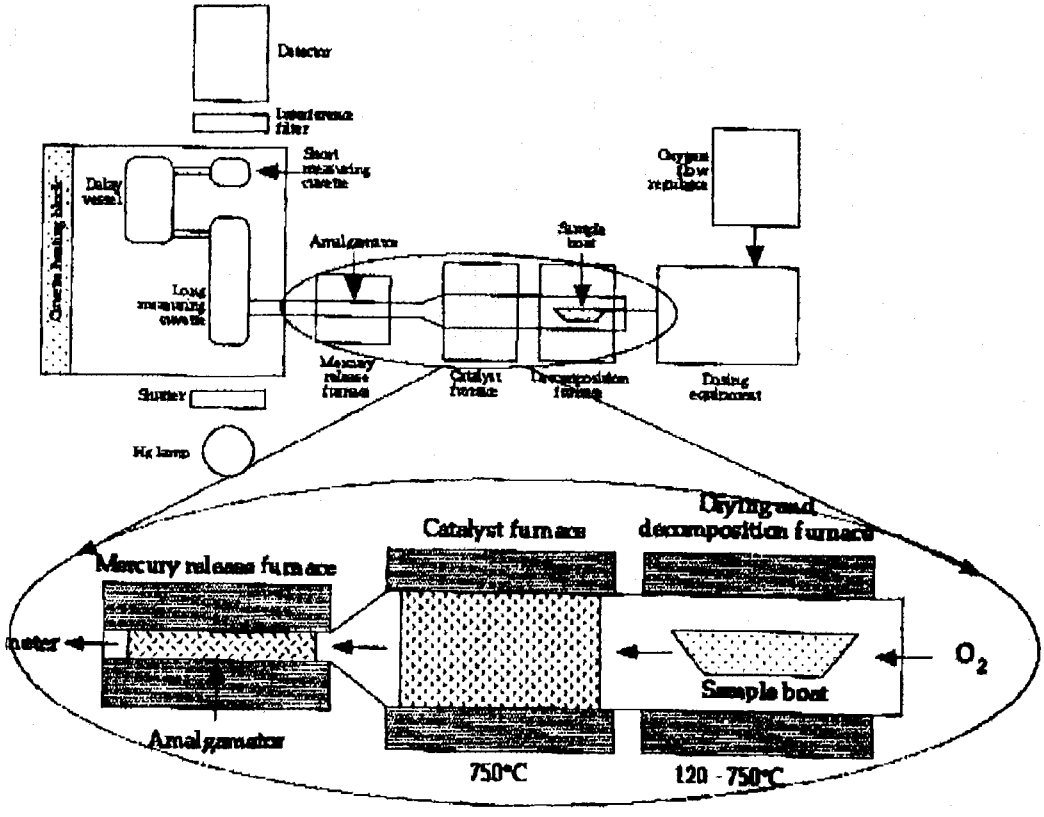

Figure 1. Schematic of the DMA-80

Table 1. Comparison of techniques use for method validation ($n \geq 5$).

EPA Method	7473	7471A	6020
Technique	direct mercury analysis	CV-AAS	ICP-MS
Average RSD	<10%	<15%	~15%
Agreement?	√	√	√

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MERCURY IN SOIL SCREENING BY IMMUNOASSAY

Mark L. Bruce and Kathleen L. Richards
Quanterra Inc., 4101 Shuffel Dr. NW, North Canton, OH 44720
brucem@quanterra.com
Lorraine M. Miller
Olin Corporation, 1186 Lower River Road NW, Charleston, TN 37310
lmmiller@corp.olin.com

Abstract
EPA SW-846 Method 7471 (Cold Vapor Atomic Absorption, CVAA) has been traditionally used for mercury analysis. This method requires several hours of labor and total processing time to prepare soil samples and analyze them. The sequential nature of the analysis step limits sample throughput and capacity. Also, the method is difficult to perform at a remediation site. In contrast, immunoassay (IA), as used in proposed Method 4500, prepares and analyzes the samples in parallel and can provide very large sample capacity in a 2-3 hour processing time. Also, the IA kit is much more field portable.

Quanterra performed an evaluation of the BiMelyze Soil Extraction and Mercury Immunoassay kit from BioNebraska for the Olin Corporation. Four different site soil samples were analyzed in quadruplicate by CVAA and IA following the New York State Department of Health (NYSDOH) Alternate Testing Procedure guidelines. Threshold standards were setup at 1 mg/kg and 15 mg/kg. No false negatives were observed. Thefalse positive rate was 6%. The overall accuracy rate was 94%.

Switching to immunoassay improves turn-around-time, sample capacity and field portability.

Introduction
Community, environmental and economic concerns are exerting pressure on the environmental market to reduce analysis turn-around time and cost. At the same time, some data end users have realized that traditional test methodologies and their QA/QC requirements are not necessary for all environmental decisions. There is a growing need to provide reliable, quick turn-around field testing in order to expedite site remediation. Accelerated testing can be instrumental in reducing the impact that remediation activities may have on the local community. It also facilitates faster site closure, thus reducing the time the excavation site is exposed to the effects of weathering.

Immunoassay has been widely used in biochemical testing for health services for decades. Several companies have adapted this technology to test environmental pollutants including organic compounds and metals. Immunoassay has proven to be a low cost, fast turn-around, high capacity analysis for the health sciences. These same characteristics make it very attractive for the environmental market. Immunoassay (IA) for metals does not provide data that is identical to the traditional inductively coupled plasma or atomic absorption tests. The specificity of IA should make it less susceptible to the interferences that limit spectroscopic analyses. However, the biochemical nature of IA may make it sensitive to new interferences. The QA/QC data normally available from IA can include replicates and matrix spikes.

This study compared the results from proposed US EPA SW-846 Method 4500 (Mercury in Soil Sample by Immunoassay) with EPA SW-846 Method 7471 (Cold Vapor Atomic Absorption, CVAA). Method 4500 was performed using the BioNebraska BiMelyze Soil Extraction and Mercury Immunoassay kit. Actual field samples

from a remediation site containing the analyte of interest (mercury) were used for this study.

Immunoassay Method Summary (excerpted from Section 2.2 of Method 4500)
"Solid samples are prepared by extraction with a mixture of hydrochloric and nitric acids for ten minutes and then buffered prior to analysis. The sample is added to a tube (treated with BSA-glutathione) and incubated at ambient temperatures for five minutes. The mercuric ions bound to the sulfhydryl groups of the BSA-glutathione are now reacted with a reconstituted antibody specific for mercury and incubated for five more minutes. A peroxidase conjugate is added to the sample, reacting with any mercury specific antibody. The substrate is then added forming a color that is in proportion to the amount of mercury originally present in the sample. The color produced is then spectrophotometrically compared with the control standards."

Experimental
This project evaluated the BioNebraska BiMelyze Soil Extraction and Mercury Immunoassay kits (BN-IA-Hg), proposed Method 4500 by comparison to the traditional mercury analysis method (cold vapor atomic absorption, SW-846 7471). NYSDOH Alternative Testing Procedure guidelines (4/1/86) were followed.

The NYSDOH Alternative Testing Procedure specifies that limited approval for a "new" test method requires the following analytical work:

1) Three samples from the soil source.
2) Analyze four aliquots of each sample with the approved method (7471).
3) Analyze four aliquots of each sample with the alternative method (4500).
4) Analyte concentrations should range from the detection limit to 20% greater than the regulatory limit.
5) The result from the alternative method must fall within the confidence interval of the approved method (based on two times the published standard deviation).

An additional sample from the soil source which had a mercury concentration previously determined to be well below the lowest action threshold was evaluated to test the likelihood of the IA kit producing false positives. False positives occur when interferences or analytical error produces a test result that is greater than the control threshold when the analyte concentration is actually below the threshold. A false positive can result in unnecessary remediation work.

Also, it is common to intentionally bias the results of semi-quantitative field tests slightly high. This reduces the false negative rate. Many organic immunoassays use a bias of 30%. A 20% bias had been used previously by others working with the BioNebraska mercury test kit. A 30% bias on the threshold standards was selected for this study.

The NYSDOH requirements described above were met as follows:

1) Four samples from the soil sample source were selected based on previous CVAA analysis to cover the appropriate concentration ranges. Approximately 150 g of each sample was frozen and then homogenized cold to reduce analyte losses. The samples were stored at 4°C until appropriately sized aliquots were removed from the sample containers for each test method. No elemental mercury was visible and the samples appeared visually to be homogeneous before sub-aliquots were removed.
2) Four aliquots of each of the 4 samples were analyzed by Method 7471.
3) Four aliquots of each of the 4 samples were analyzed by Method 4500 following the procedure described in the BioNebraska test kit product literature. The two control thresholds were 1 and 15 mg/kg since those correspond to the two action limits for theapplicable site.
4) Ideally one sample would have been available for the middle of the following ranges: $x < 0.5$ ppm, 1 ppm $< x <$ 5 ppm, 10 ppm $< x <$ 15 ppm, 15 ppm $< x <$ 20 ppm
   The quadruplicate CVAA results show that 3 of the 4 ranges were covered by the samples selected.
5) Since the alternative method is semi-quantitative, the range determined for each individual sample was compared to the corresponding average quantitative result from Method 7471.

Results and Discussion
Accuracy
The mercury field test kit is semi-quantitative for this site (e.g. $x < 1$ mg/kg or 1 mg/kg $< x <$15 mg/kg or 15 mg/kg $< x$). The concentration range determined by method 4500 (IA) was compared to the concentration

measured by 7471 (CVAA). IA results which placed the sample in the correct range were considered "accurate". Results that were too low were labeled "false negative". Results that were too high were labeled "false positive". Normal US EPA criteria for field test kits specify the false negative rate should not exceed 5%. NYSDOH criteria were not available.

Table 1. Comparison of Average Results, CVAA vs IA

Sample ID	CVAA avg mg/kg	IA avg abs	IA interpretation (mg/kg) x<1	1<x<15	15<x	Test Agreement
B41-24-102297	0.12±0.02	0.21	X			OK
B11-02-102197	9.4 ±0.88	0.43		X		OK
B44-02-102197	35.2 ±9.2	1.20			X	OK
B1-24-102197	16.9±14	0.77			X	OK

±2 standard deviation confidence interval

Table 2. Comparison of Detailed Results, CVAA vs IA

Sample ID	CVAA mg/kg	IA abs	IA interpretation X<1	1<x<15	15<x	Test Agreement
blank soil		0.07				
1 ppm threshold std*		0.24				
15 ppm threshold std*		0.70				
B41-24-102297	0.12					
	0.12					
	0.12					
	0.10					
		0.24		x		false +
		0.21	x			OK
		0.20	x			OK
		0.19	x			OK
B11-02-102197	9.6					
	9.2					
	8.8					
	9.8					
		0.45		x		OK
		0.40		x		OK
		0.43		x		OK
		0.42		x		OK
B44-02-102197	41					
	36					
	33					
	31					
		1.26			x	OK
		1.47			x	OK
		0.93			x	OK
		1.13			x	OK
B1-24-102197	27					
	16					
	12					
	13					
		1.03			x	general
		0.62		x		data
		0.77			x	set
		0.67		x		agreement

*The actual concentration of the two threshold standards was 30% lower than the stated thresholds in order to reduce the likelihood of false negative results

The average IA results agreed with the average CVAA results for each of the four samples.

As expected the individual results showed greater variability and slightly less agreement between the two analysis types. One immunoassay result from B41-24-102297 (x < 1 ppm) was a false positive since its absorbance equaled that of the 1 ppm threshold standard. Occasional results of this type are to be expected when using low biased threshold standards to reduce the false negative rate. The IA and CVAA results for samples B11-02-102197 (1 < x < 15 ppm) and B44-02-102197 (15 ppm < x) showed excellent agreement.

Sample B1-24-102197 had a concentration near the 15 ppm threshold and was apparently more heterogeneous than the other samples (despite the extensive homogenization that had been performed). Both the IA and CVAA results were more variable and were evenly split on either side of the 15 ppm threshold. As a general data set the results from the two methods are in agreement. Please note that since the individual IA and CVAA analyses were performed on separate aliquots of the same sample, it is not appropriate to directly compare the individual test results in order. Rather the quadruplicate results from each method must be considered as a set.

Given the results discussed above and shown in the table below, no false negatives (0%) and only one false positive (6%) were observed in the 16 sample assays. The agreement rate between the two tests was 94%.

The average IA kit absorbances correlated well with the CVAA average results. This indicates it may be possible to use the IA kit for quantitative analysis, particularly if standards were prepared in or made from soil samples on-site. The chart below shows IA absorbances plotted relative to the CVAA results. The IA standard soils (from BioNebraska) are also shown relative to their actual prepared concentrations. The least squares linear equation for the 4 soil samples was :

IA abs = 0.02879 (Hg conc mg/kg) + 0.2089 with an R^2 value of 0.9848.

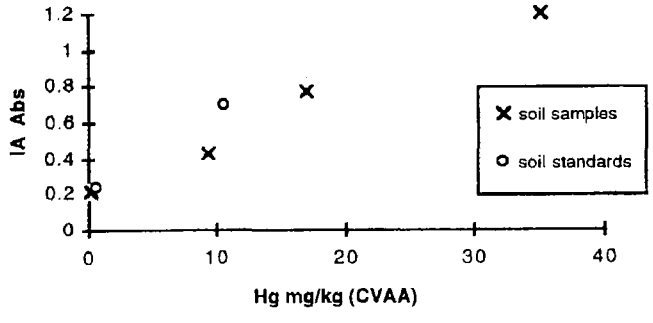

Figure 1. Comparison of IA Absorbance vs CVAA Concentration

Precision

The standard deviation of the absorbances produced by the IA test were useful when interpreting results near a control threshold. It is not practical to calculate the standard deviation of the concentration since this is a semi-quantitative test in its current configuration.

The percent relative standard deviation (%RSD) of the result (conc for CVAA and absorbance for IA) for each method was comparable. This indicates the two methods have the same precision for this group of samples. Most likely sample homogeneity was the factor which limited the precision of both methods.

Table 3. Comparison of Precision, CVAA vs IA

Sample ID	CVAA		IA	
	Std Dev	%RSD	Std Dev	%RSD
B41-24-102297	0.01	8.6	0.02	10
B11-02-102197	0.44	4.7	0.02	4.9
B44-02-102197	4.6	13	0.23	19
B1-24-102197	7.1	42	0.18	24
average %RSD		17		

Information from a BioNebraska representative indicates that the use of volumetric pipettes instead of the "eye dropper" volume measurements described in the product literature may have improved precision by a few percent.

Sample Turn-Around Time

Complete kit preparation, extraction and analysis of a batch of soil samples took approximately 3 hours for a

batch of 19 assays (16 samples). Kit preparation (including reagent prep and sample container labeling) took about 0.5 hours. Extraction and filtration of the soil samples took 1.75 hours. Performing the immunoassay took 0.75 hours. Two analysts were working together performing the soil filtrations. If a single analyst was performing all the filtrations with the filters supplied in the kit, add about 0.5 hours to the total time. Obviously smaller batches of samples would reduce the time required for kit preparation, extraction and filtration but the assay step would be only slightly shorter. Also, autopipettes and repeating pipettes were used (at client request) to improve accuracy and precision. This equipment (not included in the field kit) also shortened the time necessary for some of the liquid handling steps in the immunoassay.

Sample Capacity
The field portable version of the test kit is designed to process 13 soil samples in each batch. Smaller batches can be processed but the cost per sample increases because the test kits are used less efficiently and additional control soil samples must be purchased. The laboratory version of the test can be configured for much larger batch sizes. Using laboratory pipettes and previous experience with immunoassay, two field kits were combined to process all 16 tests (4 samples in quadruplicate) in the same batch. Laboratory kits are available to process up to 96 assays (~80 samples) in a batch.

Analyst Skill
The field test kit was designed for use by field technicians with average manual dexterity and attention to detail but limited experience with scientific instrumentation. Based on the experience during this study, this expectation is true. Appropriate hands-on training with the IA kit on known samples is essential before beginning work on unknown samples. Also, two problems occurred during sample preparation which might happen for other samples on this site.

1) B44-02-102197 produced a large amount of foam when the acid was applied to the sample at the being of the extraction. During the study, the acid was added very slowly and the bottle continuously tapped on the bench top to break the foam bubbles. Even so, 2 of 4 aliquots lost about 1% of the sample due to foaming out of the extraction bottle. This did not appear to affect the assay results but required considerable attention, persistence and time to avoid significant sample loss. An experiment conducted after the assays were complete showed that adding the recommended amount of acid solution to a 5g sample aliquot resulted in foam overflowing the normal 32 mL sample bottle and a 67 mL bottle. When a 140 mL bottle was used the foam filled 80% of the bottle before bursting and settling into the bottom of the bottle. Thus, for samples similar to this one it would be advisable to use a 140 mL bottle to avoid accidental sample loss, slow processing and increasing the skill requirements.

2) The extract filtration step was much slower for the samples collected at the site than for the standard soils supplied by BioNebraska. Sample B41-24-102297 in particular was very difficult to filter. Several samples required squeezing the sample bottle with pliers in order to force sufficient extract filter. This would make reproducible results difficult using "eye dropper" volume measurements at this point in the process. Other types of IA kits have more "user-friendly" filtration processes. It may also be possible to adapt the current filtration process to improve its performance.

Conclusion

Method 4500 (IA) produced semi quantitative results which matched the Method 7471 (CVAA) results for 15 of the 16 tests (94%) performed. There was one false positive where the immunoassay overestimated the mercury concentration. The false negative rate in this four sample evaluation study was 0%, while the false positive rate was 6%. This meets the requirements of the NY DEC Alternative Testing Procedure. In addition, the average IA absorbances from each quadruplicate set of data correlated very well with the CVAA results. This indicates that the IA kit may also be useful for quantitative analyses in the future.

Summary of Reporting Limits and Performance Results

Matrix	Mercury	Accuracy	False Negative	False Positive
soil	1 mg/kg	94%	0%	6%

Acknowledgments

The authors would like to thank Veronica Bortot from Quanterra - Pittsburgh for overall project coordination and Craig Schweitzer from BioNebraska for IA product and technical support.

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UTILIZATION OF A FIELD METHOD FOR THE SEMIQUANTITATIVE DETECTION OF SILVER IN ENVIRONMENTAL SAMPLES IN THE 0 - 50 ppb RANGE

Dan Kroll
Hach, 100 Dayton Road, Ames, Iowa 50010

Abstract
Silver is commonly used in industry, and its bactericidal properties have also lead to its use for water disinfection purposes. Excess concentrations of silver may damage human health and be toxic to aquatic life. Current methods of silver analysis, in the ppb range, require expensive equipment and careful technique. There is a need for a quick, easy screening method for silver at these levels. The procedure described employs the bromopyrogallol red/1,10-phenanthroline method, described by Dagnall and West (1964), combined with a novel concentration/detection method. At a pH of 7, a ternary complex is formed with two 1,10-phenanthroline molecules binding to each silver ion, and then two of these complexes bind to a bromopyrogallol red molecule. This results in a blue precipitate. The colored precipitate is caught on a 13 µm pore size filter, and the filter is compared to a precalibrated (0, 5, 10, 25, and 50 ppb) printed color chart for quantification. All the reagents are combined in a single powder that contains both dyes, a buffer, and a masking reagent. The system is easy to use, fast, portable, and all reagents are stable for at least one year making the system ideal for field testing. This method has been evaluated on a variety of tap water, pool & spa water, river water, and sewage effluent samples that have been spiked with known amounts of silver. Some of the river water samples and the sewage effluent required a sulfuric acid digestion, but all samples resulted in good recovery of the spikes and correlated well with numbers generated using AA techniques. Various soil samples that were spiked with 25 ppb Ag resulted in good recoveries that corresponded to the appropriate color spot on the chart. Use of this method as a screening process may help to save time and money by cutting down on the need to do more accurate analysis of all samples.

Introduction
Silver is a common contaminant of industrial process and wastewater. In private industry, silver is used in applications such as jewelry, coins, dentalware, silverware, solder, electroplating, photography, and battery production. In low concentrations, silver's antibiotic properties make it desirable for use as a fungicide and for drinking water disinfection purposes, and it has been gaining in popularity as a pool and spa biocide. However, according to the World Health Organization (WHO), continuous exposure to silver in drinking water (0.4 mg or more) in humans causes arygaria, an irreversible condition which produces a bluish-gray discoloration of the skin, hair, nails and eyes.[4] Long term continuous exposure to silver has also been implicated in liver damage and enzyme inactivation in humans.[4]

Unpolluted surface water levels of silver usually range between 0.1 4 µg/L. Drinking water levels range between 0 - 2 µg/L; average = 0.13 µg/L.[3] The WHO has not as yet set limits for safe silver concentrations in drinking water.[5] The USEPA has adopted the Public Health Service (PHS) standard that silver in domestic water not exceed 50 µg/L.[3] The USEPA-adopted PHS standard was set to protect aquatic life and human health. Canada has adopted a similar 50 µg/L standard while the EEC standard is 10 µg/L.[5] Silver is also on the list of seven priority pollutant metals that must be monitored in landfill leachate.[7]

There are many current methods to measure silver in the ppb ranges. These include atomic adsorption by flame or electrothermal techniques, inductively coupled plasma, or colorimetry. Each of these methods requires complicated and expensive apparatus, hazardous chemicals and/or a large investment in time and equipment. Each also has its drawbacks. AA is accurate at moderate concentrations, but displays sensitivity to ion interference. ICP techniques have higher minimum detection limits and are sensitive to refractory elements.

Colorimetry loses sensitivity at these ranges and uses hazardous chemicals.[6]

There is a need for a portable, rapid, easy, and safe screening method for low levels of silver. The method described in this article meets all of these requirements and requires less time than conventional methods. The user obtains an on-site reading that only takes minutes to obtain. The procedure features a simple visual comparison for obtaining semiquanitative measurements for silver between 0-50 µg/L. Single-reagent addition and quick results make this method ideal for field testing.

Method and Chemistry

This test makes use of the fact that under certain specified conditions, metals form brightly colored precipitates with certain dyes or mixtures of dyes. In the case of saver, the complex formation is with 1-10 Phenanthroline and Bromopyrogallol Red. This chemistry is an adaptation of a reaction described by Dagnall and West.[1] In this reaction each Ag ion first reacts with two 1-10 Phenanthroline molecules to form a colorless complex. Two molecules of this complex then react with a molecule of the Bromopyrogallol Red to form a blue precipitate. Dagnall and West made use of this system for the spectrophotometric detection of silver with a lower detection limit of 20 ppb. The system that I am currently using follows this chemistry until the method of detection. I make use of the fact that the blue complex is an insoluble precipitate in an aqueous sample.

A reagent powder is prepared that contains a Sodium Citrate - Citric Acid buffer system with a pH of 7. The powder also contains Tetrasodium EDTA as a masking reagent to remove interference from other metals. An excess of 1-10 Phenanthroline is added to make sure that there is more than enough present to complex the silver along with any iron that may be present. If excess 1-10 Phenanthroline is not added, it may all bind to contaminant iron leaving none available for the silver. Finally, the reagent powder contains the Bromopyrogallol Red. The final reagent powder is then packaged at a weight fill of 2.0 g in unit dose form. This is the amount needed to react with a 100 mL sample.

After the initial chemical reaction is carried out, 100 mL of the reacted sample is filtered by being forced with a syringe through a nitrocellulose microporous filter. (Schleicher & Schuell) The blue precipitate is trapped on the filter. The intensity and hue of the filter is dependent in a quantitative manner upon the original concentration of silver present in the sample. The colored filter is then compared to a color matching chart with different shades of blue corresponding to different concentrations of silver. By manipulation of the dye concentrations, filter size, pore size, and sample volume, the levels to which the test can be made effective can be altered. Using a 100 mL sample, 5 mm dia. filter size (a Gelman #4317 13mm plastic filter holder is modified with washers to expose a 5 nun surface area on the filter), and 12 µm pore size, visual levels of detection down to 5 ppb Ag can be achieved. The final color coding chart for silver has gradations of 0, 5, 10, 25, and 50 ppb Ag (See Fig. 1). This method has been validated on a number of different water matrices using NIST standard spikes (SRM3151) and compared to AA (Varian SPECTRAA 20-plus) for verification. This method allows visual detection of silver in ranges that are comparable to, and in some cases lower than, the levels of detection that are possible with more costly and time consuming methods, such as AA.

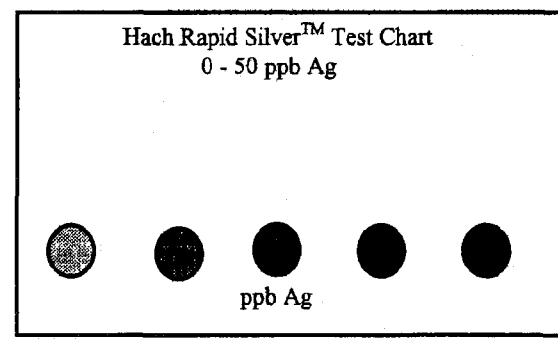


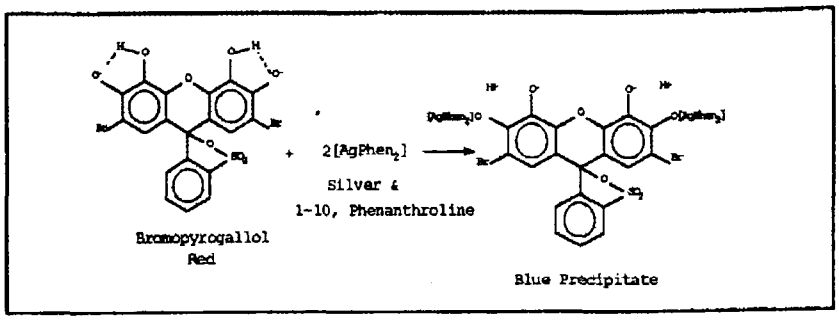
Figure 1. Color Comparator Chart

Summary of Method

Silver ions at a pH of ~7 combine with two molecules of 1,10-Phenanthroline to form a colorless water soluble complex. Two molecules of this complex then combine with a molecule of Bromopyrogallol Red to form a water insoluble blue precipitate. (See Fig. 2) This blue precipitate is then captured on a nitrocellulose filter. The filter is then compared to a color chart and matched to the appropriate spot for a semi-quantitative reading. The reagent pillow contains appropriate buffer, indicator, and EDTA as a masking reagent. A pretreatment of ascorbic acid is necessary to remove Cl_2 in excess of 2 mg/L. Digestion is needed for some samples. Other samples such as very concentrated soil digests that contain large quantities of interfering metals may require the addition of extra EDTA and or sodium citrate as chelating reagents.

Sampling and Storage

Collect samples in an acid-cleaned glass or plastic container. Adjust the pH to 2 or less with Nitric Acid (about 2



mL per liter). Store preserved samples at room temperature for up to six months. Adjust the pH to ~7 with Ammonium Hydroxide before analysis. Do not use a pH meter as silver contamination from the electrode may occur. Phenol Red may be used as an indicator. Correct the test results for volume additions.

Figure 2. Reaction Mechanism

Interferences

Interference studies were conducted by preparing a known silver solution (approximately 0.010 mg/L) and the potential interfering ion. Positive interference was tested by running blanks of deionized water that contained the potential interfering ion. The ion was said to interfere when the resulting change threw off the color match by more than 1/2 step on the chart. The following substances, at the stated levels, show no interference on a 10 ppb Ag standard test. There should be no problem with color matching or bad blanks at these levels. These tests were run at the levels indicated, although greater concentrations may be tolerated.

Table of Interference Study Results

Cation or Anion	Level	Type of Interference	Cation or Anion	Level	Type of Interference
Aluminum Al	10 ppm	none	Manganese Mn	10 ppm	none
Antimony Sb	10 ppm	none	Mercury Hg	10 ppm	none
Bismuth Bi	10 ppm	none	Molybdenum Mo	10 ppm	none
Borate $Na_2B_4O_7$	1 g/L or 215 ppm as B	none (fades with time)	Nickel Ni	10 ppm	none
Barium Ba	10 ppm	none	Nitrate NO_3 as N	250 ppm	none > amounts appear to fade color
Chlorine Cl_2	5 ppm	Dingy but readable > OK with ascorbic acid	Nitrite NO_2 as N	100 ppm	none > amounts appear to fade color
Chloride Cl^-	400 ppm	none > amounts interfere	Ammonia NH_3^+ as N	1000 ppm	none
Chlorite HOCl	1 Ppm	none	Palladium Pd	10 ppm	none
Calcium Ca^{+2}	1000 ppm	none	Phosphate PO_4 as P	1000 ppm	none
Chromium Cr^{+3}	10 ppm	none	Potassium K	1000 ppm	none
Chromium Cr^{+6}	10 ppm	none	Platinum Pt	50 ppb	none > negative interference
Cadmium Cd^{+2}	10 ppm	none	Sulfate SO_4	1000 ppm	none
Cobalt Co	10 ppm	none	Selenium Se	10 ppm	none
Copper Cu^{+2}	10 ppm	none	Silica SiO_2	1000 ppm	none
Flouride F^-	10 ppm	none	Thallium Tl	1 ppm	none
Gold Au	10 ppb	none > negative interference	Tin Sn	10 ppm.	none
Iron Fe^{+2}	10 ppm	none	Titanium Ti	10 ppm	none
Iron Fe^{+3}	10 ppm	none (lite pink tint) >with addition extra	Phenanthroline	1 ppm	none
Lead Pb	10 ppm	none	Zinc Zn	10 ppm	none
Magnesium	1000 ppm	none			

Turbid samples should be pre-filtered through a glass fiber filter. Oils and surfactants may interfere by preventing

formation of the insoluble complex; however, appropriate digestion may eradicate some of these interferences.

Materials that were not tested, that according to the literature do interfere, are Uranium (VI), Thorium (IV), and Niobium (V). They all form blue colored complexes with Bromopyrogallol Red. They can be masked at a 10-fold excess over silver by the addition of excess fluoride for Uranium and Thorium, and of hydrogen peroxide for Niobium.[1]

Precision

In a single laboratory, using a standard solution of 0.010 mg/L silver and three representative lots of reagents, a single operator performing 50 tests per lot obtained no results that were not properly matched to the 10 ppb color dot within 1/2 step. In other words all results were within a range of 7.5 to 17.5 ppb. These results were compared to results obtained on a AA (Varian SPECTRAA 20-plus). The results for the AA on 30 repetitions using the same standard gave an average of 6 ppb with a standard deviation of 4.98 ppb. The recommended lower level of detection for the AA was 20 ppb.

Assuming the worst case scenario where the standard deviation for the visual test method is 7.5 ppb a z test was performed to compare the mean results from the two methods. This resulted in a calculated z value of 2.86. This value for the z statistic indicates that the means are not the same with over 99% confidence. In this case, where the amounts of silver to be detected are below the recommended level of detection for the AA, the visual method out performs the AA.

Performance on Environmental Samples

Samples from a hot tub utilizing bromine as a disinfectant, Ames, Iowa tap water and pool water from Carr pool, also in Ames, were spiked at a level of 10 ppb silver. Tests run in the field using the visual method resulted in 100% recovery on these spiked samples. All samples matched the 10 ppb spot.

Samples run on sewage effluent from the Ames, Iowa sewer plant and surface water from the Skunk River near Ames resulted in poor or no recovery. This is probably due to the binding of the silver ions by humic or fulvic acids present in the sample, or possibly because of reduction of the silver ions to silver metal upon addition. 100% recovery on spiked 25 ppb silver samples was found after treatment of the samples with a simple sulfuric acid - hydrogen peroxide digestion procedure (Hach Didesdahl™ Procedure)2. Strongly reducing samples, samples with high organic content, and samples which contain thiosulfate or cyanide should be digested before testing.

Summary of Results

Source of Sample	Expected Conc. Ag (ppb)	Observed Conc. Ag (ppb)
Tap Water	10	10
Pool Water	10	10
Spa Water	10	10
Sewage Efluent	25	25
River Water	25	25
Crowley Silt Loam	30-32	35
Coland Clay Loam	25	25
Clarion Loam	25	25
NIST SRM 2711	25	25

Tests were run on digested samples of a Crowley Silt Loam soil obtained from the Louisiana State University Extension Service. 0.5g of the sample was digested using the Hach Digesdahl™ procedure. The digests were then filtered through a glass fiber filter and diluted to a final volume of 1 liter. These tests resulted in no recovery. After the addition of 1.5 g of extra disodium citrate as a complexing reagent to remove interfering ions, the samples were found to give a blank of ≈8 ppb for the visual test and 4.66 with a standard deviation of 5.07 ppb on the AA. 0.5g samples of the soil were then spiked with 25 µg of silver and the procedure was repeated. All of 30 samples measured by the visual test read between the 25 and 50 ppb dots for an extrapolated average of ≈35 ppb. The same samples ran on the AA gave an average result of 36.66 ppb with a standard deviation of 4.34 ppb. Assuming the worst case scenario where the standard deviation for the visual test method is 12.5 ppb a z test was performed to compare the mean results from the two methods. This resulted in a small z statistic of -0.69. This value for the z statistic indicates that the means for this sample using the visual and AA methods are

statistically the same. The initial silver content of the soil explains the differences in the spiked and recovered amounts. Tests performed on a Coland Clay Loam and a Clarion Loam obtained in the Ames area gave similar results, but with no detectable blanks.

Finally a 0.5407 g sample of Montana soil NIST SRM 2711 was digested using the Digesdahl™ procedure. This amount of test soil results in a final solution, when diluted to 100 mL, with a reported assay value of 25 ppb silver. All of the samples tested correlated well with the reported values. All samples tested matched the 25 ppb dot using the visual method.

Stability
Reagents kept at 35°C for 1 year still function properly.

Summary
The method described was utilized to test various soil and water samples for the presence of Ag. All of the matrices that were examined gave acceptable results. The results were comparable to those obtained with an AA, and in the case of levels of 10 ppb and below, the visual method was found to be superior to the AA. This method should be useful as a field method for determining trace amounts of silver in a variety of environmental samples.

The use of this method should save time and money without compromising the accuracy of analysis.

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DIAGNOSING ERRORS IN SPECIES ANALYSIS PROCEDURES USING SIDMS METHOD 6800

H.M. "Skip" Kingston, Dengwei Huo, Yusheng Lu
Duquesne University, Department of Chemistry and Biochemistry Pittsburgh, PA 15282-1503
412-396-5564

The determination of chemical species in environmental samples is difficult when the species are easily altered during the analysis process. A method has been developed to permit the species to undergo chemical reactions during analysis and correct for these changes. Speciated Isotope Dilution Mass Spectrometry (SIDMS) is especially suited for species that equilibrate in solution quickly and also degrade during extraction, oxidize or reduce during analysis or are difficult to separate quantitatively using conventional methods[1] This method is a new draft EPA RCRA method (Method 6800) that utilizes isotopically enriched speciated spikes combined with isotope dilution to accurately determine and correct for species transformations that occur in sample processing. The errors in the measurement are those that are limited by the ability of the ratio measurement and the equilibrium of the species during spiking. This method was specifically developed to address the problems of accurately quantifying different species in complicated matrices that also play a role in the stability of the species during extraction, separation or manipulation. Additionally, it is a diagnostic tool for identifying both the error and bias inherent in specific method steps prior to and during sample analysis such as sampling process, storage, sample preparation, and chemical modifications prior and during measurement. The basic SIDMS method is applicable to many species of elements with multiple isotopes and extends to various oxidation states, organometallics, and molecular forms of species. The method is used as a diagnostic tool and reference method assisting with error identification in other methods permitting their development as more accurate and precise species analysis tools.

Validation data for Cr(VI) and Cr(III) demonstrate the ability of SIDMS to examine other methods in a diagnostic manner. The extraction procedure Method 3060A and analysis Method 7196A are used to demonstrate the identification of specific chemical changes that take place in these methods. These changes can be corrected by use of this very sensitive internal speciated tracer[2].

The objective of EPA Method 6800 is to provide a new reference method that is also legally defensible as a reference method for measurements that have high degrees of uncertainty and error due to highly reactive species.

1. Kingston, H.M. Skip, Dengwei Huo, Yusheng Lu, Stuart Chalk, "Accuracy in species analysis: Speciated Isotope Dilution Mass Spectrometry (SIDMS) exemplified by the evaluation of chromium species" Spectrachemica Acta B, (accepted) 1998.
2. Yusheng Lu, Dengwei Huo and H.M. Skip Kingston. "Determination of Analytical Biases and Chemical Mechanisms in the Analysis of Cr(VI) Using EPA Protocols" ES&T (submitted) 1998.

THE USE OF ^{210}Pb DATING AND DETAILED STRATIGRAPHY TO DETERMINE THE SIGNIFICANCE AND FATE OF CHROMIUM IN SEDIMENTS NEAR A HAZARDOUS WASTE SITE

Richard Rediske
The Robert B. Annis Water Resources Institute, Grand Valley State University, Allendale, MI 49401
616-895-3047
Gary Fahnenstiel
National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Lake Michigan Field Station, 1431 Beach St., Muskegon, MI 49441
Claire Schelske
Department of Fisheries and Aquatic Sciences, University of Florida, Gainesville, FL
Marc Tuchman
USEPA Great Lakes National Program Office, 77 West Jackson Blvd., Chicago, IL 60604

ABSTRACT

An innovative investigation using ^{210}Pb dating and detailed stratigraphy was conducted to determine the significance and fate of chromium in the sediments of White Lake (Michigan). Elevated sediment concentrations of chromium, arsenic, and mercury were found in the vicinity of the historical effluent discharge point of a tannery. The chromium levels found in the sediments were among the highest concentrations reported in the Great Lakes basin (20,000 mg/kg). Since the direct discharge of effluent from the tannery was discontinued in 1976, vertical depositional patterns may reflect changes in the flux of chromium into the system. Historical levels of metals may be covered by less contaminated material or resuspended by physical events. Information on sediment stability and deposition rates was critical to the development of remediation options for the site.

Traditional sampling and analytical methods would not provide information on sediment stability and accumulation patterns. Radiodating using ^{210}Pb, a technique commonly used in linmology, was employed to determine the history of sediment deposition. This technique was augmented with detailed stratigraphy analysis to provide a current and historical record of chromium deposition in the sediments. Two piston core samples were collected in the tannery discharge area and sectioned in 2 cm intervals. Total chromium was analyzed by ICP. Radiometric measurements were made using a low-background gamma counting system with a well-type intrinsic germanium detector. Total ^{210}Pb activity was obtained from the 46.5 kev photon peak, and ^{226}Ra activity was obtained from the 609.2 kev peak of ^{214}Bi. The 661.7 kev photon peak was used to measure ^{137}Cs activity. The peak in ^{137}Cs activity was measured to evaluate its usefulness as an independent time marker for the peak period of fallout from nuclear weapons testing in 1962-63.

Chromium stratigraphy in the tannery discharge area indicated that the top 15-20 cut of sediment was less contaminated (2,000-4,000 mg/kg) than sediment located at >30 cm (>5,000 mg/kg). Radionuclide results suggested that this surface sediment layer was well mixed, however, distinct from the deeper more highly

contaminated sediments. Presently this surface sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The surface layer was followed by a region (30-80 cm) that contained chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should have been apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments suggested that the processes of mixing and resuspension continue to be active. In addition, chromium transport to the 0-20 cm sediment zone may also have occurred by other mechanisms including surface runoff of contaminated soils and possibly groundwater advection. The lack of a significant ^{137}Cs horizon in the sediments indicated that groundwater was discharging in this region; however, the linkage with chromium mobility required further investigation.

INTRODUCTION

White Lake is a 2,571 acre, drowned-rivermouth lake located on the eastern shore of Lake Michigan in Muskegon County. The Lake is part of the White River Watershed and discharges directly to Lake Michigan through a channel located on the western end. White Lake was designated an Area of Concern (AOC) in 1985 by the International Joint Commission because of historical discharges of heavy metals and organic chemicals. Chromium, mercury, arsenic, and animal hides have been discharged into White Lake by Whitehall Leather. The tannery began operating in Whitehall near the turn of the century and used wood bark as the original tanning agent. In 1940, the tanning agent was changed to chromic sulfate, and a series of six waste treatment lagoons were constructed near an area of the shoreline called Tannery Bay. Effluent from these lagoons containing heavy metals and leather byproducts was discharged directly into the bay. In addition, dredged materials from the lagoons and other process wastes were disposed of in landfill areas adjacent to the shore. The direct discharge of wastewater effluent from the tannery ceased in 1976. Previous investigations have indicated extensive contamination of sediments in White Lake. Elevated levels of chromium, lead, arsenic, and mercury were detected in the northeastern section of the lake in 1982 (WMSRDC 1982) and in 1994 (Bolattino and Fox 1995). This area was the historical discharge point for tannery effluent from Whitehall Leather. The chromium levels found in the sediments of this area were some of the highest reported from any site in the Great Lakes. Since the direct discharge of effluent to Tannery Bay was discontinued in 1976, vertical depositional patterns may reflect changes in the flux of chromium into the system. The stability of the sediments in this region was also unknown. Without more information on sediment stability and accumulation rates, it would difficult to determine the residence time of contaminants within any specific region of the sediments. Whether historical levels of metals are being covered by less contaminated material or being resuspended by physical events are critical questions that need to be answered before evaluating remediation options.

An innovative investigation using ^{210}Pb dating and detailed stratigraphy was conducted to determine the significance and fate of chromium in the sediments of White Lake. Radiodating using ^{210}Pb provides a continuous sequence of dates from a single core utilizing the natural decay of ^{210}Pb. This technique has been widely used in limnology and has been independently verified by comparisons with other techniques (e.g., Robbins et al. 1978; Appleby et al. 1979; and Wolfe et al. 1994). ^{210}Pb is a naturally occurring radioisotope that enters lakes through wet and dry deposition following the decay of atmospheric ^{222}Rn. Once in the take, ^{210}Pb is rapidly scavenged by particles and settles to the bottom. The concentration of ^{210}Pb can then be analyzed at a series of depths in the cores from the surface to the depth where excess ^{210}Pb is no longer measurable, approximately 5-8 half-lives or 150 years. From this ^{210}Pb profile, dates and sediment accumulation rates are calculated using one of several mathematical models, such as the constant rate of supply method. Using a combination of ^{210}Pb dating and detailed metal stratigraphy, critical information related to contaminant profiles and sediment stability was obtained. The technique described can be used at hazardous waste sites where the evaluation of contaminated sediments is required for remediation.

EXPERIMENTAL

The sediment cores were collected with a VibraCore device with core lengths ranging from 6 8 ft. The core samples were then sectioned in three equal lengths for chemical analysis. Ponar samples were also collected at these locations to provide an assessment of the near surface zone sediments. A piston corer (Fisher et al. 1992) was used to obtain the samples for stratigraphy and radiodating since the VibraCore causes some degree of internal mixing in the core tube. VibraCore samples were collected during 1994. The ponar and piston core samples were collected during 1996. Sampling locations are shown in Figures I and 2. All samples were collected using the USEPA *R.V. Mudpuppy.*

Piston core samples were extruded and cut into 2 cm intervals. Each interval was weighed and an aliquot was

removed for metals analysis. Sample preparation and analysis methods (EPA 1994) for metals are listed below:

Arsenic	Graphite Furnace	7060/3050
Chromium	Inductively Coupled Plasma	6010/3050
Mercury	Cold vapor	7471

All metals results were reported on a dry weight basis.

The preparation for radiometric analysis consisted of freeze drying the sediment and the grinding the sample to a homogenous mixture. Sub samples were then packed and sealed with an epoxy resin in polypropylene tubes in preparation for radiometric analysis.

Radiometric measurements were made using low-background gamma counting systems with well-type intrinsic germanium detectors (Schelske et al. 1994). To prepare samples for radiometric analysis, dry sediment from each section was packed to a nominal height of 30 min in a tared polypropylene tube (84 mm high x 14.5 mm outside diameter, 12 mm. inside diameter). Sample height was recorded and tubes were weighed to obtain sample mass. Samples in the tubes were sealed with a layer of epoxy resin and polyamine hardener, capped, and stored before counting to ensure equilibrium between ^{226}Ra and ^{214}Bi. Activities for each radionuclide were calculated using empirically derived factors of variation in counting efficiency with sample mass and height (Schelske et al. 1994). Total ^{210}Pb activity was obtained from the 46.5 kev photon peak, and ^{226}Ra activity was obtained from the 609.2 kev peak of ^{214}Bi . ^{226}Ra activity was assumed to represent supported ^{210}Pb activity. Excess ^{210}Pb activity was determined from the difference between total and supported ^{210}Pb activity and then corrected for decay from the coring date. The 661.7 kev photon peak was used to measure ^{137}Cs activity. The peak in ^{137}Cs activity was measured to evaluate its usefulness as an independent time marker for the peak period of fallout from nuclear weapons testing in 1962-63.

Sediments were aged using measurements of the activity of naturally occurring radioisotopes in sediment samples. The method is based on determining the activity of total ^{210}Pb (22.3 yr half-life), a decay product of ^{226}Ra (half-life 1,622 yr) in the ^{238}U decay series. Total ^{210}Pb represents the sum of excess ^{210}Pb and supported 2 10Pb activity in sediments. The ultimate source of excess ^{210}Pb is the outgassing of chemically inert ^{222}Rn (3.83 d half-life) from continents as ^{226}Ra incorporated in soils and rocks decays. In the atmosphere, ^{222}Rn decays to ^{210}Pb, which is deposited at the earth's surface with atmospheric washout as unsupported or excess ^{210}Pb. Supported ^{210}Pb in lake sediments is produced by the decay of ^{226}Ra that is deposited as one fraction of erosional inputs. In the sediments, gaseous ^{222}Rn produced from ^{226}Ra is trapped and decays to ^{210}Pb. By definition, supported ^{210}Pb is in secular equilibrium with sedimentary ^{226}Ra and is equal to total ^{210}Pb activity at depths where excess ^{210}Pb activity is not measurable due to decay. Because the decay of excess ^{210}Pb activity in sediments provides the basis for estimating sediment ages, it is necessary to make estimates of total and supported ^{210}Pb, activities so excess ^{210}Pb activity can be determined by difference. Excess ^{210}Pb activity was calculated either by subtracting ^{226}Ra activity from total ^{210}Pb activity at each depth or by subtracting an estimate of supported ^{210}Pb activity based on measurements of total ^{210}Pb activity at depths where excess ^{210}Pb activity is negligible.

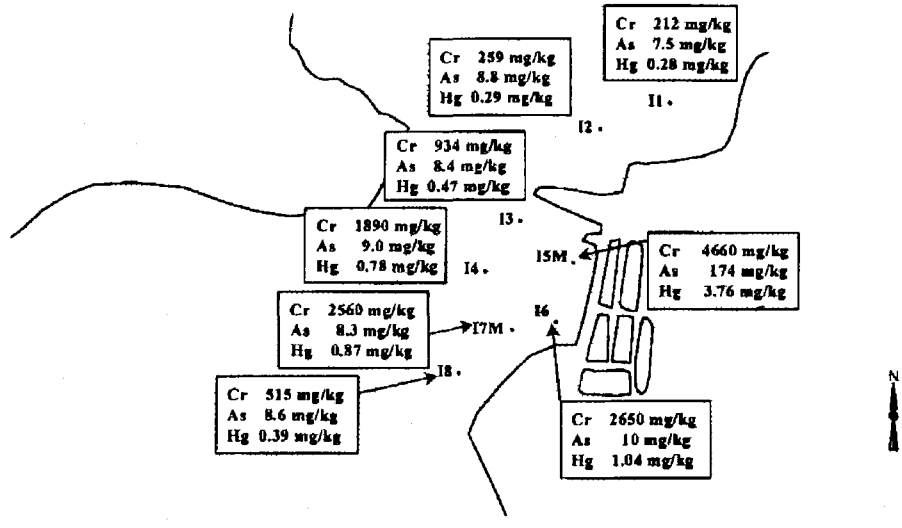


Figure 1. Conentration of chromium, arsenic, and mercury in ponar samples collected from Tannery Bay, Whitehall, Michigan (1996)

Sediment ages were calculated using a CRS model (Appleby and Oldfield 1983). This model calculates ages based on the assumption that the flux of excess ^{210}Pb, to the lake was constant and therefore that variation in ^{210}Pb activity from a pattern of exponential decrease with depth depends on variation in rate of sedimentation.

Errors in age and mass sedimentation rate were propagated using first-order approximations and calculated according to Binford (1990).

RESULTS AND DISCUSSION

The results of ponar and VibraCore samples are shown in Figures 1 and 2 respectively. Ponar samples provide an indication of the conditions present in the near surface zone of the sediments. The penetration of the ponar is variable and can range from 0-15 cm. depending on the condition of the sediment. A comparison of the results from both collection methods suggests that the highest degree of the chromium contamination is present at depths below the penetration of the ponar. In addition, the ponar results suggest that chromium continues to enter the sediments of Tannery Bay since concentrations range from 1,000 mg/kg to 4,600 mg/kg near the surface.

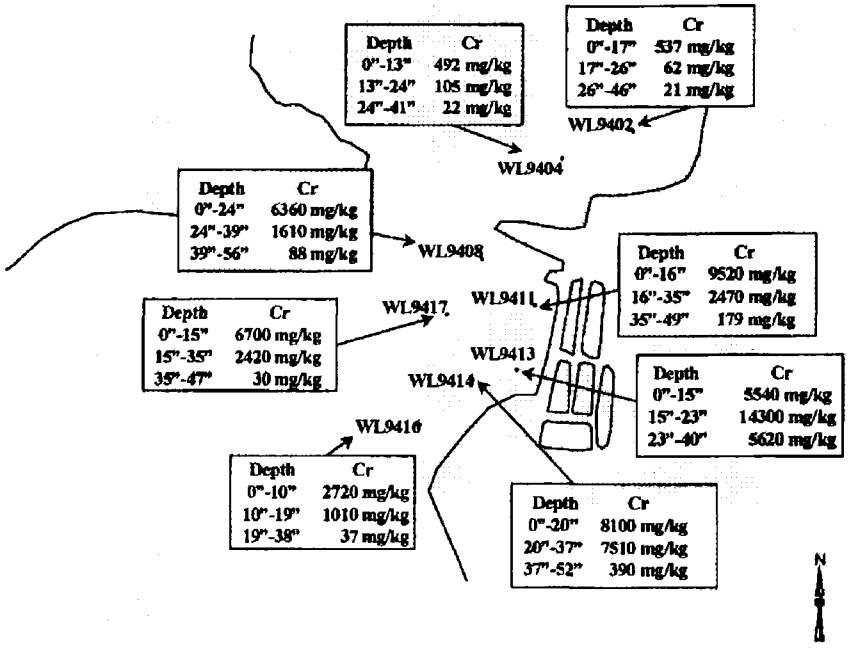


Figure 2. Concentration of chromium in core samples collected from Tannery Bay, Whitehall, Michigan (1994)

The results of the stratigraphy analyses for total chromium are given in Figures 3 and 4 for I-5M and I-7M respectively. The I-5M core shows a relatively uniform region of chromium concentrations ranging from 2,500 mg/kg to 3,600 mg/kg between 0 and 26 cm. This region is followed by more concentrated strata that vary from approximately 5,000 mg/kg to 23,000 mg/kg in the interval from 26-84 cm. Chromium in the remainder of the core decreases after 84 cm. Since this station was located in the discharge area of the waste treatment lagoons,

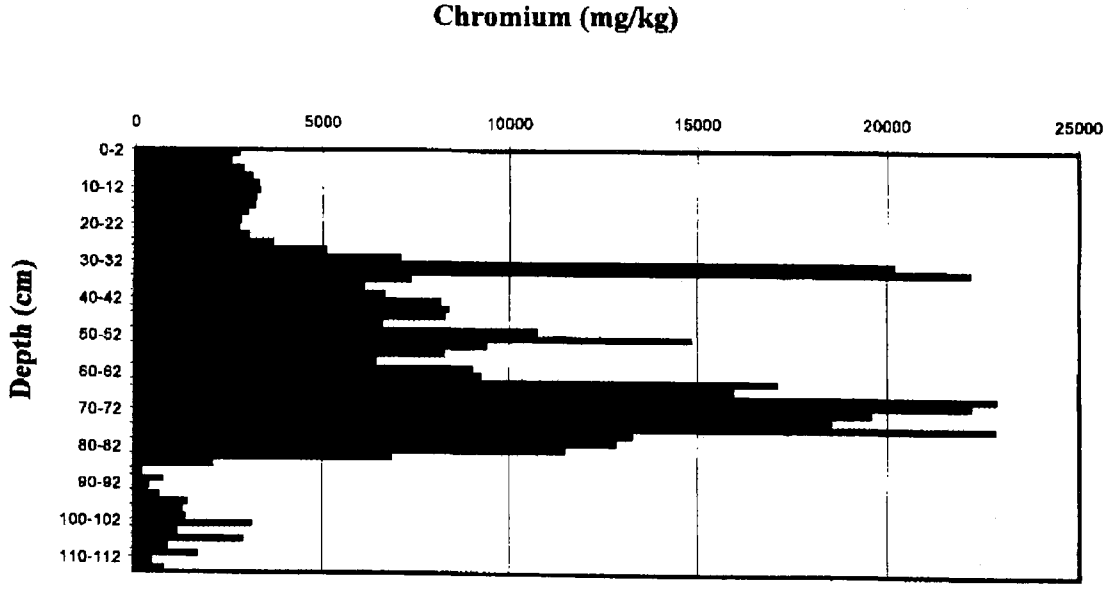


Figure 3. Results of chromium stratigraphy analysis on the core sample from I-5M

the variations in chromium concentrations observed reflect differences in effluent composition over time. Sudden

reductions in chromium levels also correspond to strata that contain animal hair and hide fragments. The I-7M core follows a different depositional pattern. Concentrations of chromium gradually increase from approximately 2,000 mg/kg to 5,000 mg/kg over the interval from 0-36 cm. Concentrations then rapidly rise and remain elevated in the region from 38-128 cm. Chromium concentrations began to decrease after 128 cm. Higher levels of chromium were found in the I-7M core than at I-5M. The highest level found at I-5M was 22,800 mg/kg while several 2 cm strata at I-7M ranged from 34,000 mg/kg to 61,100 mg/kg.

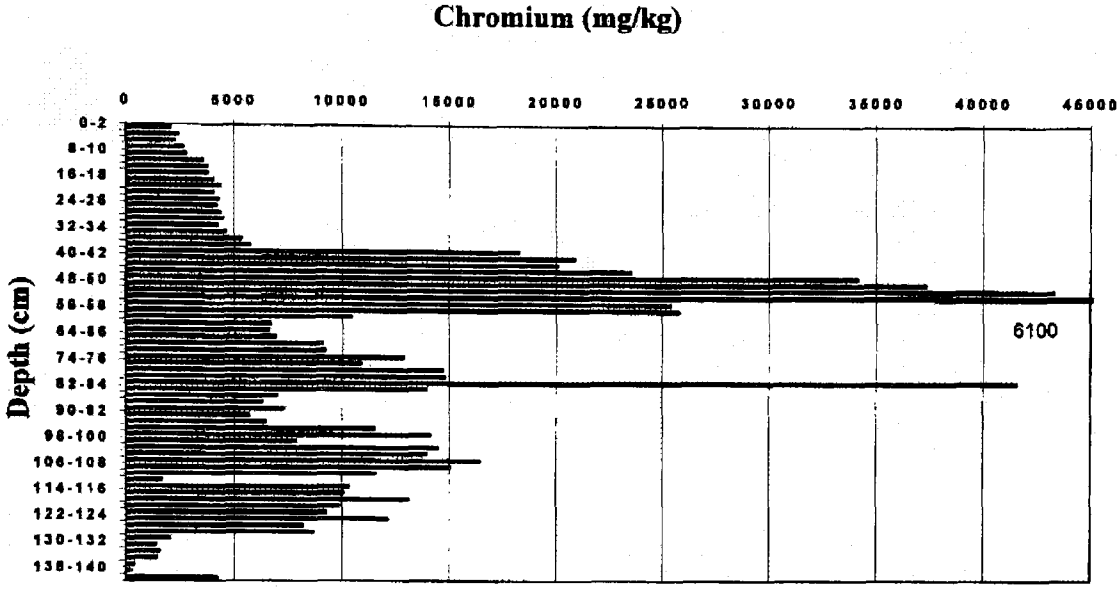


Figure 4. Results of chromium stratigraphy analysis on the core sample from I-7M

The radiochemistry data is summarized in Tables 1 and 2. The profiles of ^{210}Pb activity for Station I-5M and Station I-7M (Figure 5) provide other information about historical sedimentation at the Tannery Bay sites. First, ^{210}Pb activity generally decreases with depth. Second, several stratigraphic layers can be identified based on ^{210}Pb activity. Four layers are present in core I-5M: 0-15 cm, 15-30 cm, 30-50 cm, and 50-65 cm; and four layers can also be identified in I-7M: 0-20 cm, 20-35 cm, 35-45 cm, and 45-70 cm. The total ^{210}Pb activity in the top layer in both cores was similar, ranging from 10-12 dpm/g, and the activity in the lowest layer was also similar in both cores. Supported ^{210}Pb is by far the largest fraction in the lowest layer. Finally, because excess ^{210}Pb is generally not measurable in sediments with ages older than five or six half lives, we can conclude that the ages in sediments above the bottom layer with measurable levels of excess ^{210}Pb activity are probably not older than 110 to 130 years.

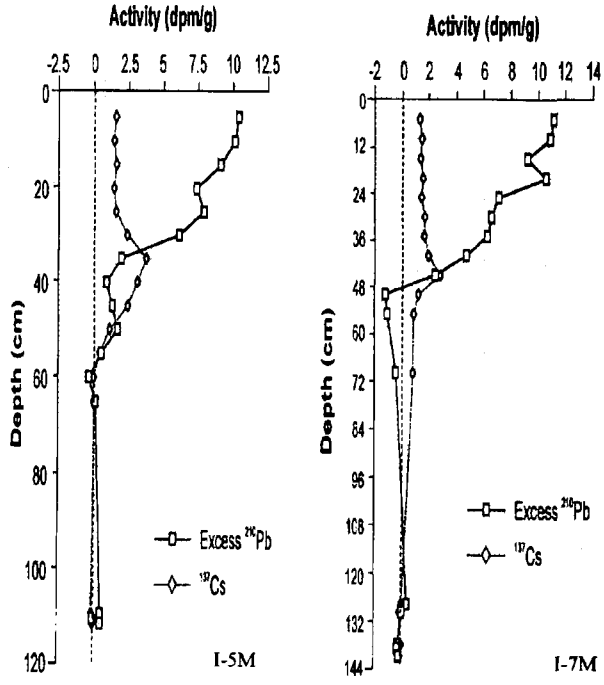
Table 1. Results of radiochemistry analysis of the core sample from I-5M.

	Total			Excess				Mass	
	Pb-210	Ra-226	Cs-137	Pb-210		Age		Sedimentation	MSR
Depth	Activity	Activity	Activity	Activity	Age	Error	Date	Rate	Error
(cm)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(years)	(1s)		(mg/cm^2/yr)	(1s)
5	11.951	1.735	1.565	10.358	3.965	1.222	1992.7	167.23	8.36
10	11.552	1.592	1.437	10.103	10.534	1.339	1986.2	145.68	7.68
15	10.70	1.73	1.614	9.1	17.992	1.490	1978.7	130.06	8.22
20	8.55	1.276	1.449	7.38	29.222	1.848	1967.5	120.21	7.18
25	8.81	1.015	1.598	7.911	46.450	2.604	1950.2	72.50	5.86
30	7.455	1.423	2.414	6.123	68.841	4.523	1927.9	50.96	5.95
35	4.931	2.967	3.769	1.996	81.028	5.603	1915.7	89.93	22.61
40	2.641	1.753	3.142	0.904	90.010	5.747	1906.7	142.5	61.92
45	2.696	1.398	2.468	1.32	104.612	6.991	1892.1	67.94	22.25
50	2.889	1.224	1.139	1.689	149.286	21.588	1847.4	22.63	9.26
55	1.243	0.703	0.437	0.549					
60	0.44	0.757	0.024	-0.322					

Combined plots of chromium stratigraphy and radiochemistry data are shown in Figure 6 for I-5M and I-7M. The four regions in each core described earlier suggest distinct layers. Sediments that are well mixed would have relatively uniform ^{210}Pb activity as illustrated from the surface to the 10-20 cm zone. These results are significant as the ^{210}Pb profile demonstrates a mixed zone near the surface that is isolated from the sediments below approximately 20 cm. Levels of chromium in excess of 20,000 mg/kg begin at 40 cm at I-7M and at 30 cm at I-5M. Based on the ^{210}Pb profile, a region of unmixed sediment lies between the heavily contaminated strata and the mixed sediment zone. The zones of greatest chromium contamination therefore appear to be isolated from the surface sediments that are subject to mixing. Sedimentation rate data for both Table 1. Results of radiochemistry analysis of the core sample from I-5M stations suggest that I-7M has a greater rate (225 mg/cm^2/yr) than I-5M (167 mg/cm^2/yr). This observation is supported by the chromium profile discussed above.

Total 2. Results of radiochemistry analysis of the core sample from I-7M.

Depth (cm)	Total Pb-210 Activity (dpm/g)	Ra-226 Activity (dpm/g)	Cs-137 Activity (dpm/g)	Excess Pb-210 Activity (dpm/g)	Age (years)	Age Error (1s)	Date	Mass Sedimentation Rate (mg/cm^2/yr)	MSR Error (1s)
5	12.510	1.550	1.280	11.110	2.410	1.710	1994.3	225.77	14.85
10	12.700	1.990	1.440	10.860	5.460	1.790	1991.2	212.07	16.31
15	11.090	2.030	1.350	9.190	11.620	1.940	1985.1	217.52	19.10
20	12.150	1.730	1.530	10.570	21.900	2.380	1974.8	146.84	9.77
25	8.770	1.740	1.420	7.130	31.670	2.870	1965.0	159.07	16.91
30	8.320	1.840	1.660	6.580	44.500	3.740	1952.2	121.58	15.67
35	7.980	1.800	1.640	6.270	65.110	6.130	1931.6	76.58	12.89
40	7.000	2.350	1.950	4.710	101.820	16.450	1894.9	43.32	13.97
45	5.780	3.380	2.820	2.440					
50	5.440	3.640	1.220	-1.220					
55	2.300	3.360	0.850	-1.080					



The peak input of fallout ^{137}Cs in the late 1950s and early 1960s has been used to provide a time-dependent horizon in cores. This approach was used to verify CRS dates in Lake Erie cores (Schelske and Hodell 1995). Neither a sharp peak nor a large peak in ^{137}Cs activity was found in the Tannery Bay cores. Therefore, this measurement was not useful in establishing the ^{137}Cs horizon. The low inventory of ^{137}Cs activity in both cores is in sharp contrast to the high inventory of ^{210}Pb activity. These results indicate that ^{137}CS was deposited and not retained at these sites for the following reasons:

- sediment resuspension focused the ^{137}Cs to other locations
- the ^{137}Cs was diluted by the introduction of large quantities of tannery wastes
- ionic ^{137}Cs was advected with pore waters from the core site

Figure 5. Activity versus depth of excess ^{210}Pb and ^{137}Cs at stations I-5M and I-7M

The latter mechanism is prevalent at locations where groundwater is moving through deposited sediments. It seems unlikely that resuspension or dilution was a primary mechanism because of the large inventories of ^{210}Pb activity at both sites. The most plausible explanation for the absence of the ^{137}Cs horizon is, therefore, groundwater advection.

The influence of groundwater advection on chromium may also be a factor in its fate and transport. As discussed previously, the absence of the ^{137}Cs horizon suggested that the movement of local groundwater through the sediments was responsible for advective losses. Since the local groundwater is known to discharge in the near shore area of Tannery Bay, chromium may also be mobilized from the deeper layers and transported to the surface. While the solubility of trivalent chromium is generally limited due to the precipitation of insoluble hydroxides, the formation of organic complexes has been shown to increase its solubility. Kaczynski and Kleber (1994), James and Bartlett (1983), and Hassan and Garrison (1996) noticed that the solubility of trivalent chromium was increased in the presence of organic complexing agents. The latter authors noticed an increase in solubility in the presence of cysteine under low Eh conditions. The low Eh environment present in the sediments of Tannery Bay, in addition to the organosulfur compounds produced during the decomposition of animal hides and hair, may produce conditions that promote chromium complexation. It was also noted that a large amount of humic material was released from the Tannery Bay sediments during alkaline digestion. These materials may also serve as complexing agents to increase chromium complexation. The presence of a complexed chromium fraction in the sediment pore water and its potential role in the advection of chromium needs to be evaluated as long as groundwater continues to enter Tannery Bay.

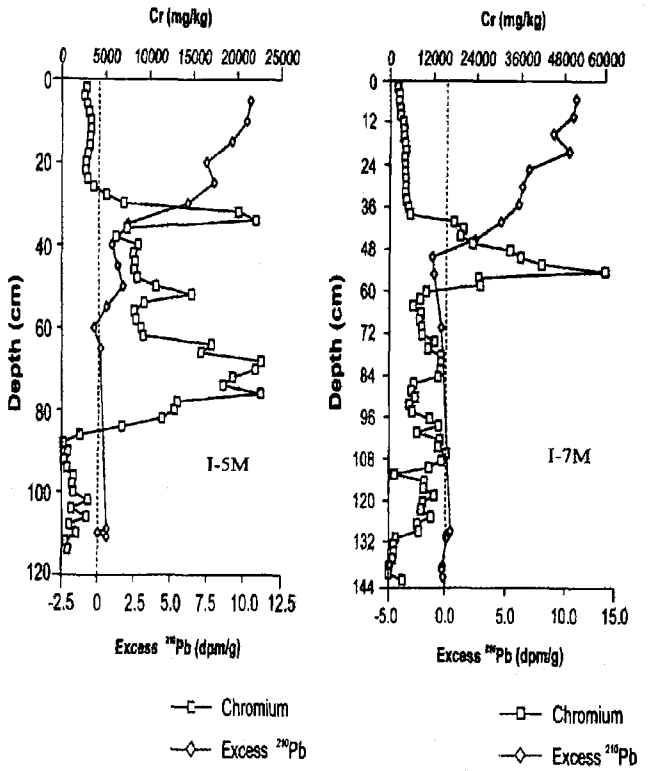


Figure 6. Chromium concentrations and excess ^{210}Pb versus depth at stations I-5M and I-7M

Since the direct discharge of tannery effluent to Tannery Bay ceased in 1976, evidence of the deposition of sediments with less chromium contamination should be evident. The lack of a decreasing gradient of chromium concentrations in the surface zone sediments (0-20 cm) may be explained by several mechanisms:

- continued surface runoff
- groundwater advection
- continual sediment mixing and resuspension in the 0-20 cm zone

Since the levels of excess ^{210}Pb in the surface zone sediments are normal and do not reflect excessive dilution with terrestrial soil, surface runoff would only be significant if small amounts of highly contaminated material were continuously eroding into Tannery Bay. As discussed previously, groundwater advection may be responsible for some migration of chromium from deeper sediment layers to the surface. It is, however, doubtful that this mechanism would be responsible for chromium levels in excess of 2,000 mg/kg. The most likely process that would produce the observed chromium levels is that of sediment mixing and resuspension. The flocculent, fine-grained sediments in Tannery Bay may be mixed to a degree that prohibits the formation of concentration gradients. The continued mixing of flocculent materials would result in unstable, resuspended sediment that could readily be exported into White Lake by currents and wave action. The prevalence of the high levels of chromium in the White Lake samples collected down gradient from Tannery Bay would support the continued export of resuspended sediments (Rediske et al. 1998)

The CRS model (Appleby and Oldfield 1983) was selected to calculate ages because of the absence of an exponential ^{210}Pb gradient (Table 1). Ages calculated from the model placed 1892 at 45 cm and 1847 at 50 cm for core I-5M, and 1895 at 40 cm for core I-7M. These ages, however, were much younger than expected based on other information available from the core. For example, the chromium concentration exceeded 10,000 mg/kg from 62-82 cm in I-5M or in sediments older than 1847 according to the calculated ^{210}Pb ages. The chromium concentration exceeded 10,000 mg/kg at depths down to 84 cm in I-7M. By contrast only the upper 40 cm of this core contained sufficient levels of excess ^{210}Pb for dating. This lack of conformity shows that the calculated ages

are not credible. Results from the CRS ^{210}Pb age model that are not credible can be a product of the point transformations that are used in the CRS model (Robbins and Herche 1993). Independent assessment of dating is therefore required for the CRS model. For the piston cores, data for chromium and tannery waste by-products provide independent time markers that are at variance with the calculated ^{210}Pb ages. Since high levels of chromium and tannery waste byproducts (hair and dye coloration) persist well below the calculated 1847 date, the dating chronology must be rejected. Large inputs of waste materials could confound the chronological record by diluting the natural sediments and by altering the physical-chemical environment.

Given the insolubility of trivalent chromium in natural water (Palmer and Puls 1994), the predominant mechanism driving the flux of this metal in White Lake appears to be sediment export. The hydrodynamics of White Lake support the progressive transport of sediments in a westerly direction following the natural water currents. Prevailing winds function to mix the near shore sediments and move the resuspended material out into the main lake. The 0-20 cm zone of sediment mixing determined by the ^{210}Pb data reflects the action of the prevailing winds and the wave induced resuspension. The well mixed nature of the top 20 cm zone also suggests that these sediments are unstable and easily exported. In addition, the differences in stratigraphy between I-5M and I-7M are consistent with wind induced wave action. Station I-5M has a greater exposure to the westerly wind and has a lower calculated sedimentation rate (167.23 mg/cm^2/yr) and a shallower interval of sediment above the highly contaminated zone. In contrast, station I-7M is more protected from wave action and exhibits a greater calculated sedimentation rate (225.77 mg/cm^2/yr) and a stratigraphy profile reflecting a greater depth of less contaminated material.

The discharge of tannery waste was located near the shore of Tannery Bay in the northeast corner. The EPA/MDEQ core samples indicate heavy sediment contamination with chromium in the near shore and middle areas of Tannery Bay. Stations near the confluence with White Lake have considerably less chromium in the sediments. This pattern reflects a discharge of insoluble chromium that was rapidly incorporated into the sediments. Based on this information, the historical and current mechanism for chromium transport in White Lake is sediment export from Tannery Bay by the prevailing circulation pattern and wave action. Chromium export from Tannery Bay into White Lake proper will continue as long as the contaminated sediments are influenced by hydrodynamic circulation patterns.

CONCLUSIONS

By using a combination of combination of traditional chemical analyses, radiometric determinations, and stratigraphy, important information concerning the nature and fate sediment contamination in the Tannery Bay area of eastern White Lake was obtained. Chromium stratigraphy in indicated that the top 15-20 cm of sediment were less contaminated (2,000-4,000 mg/kg) than sediment located at >30 cm (>5,000 mg/kg). Radionuclide results suggested that this surface sediment layer was well mixed, however, distinct from the deeper more highly contaminated sediments. Presently this sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The surface layer was followed by a region (30-80 cm) that contains chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should have been apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments suggests that the processes of mixing and resuspension continue to be active in Tannery Bay. In addition, the high inventories of ^{210}Pb in the 0-20 cm zone show that surface runoff from the waste piles has not contributed significantly to the recent sediment record. The lack of a significant ^{137}Cs horizon in the sediments indicates that groundwater is discharging in this region; however, the linkage with chromium mobility requires further investigation. While traditional chemical analyses provide important information for determining the spatial extent of contamination, additional techniques are required to describe chemical fate and transport. Stratigraphy and radiometric analysis using ^{210}Pb can provide critical information related to sediment stability, depositional patterns, and chemical flux that is essential for the analysis of remediation alternatives.

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AIR-FORCE WIDE BACKGROUND CONCENTRATIONS OF INORGANICS OCCURRING IN GROUND WATER AND SOIL

Philip M. Hunter
Air Force Center for Environmental Excellence, Consultant Operations Division,
3207 North Road, Brooks AFB, Texas 78235

ABSTRACT
Background concentrations of naturally occurring inorganics are important to site characterization, establishing cleanup levels, conducting risk assessments, designing and operating long-term monitoring programs, and the like. The Air Force Center for Environmental Excellence (AFCEE) has streamlined the process for determining background concentrations by using computer algorithms that interrogate the Air Force's Environmental Resources Program Information Management System (ERPIMS). Analysis of this database reveals that there are a wealth of existing sampling locations that are known to be uncontaminated and available for use in these important calculations. Air-Force wide background concentrations for ground water and soil have been calculated

for inorganics using all available sampling data from the ERPIMS Database. Insight can be gained by using these concentrations as a representative baseline of numbers for ongoing and future investigations concerned with monitoring and remediation of inorganic contamination.

INTRODUCTION

Analysis of the ERPIMS database reveals that most contamination across the Air Force is organic in nature and is typically associated with chlorinated solvents and fuels (i.e. BTEX and related compounds). The presence of key organics detected in groundwater and soil samples is a good indicator of both inorganic and organic contamination. Often Air Force resources are expended needlessly to perform a separate background investigation at individual installations using newly-captured data rather than relying on existing data. AFCEE-developed computer algorithms were used to automate the process of identifying background locations using ERPIMS data. Over 10 years worth of project data is available as an existing resource for background determinations at installations across the Air Force. This methodology reduces and some cases eliminates the need to perform a separate background investigation which can cost hundreds of thousands of dollars to accomplish. This paper will discuss AFCEE's automated approach for identifying background locations, the statistical methodology used to calculate Air-Force wide background concentrations, and the nature of these background concentrations for both ground water and soil.

ERPIMS DATABASE

ERPIMS (previously known as IRPIMS) stores some 12.5 million analytical sampling results from 196 Air Force installations. Data from 40,000 distinct sampling locations (wells, borings, etc.) is captured by the system. The ERPIMS hardware consists of a Digital Equipment Corporation (DEC) Alpha® 4100 computer that runs Oracle® 7.3 on a VMS operating system. The system has been operational since 1987 and is managed by AFCEE/MSC.

DETERMINATION OF BACKGROUND LOCATIONS

Even when investigations specifically target contamination by drilling wells and borings into areas known to be hazardous waste sites, the non-detect (ND) rates for organics are surprisingly high. For example, the ND rates for TCE, which is highly mobile and known to be the most ubiquitous constituent found on Air Force installations, are on the order of 65% in ground water. For most other organic constituents, the ND rates are approximately 90% for ground water. For soil, the ND rates for organics tend to be even higher. As a result, a wealth of existing sampling locations are known to be uncontaminated and available for use as locations for background calculations. This knowledge was used to construct a computer algorithm that identifies background locations across the entire Air Force. The algorithm, which was written in Structured Query Language (SQL), searches out all locations that have been sampled for both inorganics and organics. Sampling locations showing evidence (i.e. detects) of organic contamination are then eliminated from the search and those remaining are retained for further consideration as background locations. Both upgradient, downgradient, and sidegradient locations could potentially be identified as background sampling locations. There were substantially more background locations identified for soil as opposed to ground water. On average, at least 25 background well locations and 50 background borehole locations per Air Force installation have been identified using these procedures. As indicated in the next section that follows, the magnitude of distinct sample locations and the sample sizes generated from these locations will more than adequately meet the requirements for the statistical calculations used to determine background levels.

DATA ANALYSIS AND CALCULATION OF BACKGROUND LEVELS

For calculation of background levels at individual installations and sites, AFCEE's approach and statistical methodology are similar to guidance published by EPA (EPA 1989, 1992), ASTM (1996), and Gibbons (1994). Using this guidance, normal 95% confidence 95% coverage upper tolerance limits are used. Depending on the distribution of individual data sets and the percentage of detects, nonparametric tolerance limits are also typically used. AFCEE, like EPA and others, requires at least 2 sampling locations to minimally account for spatial variability and a total sample size of at least 8 ($n = 8$ for each constituent) to provide ample statistical power for the background calculations. However, Air-Force wide inorganic data is complicated by multiple detection limits, diverse hydrogeologic terranes, variability over 3-dimensional space, a variety of types of hazardous waste sites, multiple Air Force bases, different waste handling practices, and the like. All of these issues force one ultimately to discriminate background levels across more than one hydrostratigraphic unit or more than one soil horizon. As a result and for the purposes of this investigation, the 95th percentile (Prc95) of the data associated with each analyte was used as the statistic of choice to best represent background. This approach parallels AFCEE's guidance for individual installations in that the 95% upper tolerance limit focuses on the 95th percentile of the data (i.e. a tolerance limit is similar to an upper confidence limit on a specified percentile or coverage of the

data, in this case the 95th percentile). Calculation of the median and the 99th percentile of background levels for analytes detected in both ground water and soil were also calculated and can be found in Tables 1 and 2. These tables also provide information that qualifies the results of the background calculations including: sample size, the number of distinct background well locations, the number of Air Force bases having background locations, and the detection frequency. All statistical analysis was performed using SAS® statistical software.

Table 1. Air-Force Wide Background Levels of Inorganics in Ground Water
As of May 1998

Analyte	Sample Size	Wells Sampled	AF Bases	Detection Freq (%)	Median (mg/L)	Prc95 (mg/L)	Prc99 (mg/L)
Aluminum	5656	2493	86	54	0.0735	44	201
Antimony	5839	2843	97	7	ND	0.014	0.2
Arsenic	7259	2996	107	32	ND	0.044	0.171
Barium	6828	2750	98	83	0.07715	0.6	2.03
Beryllium	5891	2843	98	9	ND	0.002	0.009
Boron	812	461	26	65	0.042	1.46	12
Cadmium	7153	3202	110	9	ND	0.0049	0.017
Chromium	7892	3169	112	35	ND	0.195	1.52
Cobalt	5121	2538	83	13	ND	0.031	0.12
Copper	6412	2873	102	29	ND	0.086	0.371
Cyanide	1796	987	49	2	ND	ND	0.015
Fluoride	2132	1351	60	61	0.24	2.263	4.9
Iron	6844	2838	93	78	0.56	54.4	240
Lead	8916	3552	118	33	ND	0.047	0.23
Manganese	6465	2718	92	83	0.0708	2.840	9.2
Mercury	6017	2808	105	9	ND	0.00036	0.0017
Molybdenum	3481	1779	58	17	ND	0.021	0.147
Nickel	6471	2915	104	25	ND	0.2	0.83
Nitrate	1788	1074	61	67	0.8	24.600	67
Nitrite	662	468	33	6	ND	0.02	1.1
Potassium	6561	2750	91	98	27.4	452	4050
Selenium	6794	2934	105	12	ND	0.0081	0.1
Silver	6812	3165	108	4	ND	ND	0.0155
Sodium	6561	2750	91	98	27.4	452	4050
Strontium	31	22	2	100	0.17	3670	9070
Sulfate	3175	1794	77	92	36.09	430	2420
Sulfide	176	122	14	11	ND	0.14	9.3
Thallium	5698	2780	97	4	ND	ND	0.16
Vanadium	5378	2443	84	37	ND	0.11	0.464
Zinc	6820	2863	104	67	0.02	0.33	1.67

BACKGROUND LEVELS FOR GROUND WATER

The universe of distinct monitoring wells that were sampled simultaneously for both inorganics and organics across the Air Force is approximately 4000 wells as of this writing. The query used to identify the background data set resulted in the analysis of over 145,000 analytical records. Depending on the analyte, the number of background wells used in the analysis varied from 22 (strontium) to 3552 (lead) and sample sizes varied from 31 (strontium) to 8916 (lead). Background data was captured from as many as 118 Air Force installations for lead and as little as 2 installations for strontium. Potassium and sodium were detected 98% of the time while cyanide was detected 2% of the time. Other analytes such as strontium and sulfate were detected over 90% of the time; however, the detection frequency for strontium was represented by only 2 Air Force bases and 22 monitoring wells. Some constituents were not typically detected at background locations. The following analytes had median concentrations that were below the method detection limit (MDL): antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, cyanide, lead, mercury, molybdenum, nickel, nitrite, selenium, silver, sulfide, thallium, and vanadium. The 95th percentile of the data sets for cyanide, silver, and thallium were also below MDL. This indicates that they are rarely detected in ground water and was substantiated by detection frequencies that were found to be in the neighborhood of 2% - 4%. Conversely, some inorganic constituents were detected frequently and at levels that exceeded important environmental thresholds such as Maximum Contaminant Levels (MCLs)

or Action Levels for drinking water. The following analytes had background levels (95th percentile) that exceeded MCLs: antimony, chromium, and nitrate. The background level for lead exceeded the Action Level of 0.015 mg/L set for drinking water measured at the tap. This may suggest that some regulatory limits are placed artificially close to observed background levels.

Table 2. Air-Force Wide Background Levels of Inorganics in Soil
As of May 1998

Analyte	Sample Size	Wells Sampled	AF Bases	Detection Freq (%)	Median (mg/L)	Prc95 (mg/L)	Prc99 (mg/L)
Aluminum	13077	4840	80	99	6,510	23700	84600
Antimony	15051	5683	90	8	ND	5.5	29.3
Arsenic	17212	6165	101	66	1.6	13.8	43.3
Barium	15290	5765	98	98	56.25	332.64	995
Beryllium	14724	5513	89	64	0.3	1.1	2.4
Boron	790	396	16	63	24.7	108	201
Cadmium	17464	6738	103	20	ND	2.56	10
Chromium	17549	6689	103	93	9.1	51.8	388
Cobalt	11815	4359	81	60	3	15.2	28.4
Copper	15396	5764	89	83	7.9	53	230
Cyanide	3220	1299	47	5	ND	0.155	2.3
Fluoride	1270	224	8	79	3.4	9.9	17
Iron	13719	4939	82	99	9180	33600	82900
Lead	20784	7523	113	76	5	54	340
Manganese	13495	4837	80	99	187	856	2380
Mercury	15465	5492	94	8	ND	0.11	0.58
Molybdenum	10584	3581	56	8	ND	1.8	7.99
Nickel	15167	5677	92	68	6.1	38.3	160
Nitrate	1400	273	12	47	ND	7.95	42.75
Nitrite	107	30	4	50	0.008	0.499	1.1
Selenium	16966	6019	99	8	ND	0.87	23.3
Silver	17600	6598	103	7	ND	0.93	7.35
Sodium	12161	4466	81	64	120	1300	3260
Strontium	92	24	2	100	25.1	111	8020
Sulfate	1416	273	7	96	13	200	1340
Sulfide	204	162	10	12	ND	24	99.7
Thallium	15186	5580	89	6	ND	0.352	19
Vanadium	12342	4645	80	97	18.6	66.6	142
Zinc	16017	5996	90	98	25.2	111	540

BACKGROUND LEVELS FOR SOIL

The universe of distinct boreholes sampled for both inorganics and organics across the Air Force was approximately 8100 boreholes. The query used to identify the background data set resulted in the analysis of over 325,000 analytical records. Depending on the constituent, the number of background boreholes used in the analysis varied from 24 (strontium) to 7523 (lead) and sample sizes varied from 92 (strontium) to 20784 (lead). Background data was captured from as many as 113 Air Force installations for lead and as little as 2 installations for strontium. Since inorganics tend not to be particularly mobile in ground water, it is not surprising that they are detected at higher frequencies in soil vis a vis ground water. The following constituents had detection frequencies exceeding 95%: aluminum, barium, chromium, iron, manganese, strontium, sulfate, vanadium, and zinc. The high detection frequencies for strontium and sulfate, however, are misleading since the number of Air Force bases represented is 2 and 7, respectively. Strontium, in particular, had only 24 boreholes that were sampled and identified as background locations across the Air Force. Some analytes were not commonly detected at background locations. The following analytes had median concentrations that were below MDLs: antimony, arsenic, cadmium, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. These same constituents also had median concentrations below MDLs for ground water. None of the 95th percentiles of any of the data sets for soil fell below MDLs, unlike the situation found for ground water. The following analytes had detection frequencies that were below 10%: antimony, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. On rare occasion, inorganic constituents were detected at levels that exceeded important

environmental thresholds (using residential criteria) such as Preliminary Remediation Goals (PRGs), Human Health Screening Levels (HHSLs), and Risk-Based Concentrations promulgated by various EPA regions. The background level for both arsenic and beryllium exceeded the PRGs and HHSLs for EPA Region 9 and Region 6, respectively. Iron exceeded both the HHSLs and the PRGs for EPA Regions 6 and 9, respectively. As in the case for ground water, these results also suggest that regulatory limits may be artificially placed too close to observed background levels.

SUMMARY

Computer algorithms developed by the Air Force were used to automate the process of identifying background locations for inorganics occurring in ground water and soil. These procedures identified large numbers of background locations and a more than adequate sample size which was used to determine Air-Force wide background levels for some 30 inorganic constituents. This baseline of numbers which was calculated in this study provides insight on the nature of background variability across the Air Force and gives decision makers a "feel" for representative background levels. The 95th percentile statistic calculated from individual constituent data sets is believed to best represent background levels given the inherent complexities associated with analyzing these large and diverse data sets. Potassium and sodium were highly detected in ground water; while aluminum, barium, chromium, iron, manganese, strontium, sulfate, vanadium, and zinc were frequently detected in background soil. Some constituents were not commonly detected at background locations across the Air Force. The following analytes were not typically found in ground water: antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, cyanide, lead, mercury, molybdenum, nickel, nitrite, selenium, silver, sulfide, thallium, and vanadium. For background soil, the following analytes were not typically detected in soil: antimony, cyanide, mercury, molybdenum, nitrate, selenium, silver, sulfide, and thallium. The results of this investigation suggest that some regulatory limits may be placed too close to observed background levels for selected analytes. Analytes that may fall into this category include antimony, chromium, and nitrate for ground water; and arsenic, beryllium, and iron for soil. Background levels of these constituents were found to exceed important environmental thresholds. This automated approach of performing background investigations using existing data which has already been paid for, affords the Air Force many cost benefits. Use of this methodology can eliminate the need to conduct a separate background investigation for individual sites or at the installation level and can save hundreds of thousands of dollars that would otherwise be needlessly spent.

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NEW TOOLS FOR LIQUID SAMPLING

"Evaluation and Comparison of the Performance of Liquid Sampling Devices In Stratified Liquids"

James D. Hoover
Department of Civil and Environmental Engineering,
Washington State University Tri-Cities, 100 Sprout Road, Richland, WA 99352
509-372-6972
Scott R. Somers
Advanced Concepts & Design, Inc., 77 Symons Street, Richland, WA 99352
509-943-1431

EXECUTIVE SUMMARY

Systematic differences in sampling performance were found to exist between the Drum Thief, COLIWASA, and ACD liquid sampling devices in laboratory tests simulating the containerized sampling of stratified liquids. The study involved two phases of testing: (1) the collection of 250 samples with these devices using water and corn oil at a ratio of 1:1 by 17 professional and 35 inexperienced sampling personnel, and (2) the collection of 216 test samples at water:oil ratios ranging from 95:5 to 5:95 by a single user. Both small volume (≤250 ml) and large volume (≈1000 ml) device models were evaluated. Statistically significant differences in the accuracy, precision, spillage, and time of sampling were found to exist among these devices. The relative performance of the devices were also found to coincide with the rating of the devices by 52 volunteer users.

Nearly all differences in sampling performance were found to vary systematically with device type. Differences in sampling accuracy between devices range from 18% to 175%, and sampling accuracy was found to be highly dependent on the liquid ratio for some devices. Sampling accuracy with tile COLIWASA and Drum Thief decreased sharply when the proportion of either liquid was <30%, indicating that there are limits on the liquid proportions that can be sampled with these devices. Sampling reproducibility among users also varied systematically with device type, but when used by a single individual, precision was >97% for all devices. The amount of spillage associated with sampling ranged from zero with some devices to as much as 10% of the sample volume with others. Sampling time among devices differed by as much as 300%.

The performance of the small volume and large volume models of the ACD devices exceeded that of the other devices in essentially all categories of evaluation. Nearly all aspects of sampling performance appear to be dominated by differences in the inherent design and function of the devices, which cause some devices to also be more user intensive than others. Among the devices tested, sampling performance with the ACD devices was found to be the least dependent on user factors, including experience. The ACD devices also received the highest ratings in the user survey.

These results have important implications for the sampling of liquids that is routinely performed for the purpose of characterizing their composition and potential hazard. These implications include health, safety, economic, legal, and practical considerations for the handling and disposition of the sampled liquids. These results also provide a quantitatively basis for comparing the performance of liquid sampling devices used in the environmental industry and to provide a basis for improving sampling performance and sampler design.

PURPOSE AND BACKGROUND

The sampling of liquids is an activity that is performed thousands of times daily by numerous federal, state, and local and agencies for the purpose *of* characterizing type, nature, and/or hazard of unknown liquid substances. Environmental regulations also require that essentially all liquid waste materials be sampled and appropriately characterized for the purposes of appropriate handling, transportation, treatment and/or disposal. Although a relatively small number of sampling devices are used to collect these samples, there is little documented information regarding the performance of these sampling devices or a quantitative comparison to serve as a benchmark for assessing quality control or product improvement

These studies were undertaken to assess the performance of five liquid sampling devices, The purpose of these studies was to establish a quantitative baseline for the evaluation and comparison of liquid samplers used in the acquisition of representative samples of stratified liquids. These studies were motivated by the need to establish a quantitative basis for evaluating the quality of samples that are obtained with various sampling devices.

The sampling and analysis of waste materials, contaminated media, and other materials of unknown composition are integral components of many environmental activities including regulatory compliance in accordance with the Resource Conservation and Recovery Act (RCRA; 1976) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA; 1980). Sampling protocols have been established to ensure uniformity in the generation on of sampling data (e.g., Environmental Protection Agency's (EPA's) Office of Solid Waste and Emergency Response (OSWER (e.g., EPA, 1986). Although general guidelines and procedures for liquid sampling exist (e.g., ASTM 1994; EPA 1991), there are no standards pertaining to sample quality (e.g., accuracy), and essentially no information on the quality of the samples that call be obtained with various types of sampling devices.

EXPERIMENTAL DESIGN AND TEST METHODS

This Study focused on the evaluation of three types of liquid sampling devices for the sampling of stratified

liquids from containers such as drums. The three types of liquid sampling devices evaluated were the Drum Thief, the COmposite Liquid WAste SAmpler (COLIWASA), and a new product, the Advanced Concepts & Design (ACD) liquid samplers. Further description of the sampling devices is provided in Attachment 1. These liquid sampling devices were chosen because they have all been recognized by the standards organizations as devices appropriate for liquid sampling (e.g., ASTM 1994, 1995, 1996, 1998; EPA 1986). The Drum Thief and the COLIWASA have also been the most commonly used liquid sampling devices in the collection of composite liquid samples. The Drum Thief and small volume models of the other two devices (COLIWASA-S and ACD-S) were evaluated for the collection of small volume liquid samples ≤250-ml. The COLIWASA-L and ACD-L models were evaluated for the collection of larger volume samples (i.e., 1000 ml).

Conditions of stratified liquid sampling were chosen because most data quality issues in containerized liquid sampling involve representative sampling of segregated liquids with different physical and chemical properties. Two essentially immiscible liquids, distilled water (ρ=1.0) and more viscous corn oil (ρ=0.9), were used in these tests to simulate simplified test conditions for stratified liquids. The evaluation involved two phases of study. In the first phase of testing, accuracy, precision, spillage, and sampling time were evaluated for samples collected from simulated waste drums containing equal proportions of water and oil (ratio - 1:1). Phase II tests involved the assessment of the accuracy and precision of the sampling devices for seven different water:oil ratios ranging from 95:5 to 5:95.

Test Conditions

All samples were collected under controlled laboratory conditions simulating the sampling of stratified liquids from 55-gallon waste drums. In the Phase I tests, 17 professional and 35 inexperienced volunteers collected samples with each of the five sampling devices from simulated waste drums under the supervision of laboratory personnel. The simulated waste drums consisted of cut-away 55-gallon barrels fitted with 4" ID acrylic cylinders 34" in length (5.6 liter capacity per cylinder) sealed on the bottom and mounted below the bung hole. In the Phase II tests, samples were collected from freestanding acrylic cylinders by a single individual. Measured volumes of water and corn oil were placed into the cylinders to simulate stratified liquid conditions. A user survey was also conducted in conjunction with the Phase I tests to obtain all independent assessment of the overall performance of each device from the perspective of user personnel. Details regarding, the experimental procedures of the Phase I and II tests are described in Attachment 2.

RESULTS

Nearly all aspects of liquid sampling performance were found to differ with the type of device used. Systematic under-sampling and/or over-sampling, of the liquids (bias), and spillage occurred with some devices. Most aspects of device performance appear to be attributable to the inherent design of the devices and the extent to which device performance is affected or influenced by the user. The magnitude of sampling error and spillage with some devices also appears to depend on the viscosity and proportions of the liquids.

Accuracy

The more viscous of the two liquids (oil) was systematically under-sampled with the Drum Thief and COLIWASA devices. Systematic differences in the accuracy of the sampling devices were observed across the range of water:oil ratios investigated (Figure 1a,b; Figure 2). Sampling accuracy with the Drum Thief and COLIWASA was found to be highly dependent on the water:oil ratio. The differences in sampling accuracy among the devices ranged to 18% at a water:oil ratio of 1:1 (Figure 2), and increased as the fraction of either liquid became smaller. The largest errors and differences in sampling accuracy occurred with the smallest liquid fractions (5%). At a water:oil ratio of 5:95, samples obtained with the COLIWASA-S were nearly 90% *larger* than the actual the proportion of water, and about 85% *smaller* with the Drum Thief (Figure 1a,b). This pattern of antipodal bias typically occurred with the Drum Thief and COLIWASA. Sampling accuracy was routinely high with the ACD devices among all users for both small and large volume models, with >96% accuracy across most of the range of water:oil ratios. For tests performed with a water:oil ratio of 1:1, under-sampling of one liquid resulted in complementary oversampling, of the other liquid by an equivalent amount. Sampling biases for tests performed at other ratios were not complementary (Figure 1).

Precision

Measurement reproducibility, i.e., precision, varied systematically with device type among multiple users, but varied little when used by a single individual. For the tests performed with a water:oil ratio of 1:1, the ACD devices produced the greatest precision among both experienced and inexperienced users. For the tests with a water:oil ratio of 1:1, measurement uncertainty (at the 95% confidence interval) with the Drum Thief and

COLIWASAs were about twice as large as that with the ACD devices (Figure 2). However, when all samples were collected by a single user, the sampling precision (at the 95% confidence interval) for all devices was >97% for all water:oil ratios. Thus, the level of precision produced by an individual user was significantly better that that produced among multiple users. Sampling precision appears to be only slightly influenced by user experience and to be generally insensitive to differences in liquid ratios.

Spillage
The amount of spillage from sampling and the variability in the spillage measurements differed systematically with device type. The average spillage with the small volume devices ranged from essentially zero with the ACD device (0.006 ml, 1σ = 0.02 ml), to as much as 10% of sample volume (24 ml, 1σ =13 ml) with the Drum Thief (Figure 3). For the tests with large volume devices. the COLIWASA-L yielded the greatest spillage and variability (up to 11 ml, 1σ =6.7ml), and the ACD-L yielded the least spillage and variability (0.02 ml, 1σ =0.07 ml) (Figure 3). The variability in spillage was generally observed to increase with the volume spilled. User experience resulted in reduced spillage only with the Drum Thief (by about 30%).

Sampling Time
The time required to collect samples with each of the devices varied systematically with the type of device used, and was lower among experienced users. Average sampling times for the devices ranged from 40 seconds to 120 seconds. The small volume samples obtained by inexperienced users were collected fastest with the ACD device. The COLIWASA-S required about 30% longer, and the Drum Thief took nearly three times as long (Figures 4). The same pattern of device performance was found for samples collected by experienced users, but with a 20%-30% reduction in sampling times with all devices. The sampling times with the larger volume devices required only about 10-15 seconds longer. Sampling with the ACD-L was consistently about 10 seconds (10-12%) faster than with the COLIWASA-L.

User Ratings
The ratings of specific devices by experienced and inexperienced users were nearly identical. The small and large volume ACD devices received the highest ratings (4.2 and 4.3 out of a maximum of 5.0: Figure 5). The two COLIWASA devices received the second highest ratings; about 3.0 for the smaller device. and 2.7-3.2 for the larger device. The Drum Thief was ranked lowest by both groups of users, receiving average scores of 1.3-1.5. The average ratings and the 95% confidence intervals for these scores are shown in Figures 5.

Other Comparisons
It was hypothesized that some aspects of sampling performance may be related to factors such as the height of the user and/or arm length for devices requiring 42" tubes to be lifted clear of the sampling vessel for the collection of the sample. However, no obvious correlation was found between any of the sampling performance parameters and physical characteristics of the user including height, user stature, or sex.

SUMMARY AND INTERPRETATIONS

The relative performance of the five liquid sampling devices evaluated in these tests is summarized in Table 1. As indicated in Table 1, the performance of the ACD-S device exceeded that of the Drum Thief and COLIWASA in essentially all categories of evaluation for small volume sampling devices, and the performance of the ACD-L exceeded that of the COLIWASA-L for large volume devices. The performance of the COLIWASA-S was somewhat better than that of the Drum Thief for most test parameters, but the accuracy obtainable with these two devices appears to vary from user to user. The relative performance of all five devices is also consistent with the ranking of device performance based on the survey of 17 professional and 35 inexperienced users. The two ACD devices received the highest ratings, followed by the two COLIWASA devices, with the Drum Thief receiving the lowest user ratings.

The systematic differences in sampling performance among the devices can largely be attributed to their design and function. Design factors that affect performance include the relative size of the opening through which liquids enter the sampler, closing mechanisms, and the tendency for sample leakage. These factors also appear to control the extent to which device performance is affected by the user.

Much of the sampling error with the COLIWASA and Drum Thief is related to the relatively small diameter opening on the sampling tube, which causes disproportionate amounts of the liquids to enter the tube. The magnitude of this error appears to depend on the opening diameter, the rate of insertion of the sampling tube into the liquids, and on the proportions and viscosities of the liquids sampled. Although the guidelines for use of the

COLIWASA and Drum Thief recommend a slow insertion, the rate of insertion necessary to minimize this error is never known in blind sampling. In practice, disproportionate amounts of water and oil were obtained with these devices by all users. These relationships are discussed further in manuscripts being prepared for publication.

Another important manifestation of this source of bias is the dependency of sampling accuracy on the water:oil ratio with the Drum Thief and COLIWASA because this error is magnified as the proportion of a liquid becomes smaller. Although sampling accuracy for all devices was >80% when the proportions of both liquids were greater than 10%, accuracy with the COLIWASA and Drum Thief decreased substantially when the fraction of the liquid was less than 30% (Figure 1a,b). At extreme water:oil ratios (e.g., 95:5) the accuracy with these two devices was as low as 10%. These results indicate that there are limits on the proportions of a liquid that can be sampled with these devices. Sampling accuracy with the ACD devices, however, was >96% for most liquid ratios and >85% for extreme liquid proportions. Although there may also be sampling limits with the ACD devices for other testing conditions, these limits appeal to be much smaller than those for Drum Thief and COLIWASA. Liquid viscosity is expected to affect the accuracy and limits of sampling with all these devices at some point. However, it is indicated from the results of this study that sampling accuracy with the ACD devices should be significantly greater than with the Drum Thief or COLIWASA for most sampling conditions.

These design and function factors also affect sampling accuracy with the Drum Thief and COLIWASA because they cause performance of these devices to vary from user to user. It is possible for individual users to obtain highly reproducible results with the COLIWASA and Drum Thief, whether or not they are accurate. But it is indicated from the results of this study that the uncertainty in sampling accuracy among users is two to three times higher with the COLIWASA and Drum Thief than with the ACD devices. The Drum Thief appears to be the most prone to user errors. The high sampling accuracy and precision obtained with the ACD devices among all users indicates that sampling quality with these devices is essentially independent of user factors, including user experience.

Design-related performance factors unique to the Drum Thief include the leakage of liquid from tire Drum Thief and the small tube volume necessitating multiple strokes for the collection of samples. Spillage and the potential for sampling error related to spillage is greatest with the Drum Thief because significant leakage of liquid from this device during transfer is inherent to its' use. Although leakage is negligible with the COLIWASA and ACD devices, spillage resulting from liquid on the outside of the sampling tube occurs with both the COLIWASA and Drum Thief. This Source of spillage occurs because the 42-inch tubes must be removed from the vessel being sampled, and lifted above eye-level to transfer the liquid to a sample container. With the Drum Thief, both types of spillage are compounded because multiple strokes are required to obtain a sufficient sample volume all forms of spillage are essentially eliminated with the ACID devices because they are designed for transfer of the liquid directly to a sampling container without removal of the tube from the vessel (e.g., drum). These factors also affect the time required to collect a sample. Samples were systematically collected more rapidly with the ACD devices than with the COLIWASA or Drum Thief because direct transfer of samples requires less time than removal of the tube for transfer. Sampling times with the Drum Thief are also up to three times longer because multiple strokes are required to obtain samples.

Although statistically significant differences were found in the performance of liquid samplers, these differences are specific to these test conditions. Based on the evaluation of these results, similar patterns of performance are expected for most other sampling conditions. The magnitude of the differences in device performance is expected to vary systematically with changes in physical properties of liquids such as viscosity and density. However, these relationships, and the effects of other factors such as suspended solids oil device performance are not presently known, and are the subject of further investigations.

There are many potentially important implications for the results obtained in this study. Although the practical significance of the differences in device performance must be assessed oil a case-by-case basis, these results have a number of broad implications for liquid sampling. The implications for significant differences in sampling accuracy are important because the objective of sampling is to determine the types and amounts of liquids present so they can be properly (and legally) handled and dispositioned. Representative sampling has safety, economic, legal, and practical implications because the accuracy of sampling determines, correctly or incorrectly, the type and level of hazards associated with the liquids. Errors in sampling accuracy have direct and indirect economic implications involving billings and associated costs that are based on the amounts of specific chemicals that must handled or otherwise dispositioned. The level of sampling accuracy required also depends on the inherent hazard of the materials which is usually not known prior to sampling. Thus, sampling should be

carried out in a manner capable of providing the highest practicable accuracy. The indication that the proportion limits on sampling with the Drum Thief and COLIWASA are relatively high (5%-30%) is especially notable because this implies that liquid fractions smaller than 30% are subject to significant sampling errors with these devices. Sampling precision requirements may also vary from case to case, but it is important that the quality of sampling be comparable and reproducible from user to user. Spillage has direct implications for worker safety and for the costs of handling spillage and any subsequent contamination in accordance with regulatory requirements Sampling time differences of up to 300% can have cost-benefit implications, but only if the quality of sampling is not compromised. Sampling time and ease of use can also be important when sampling must be performed in personal protection equipment (PPE) or under adverse (e.g., weather) conditions. Long-term implications of sampling performance also include the integrated cost savings associated with improved sampling efficiency and minimizing the negative implications of poor quality sampling.

CONCLUSIONS & RECOMMENDATIONS

Systematic differences in sampling performance were found between the Drum Thief, COLIWASA, and ACD liquid sampling devices in tests simulating the sampling of stratified liquids. Accuracy and precision were found to be highest, and spillage and sampling time least, with the small volume ($\leq$ 250 ml) and large volume (1000 ml) ACD devices. Sampling accuracy with the COLIWASA and Drum Thief appear to depend on the relative proportions of the liquids, viscosities, and on the users themselves. The ACD devices were found to be largely independent of user factors, including user experience for the test conditions evaluated, and to exhibit high sampling accuracy for proportions ranging from 5% to 95% of each liquid. The Drum Thief and COLIWASA appear to have limitations on proportion of a liquid that can be reliably sampled between 5%-30%. The overall performance of the devices based on a survey of 17 professional samplers and 35 inexperienced nolunteer samplers indicate that both groups of users rated the ACD devices highest followed by the COLIWASA, and the Drum Thief.

These results have potentially important implications for the handling and disposition of potentially hazardous liquids, and immediate implications for sampling efficiency and the reduction of risk to sampling personnel from spillage. The results provide a baseline for quantitatively comparing the performance of liquid sampling devices, for matching sampling needs with product performance, and also provides a basis for the improvement of sampling performance and sampler design.

Although these tests are specific to the test conditions used, these results provide insight regarding the factors that affect liquid sampling under these and other conditions. Tests with liquids over wider range of densities, viscosities, and liquid conditions including suspended solids, and numbers of liquids, will be required to establish functional relationships for the performance of these devices over the range of sampling conditions encountered in the field. Based on the results of this study, the ACD devices appear to provide significantly better sampling performance and data quality than the COLIWASA and Drum Thief for most conditions of stratified liquid sampling.

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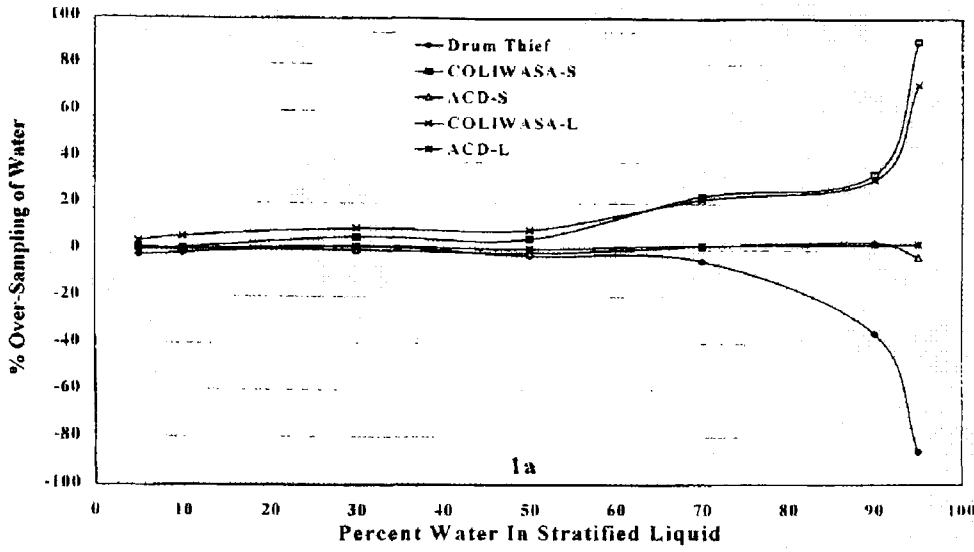

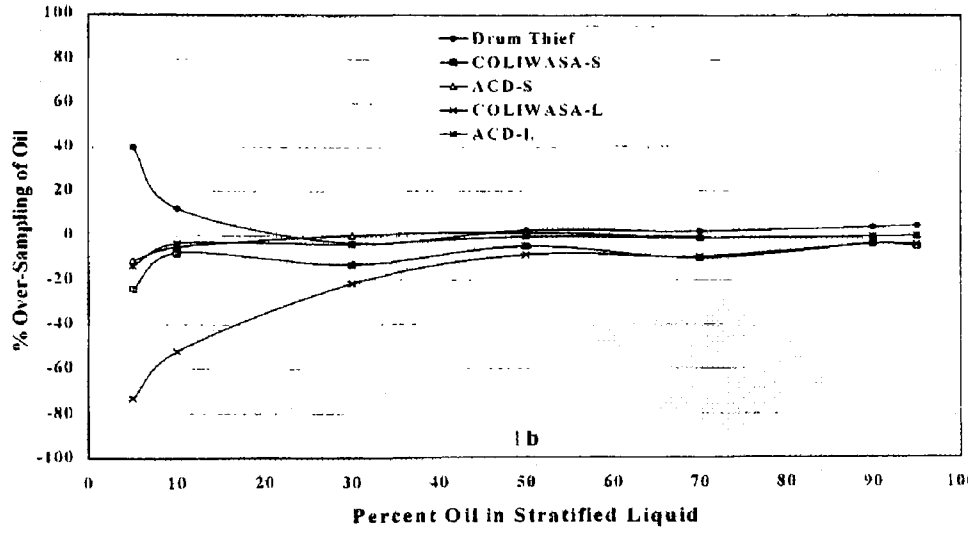

Figure 1a,b. Accuracy for test results at various water:oil ratios.
Accuracy of sampling for five liquid sampling devices at water:oil ratios ranging from 5:95 to 95:5. Sampling accuracy is indicated by the percent of over-sampling or under-sampling (bias); e.g., zero bias corresponds to 100% accuracy. Figure 1a shows the amount of over-sampling and/or under-sampling of water obtained with each device as a function of the amount of water present in the stratified liquids that were sampled. Figure 1b shows the amount of over-sampling and/or under-sampling of oil obtained with each device as a function of the amount of oil present in the stratified liquids that were sampled.

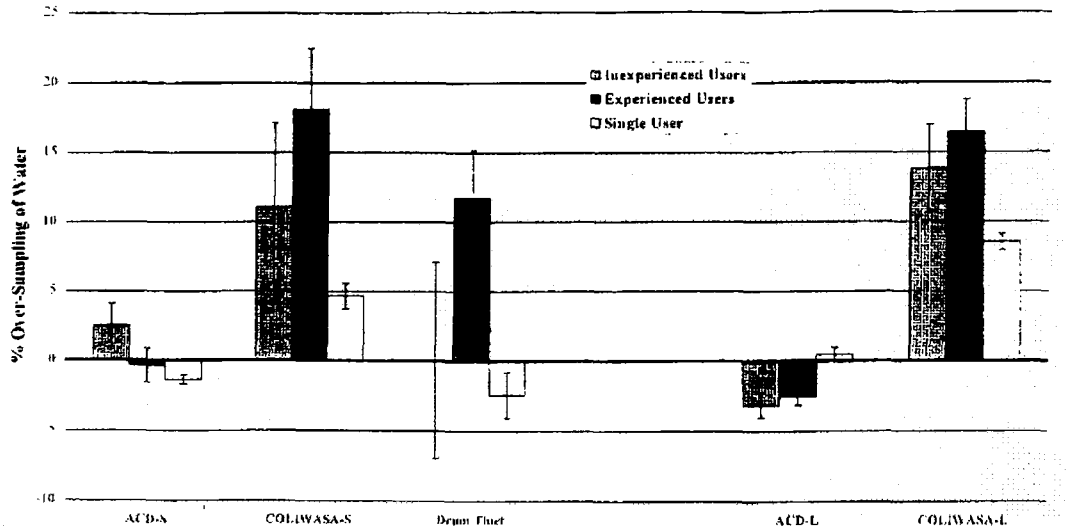

Figure 2. Accuracy and precision test results.
Accuracy and precision for liquid samples collected with five sampling devices by experienced inexperienced, and individual users. Sampling accuracy is indicated in terms of the average percent of over-sampling and/or under-sampling (bias) for water at a water:oil ratio of 1:1. Zero over-sampling corresponds to 100% accuracy. Bias levels for water mirror bias levels for oil (i.e., 10% over-sampling of water corresponds to 10% under-sampling of oil). The vertical lines at the top of each bar represent tile precision of the measurements at the 95% confidence interval (i.e., 95% confidence that the mean values lies within the range of these error bars).

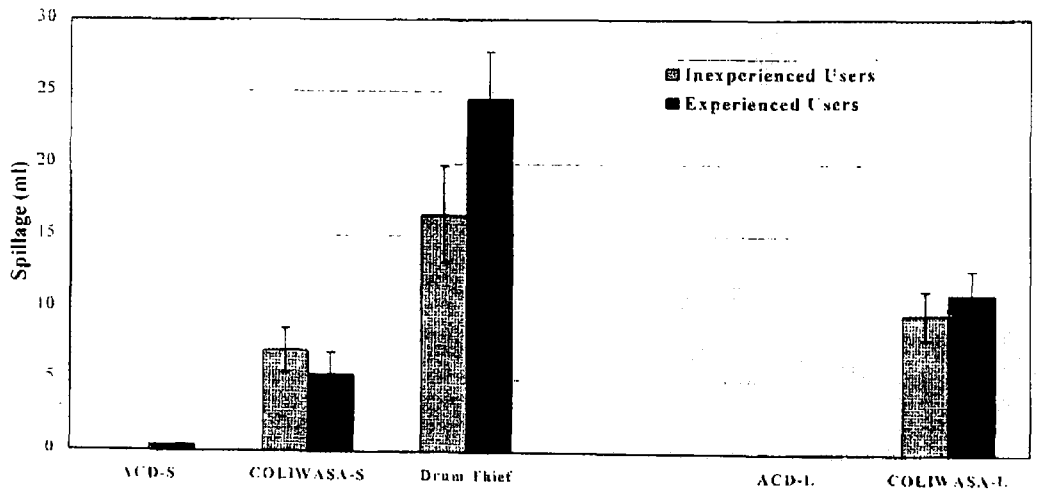

Figure 3. Spillage Test Results.
Amount of spillage resulting from the collection of liquid samples with five sampling devices. The height of the columns denote the average volume of liquid spilled (ml) by experienced and inexperienced in the process of collecting samples from simulated waste drums. Vertical lines at the top of each bar represent the 95% confidence intervals for the measurements.

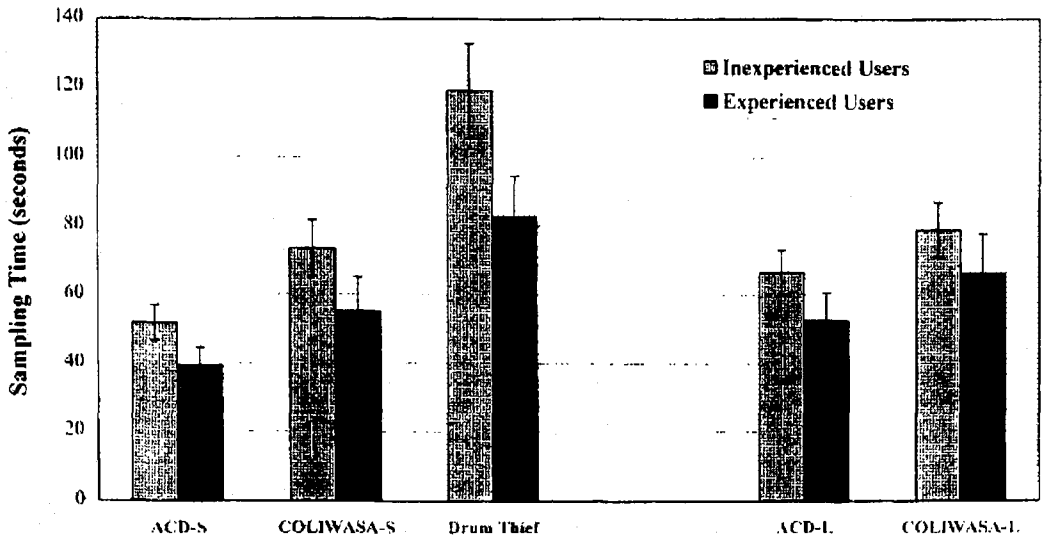

Figure 4. Sampling Time Test Results.
Time required for the collection of a sample with each of five sampling devices. The height of the columns denote the average time (in seconds) required for experienced and inexperienced users to collect a liquid sample from a simulated waste drum and transfer the liquid to a sampling container. Vertical lines at the top of each bar represent the 95% confidence intervals for these measurements.

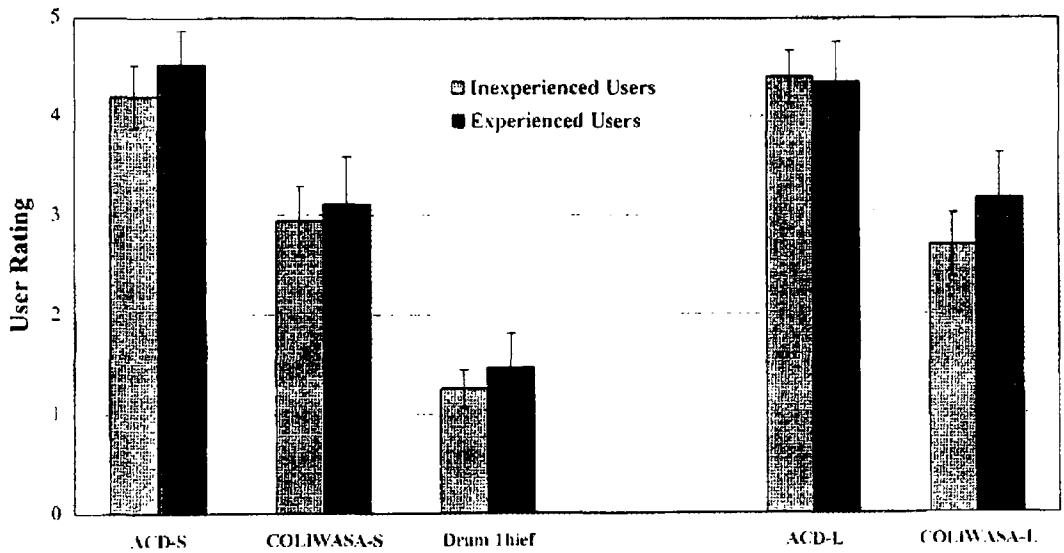

Figure 5. *User Rating Results*
Results of a survey of 17 professional and 35 inexperienced users regarding the performance of five liquid sampling devices. After collecting samples with each device, users scored each device on a scale of 1 to 5, with 5 = best, and 1 = worst. The heights of the columns denote the average user score. Vertical lines at the top of each bar represent 95% confidence intervals for the mean values.

	SMALL VOLUME SAMPLERS			LARGE VOLUME SAMPLERS	
	ACD-S	COLIWASA-S	Drum Thief	ACD-L	COLIWASA-L
EXPERIENCED USERS (n=17)					
Accuracy	○	●	◎	○	◎
Precision	○	●	◎	○	◎
Spillage	○	◎	●	○	◎
Sampling Time	○	◎	●	○	◎
User Ratings	○	◎	●	○	◎
INEXPERIENCED USERS (n=35)					
Accuracy	○	◎	○	○	◎
Precision	○	◎	●	○	◎
Spillage	○	◎	●	○	◎
Sampling Time	○	◎	●	○	◎
User Ratings	○	◎	●	○	◎
SINGLE USER (n=80)					
Accuracy					
Fraction = 1.1	○	◎	○	○	◎
Fraction 10% to 90%	○	●	◎	○	●
Fraction <10% or >90%	○	●	●	○	●
Precision (all ratios)	○	◎	◎	○	○

○ High Performance

◎

● Low Performance

Table 1. Performance Summary for Liquid Sampler Tests.
Summary of results for tests with five liquid sampling devices. Level of performance of the three small-volume and two large-volume devices in each of the categories shown are indicated by symbols defined in the legend.

ATTACHMENT 1

Devices Tested

The liquid sampling devices evaluated in this study are all commercially available and were not modified or altered.

Drum Thief

The Drum Thief is a small diameter hollow tube (typically 0.42" ID) manufactured by Wheaton Scientific Products, which is used essentially like a large capillary tube or pipette. The Drum Thief model used in these tests was 42 inches long. Samples are collected with the Drum Thief by inserting the tube into a liquid container and liquid is allowed to enter the tube. The sample is collected by covering the exposed end of the tube with a finger/thumb or stopper, removing the tube from the container, and transferring the sample to an empty container. The sample volume varies with the size of the device, but about 75-100 ml of liquid can be obtained per stroke with the 42 inches long model. Multiple aliquots are collected if larger volume samples are required.

COLIWASA

The COLIWASA, an acronym for COmposite LIquid WAste Sampler, manufactured by Wheaton Scientific Products, is constructed as a larger diameter open tube with a closure mechanism at the lower end. The COLIWASA is typically 42" long and 0.7" ID for the small volume model (~200 ml), and 1.5" for the larger volume (~1000 ml) models. The tube is tapered at the lower end, or fitted with a reduction plug about half of the tube diameter. Liquid samples are collected with the COLIWASA in a similar manner as with the Drum Thief, except that lower end of the tube is manually closed from inside the tube using a tapered plug attached to a small diameter tube (or rod) somewhat longer than the collection tube. After liquid has entered the collection tube and the lower end plugged, the device is removed from the container, and the sample is drained into a sample

jar.

ACD Samplers
The third type of sampling device tested was a product developed and manufactured by Advanced Concepts & Design (AC&D), Inc. The ACD devices are essentially have an open tube design (0.87" and 1.5" ID) in which fluid in the sample tube is manually drawn by pulling a small cone-shaped plastic plunger upward from the bottom of the tube using an attached rod or cord extending the length of the collection tube. A sample container (jar) adapter is attached at the upper end of the tube to receive the sample. Samples are obtained with this device by lowering the collection tube into the liquid and transferring the liquid from the tube to the sampling container (jar) by pulling the plunger up through the tube with the rod or cord, essentially pumping the liquid from the tube into the aligned sample jar without removing the collection tube from the sampled vessel (e.g., drum).

The COLIWASA and the ACD devices both have small volume (~200-250 ml) and large volume (~1000 ml) models. All three devices are available in glass and high density polyethylene (HDPE) models.

ATTACHMENT 2
Laboratory Procedures
Phase I Testing
Samples were collected with each of the five sampling devices from simulated waste drums under the supervision of laboratory personnel. The simulated waste drums consisted of cut-away 55-gallon barrels fitted with 4" ID acrylic cylinders 34" in length (5.6 liter capacity per cylinder) sealed on the bottom and mounted below the bung hole. Sampling was performed by two groups of volunteer. A total of' 250 samples were collected by 17 experienced (professional) samplers, and 35 inexperienced participants with no prior sampling experience. A description of the study and procedures for the use of each device was provided to each participant (herein referred to as users) prior to testing. Each user was tasked with drawing a sample from each of five simulated waste drums using one of the five liquid sampling devices at each drum station, and transferring the samples to clean sampling containers (jars) placed on top of the drum.

Data on the sample volume, liquid ratios, sampling time, and spillage were obtained for each sample collected. Pre-weighed drip trays and absorbent material (e.g., paper towels) were placed on the top of the barrels to capture spillage associated with the transfer of liquid from the drum to the sampling jars. At the conclusion of each sampling series, laboratory personnel measured the water:oil volume ratio and total volume in each sampling jar in graduated cylinders. The drip trays were then re-weighed to quantitatively assess the spillage associated with each device. The sequence in which the devices were used was rotated randomly between users to minimize bias due to the sequence in which the devices were used. All devices and testing materials were thoroughly cleaned between sampling series, liquid columns refilled and recalibrated, and pre-measured spill trays replaced.

All participants completed a user survey at the conclusion of their sampling series. In the survey, users rated each device in terms of overall performance, and commented on device features, attributes, and shortcomings. Users also provided personal information on experience and physical characteristics such as height, sex, and age. Measurements were also made of wrist girth and forearm length to assess correlation between sampling performance and physical characteristics of the users.

Phase II Tests
Sampling procedures similar to those used in the Phase I tests were employed in the Phase II tests. However, all samples were collected from freestanding acrylic cylinders by a single individual. Multiple samples were collected with each sampling device for water:oil ratios ranging from 95:5 to 5:95. A total of 216 samples were collected in Phase II testing. The following are the water:oil ratios, and the number of measurements made at each ratio.

<u>Numbers of samples collected in Phase II testing at each water:oil ratio</u>
Preliminary test, were performed with glass and plastic models of the COLIWASA and Drum Thief to assess performance among these models of the same brand. The samples were collected with each of the seven device models at a water:oil ratio of 50:50, including ten single-stroke and double-stroke samples with both of the COLIWASA-S models. The best performing models of the Drum Thief and COLIWASA-S were then used in tests at other water:oil ratios. The glass model of the Drum Thief was selected based on slightly better sampling accuracy than the high-density polyethylene (HDPE) model. The COLIWASA-S with the (HDPE) plunger head

was selected for use in the remaining tests because its' sampling accuracy was slightly better than that with the model with a borosilicate plunger head. The COLIWASA-L and ACD devices tested were all composed of HDPE. Single stroke measurements were also made for the purpose of independently evaluating the accuracy and uncertainty of samples obtained from multiple stroke composites.

RATIO	COLI WASA-Small - Glass head - Plastic head		Drum Thief - Glass model - Plastic model		COLIWASA Large	ACD Small	ACD Large
water/oil	Single stroke	Double stroke	Single stroke	Five stroke	Single stroke	Single stroke	Single stroke
95/5	3	3	3	3	3	3	3
90/10	3	3	3	3	3	3	3
70/30	3	3	3	3	3	3	3
50/150	10	10	10	10	10	10	10
30/70	3	3	3	3	3	3	3
10/90	3	3	3	3	3	3	3
5/95	3	3	3	3	3	3	3

The following steps were routinely followed in the conduction of Phase I and Phase II testing:

- Each sampler was cleaned before use.
- The plunger head was consistently lifted to a height of 4-inches prior to inserting tile sampling tube into the liquid-filled acrylic cylinder.
- A constant insertion rate of approximately 0.5 inches per second was used with all devices.
- Sampling devices were closed and sample transfer was initiated immediately after the head of the sampling tube reached the bottom of the acrylic cylinder.
- The Drum Thief and COLIWASA samplers were removed from the acrylic cylinder by pulling them up through a rag to wipe out excess fluid on the outside surface.
- Samples obtained with the Drum Thief and COLIWASA devices were transferred directly to graduated cylinders.
- Samples obtained with the ACD-S and ACD-L devices were first collected in 250ml and 1000ml jars respectively, and then transferred to graduated cylinders. The jars were allowed to drain into the graduated cylinders for up to 60 seconds so that transfer loss was negligible.
- Sufficient amount of time (up to 20 minutes) was allowed for the sample in the graduated cylinder to be segregate into layers of water and oil prior to recording the total volume and water and oil volumes of.
- Ambient room temperature was recorded at the beginning of each series of tests. An ambient room temperature from 19-21°C was maintained for all tests.
- The density of oil in each simulated waste cylinder was determined on daily basis at the beginning of each experiment. Distilled water was used in all tests.

ANALYSIS OF CHEMICAL WARFARE AGENT DECONTAMINATION BRINES FOR LEWISITE DEGRADATION PRODUCTS USING GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTION

Kevin M. Morrissey, Theresa R. Connell, and Jeffrey Mays
EAI Corporation, 1308 Continental Drive, Suite J, Abingdon, Maryland 21009
Tel: (410) 612-7332/Fax: (410) 612-7317
E-mail: kmmorris@eaicorp.com
H. DuPont Durst
US Army, CBDCOM, Edgewcod Research, Development, and Engineering Center, Edgewood, Maryland 21009
Tel: (410) 671-5270/Fax: (410) 671-2081
E-mail: hddurst@cbdcom.apgea.army.mil

Bulk chemical warfare agent (CWA) storage containers which contain decontaminated CWA waste are stored at several locations throughout the United States. Most of these containers have been in storage since the mid 1970's, and little analytical work has been performed to characterize the contents. This work reports on the efforts to determine whether these ton containers may have contained Lewisite (L, 2-chlorovinylarsonous dichloride, CAS No. 541-25-3), an arsenic containing CWA. This work summarizes the efforts at analyzing 250 ton containers stored at a single location.

In the presence of water, Lewisite quickly hydrolyzes to 2-chlorovinylarsenous acid (CVAA, CAS No. 159939-86-3), and this hydrolysis product is not directly amenable to gas chromatographic analysis. The CVAA was derivatized with 1,3-propanedithiol (PDT, CAS No. 109-80-8), and analyzed by gas chromatography/atomic emission detection (GC/AED). Quantitation was accomplished using response in the arsenic channel, with supporting data collected in the sulfur and carbon channels. Spike recovery experiments were performed at 7 different levels, and data will be reported. In addition, total arsenic was determined by ICP/MS, and supporting techniques of GC/MSD, LC/MS and CE were used to confirm the presence of CVAA and other L hydrolysis products.

Detectable levels of total As were observed in 25 of the ton containers by ICP/MS. The total As values ranged from just over the detection limit of 1 ppm, to well over 7800 ppm. Detectable levels of CVAA were observed in 17 of the ton containers by GC/AED. The CVAA levels ranged from just over the detection limit of 0.008 ppm to 2.4 ppm. In addition to the CVAA, additional organo-arsenic compounds were detected in several of the ton container samples. These additional organo-arsenicals may be indicative of the presence of other As containing CWA, interaction of CVAA with sulfur mustard (HD, CAS No. 505-60-2) hydrolysis products, or As containing industrial waste. Correlations will be made between the presence of CVAA and other CWA hydrolysis products.

EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM

INTRODUCTION, SESSION SCOPE AND PURPOSE

William Stelz
US EPA, Office of Research and Development, 401 M St., SW, Washington, DC

NO ABSTRACT AVAILABLE

BIOAVAILABILITY AND RISK ASSESSMENT OF COMPLEX MIXTURES

K.C. Donnelly, W.R. Reeves, T.J. McDonald, L.-Y. He and R.L. Autenrieth
Departments of Veterinary Anatomy & Public Health and Civil Engineering,
Texas A&M University, College Station, TX

There is an urgent need to develop an accurate method to assess the risk associated with contaminated soils and complex mixtures. Perhaps more importantly, this method should provide a means of defining acceptable residue levels to allow a more cost effective approach to site remediation. This research program is developing a methodology which can be used to estimate bioavailability. Two soils have been prepared for evaluating the bioavailability extraction method. One soil is a Weswood silt loam amended with model chemicals, including chrysene, pyrene, phenanthrene and anthracene; while the second soil is a Weswood silt loam amended with 10% (wt/wt) wood preserving waste (WPW). The soil was spiked with either the model chemicals or the complex mixture and samples collected immediately after spiking, as well as after 60 and 360 days of incubation (note day 360 samples will be collected in the fall of 1998). Soil was extracted with pH 7 water or a 1:1 methanol:water mixture. Other solutions to be tested will include a gastric solution (pH 2) and an intestinal solution (pH 7) and a 3:1 methanol:water mixture. Extractions are performed by shaking 40 g of soil with a 200 mL volume of extracting solution for 2, 3, or 5 hours (depending on the extractant) at 37°C. Recoveries were determined using GC-FID. In addition, these extractions will be compared to results from desorption kinetics studies. Results from the digestive fluid extractions indicate that the stomach to intestinal fluid conversion (GI) extracted only 5.4% and 0.11% of that recovered by standard methods for chrysene and pyrene, respectively. Using these numbers as an estimate, the hypothetical excess lifetime cancer risk for the hexane:acetone extraction would be 7.1E-5, while the estimate for the GI fluid was 1.3E-7. The desorption study reveals two compartments: one slowly desorbing and solubility limited, and one limited by desorption/diffusion, which increases in size as the soil ages. An animal study is planned for this summer using the soil from this study as a means of evaluating these methods in a rodent model. This research is supported by USEPA Grant No. R825408.

FIELD DETERMINATION OF ORGANICS FROM SOIL AND SLUDGE USING SUB-CRITICAL WATER EXTRACTION COUPLED WITH SPME AND SPE

Steven B. Hawthorne, Carol B. Grabanski, Arnaud J.M. Lagadec, Martin Krappe,
Cedric L. Moniot, and David J. Miller
Energy and Environmental Research Center, University of North Dakota,
Grand Forks, North Dakota, USA 58202

We have demonstrated that subcritical water (hot water maintained as a liquid by a few bar pressure) is an excellent solvent to quantitatively extract polar and non-polar organics from soils and sludges. Subcritical water extractions can be highly selective; polar organics extract at lower temperatures (e.g., phenols and amines extract at 50 to 100 °C), and non-polar organics extract at high temperatures (e.g., 200 to 250 °C). By heating water under low pressure, solubilities of polar organics increase dramatically, and even non-polar organics such as PAHs can increase solubilities by > 10^6-fold.

For water samples, both SPE (solid phase extraction) and SPME (solid phase microextraction) can be used to extract and concentrate organics in the field for subsequent analysis (e.g., field-portable GC), but are not applicable to extracting organic pollutants from solid samples. If organic pollutants on soils and sludges could be efficiently transferred to water, both SPE and SPME could be very useful for field determinations of organic pollutants from solids. The primary purpose of the proposed investigations is to couple SPE and SPME with subcritical water extraction of soils and sludges to allow field-portable water methods to be applied to contaminated solids.

We have coupled subcritical water extraction with SPME using very simple, inexpensive, and field-portable equipment. The method uses a static extraction (no pump), no flow restrictor, and no organic solvent. Soil, water, and internal standards are placed in an extraction cell and heated for 15-60 minutes. The cell is then cooled and the water extracted using a SPME fiber followed by direct desorption in a GC injection port. Although the method involves multiple partitioning steps (water/soil, and water/SPME), quantitative results can be obtained using proper internal standards, e.g., deuterated PAHs are added to calibrate for PAH determinations. Methods have been developed for PCBs, PAHs, and aromatic amines which give good quantitative comparisons to conventional (Soxhlet) extraction. Typical sample preparation time is < 1 hour, and detection limits of < ppb are obtained.

In contrast to the multiple partitioning steps involved in the coupled subcritical water/SPME method, coupling subcritical water with SPE discs (e.g., "Empore" discs) should allow quantitative extraction and collection of organic analytes. For example, when a static extraction cell contains the soil, water, and an SDB disc, PAHs extract from the soil into the water during the 250 °C heating step, but then are efficiently collected (ca. 90 %) on the sorbent disc as the extraction cell is cooled to room temperature. The PAHs are then eluted from the disc in a few mL of solvent, and the extracts analyzed by conventional GC methods. Similar approaches are being developed for PCBs. In addition, the use of subcritical water to aid in derivatization reactions for the SPME or SPE collection and analysis of more polar solutes (e.g., acid herbicides, natural pyrethrins) will be presented.

A FIELD PORTABLE CAPILLARY LIQUID/ION CHROMATOGRAPH

T. Scott Kephart, C. Bradley Boring and Purnendu K. Dasgupta
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061
James N. Alexander, IV
Rohm and Haas Company, 727 Norristown Road, P.O. Box 904, Spring House, Pennsylvania 19477-0904

INTRODUCTION

The need for on-site, real time characterization of environmentally hazardous sites has led to a considerable interest in the development of self-contained field-portable instrumentation. Presently, two factors limit the use of field portable instruments for environmental analysis. First, most portable instruments do not compare favorably to laboratory-based instruments with respect to reliability and performance. Second, the availability of stand-alone field portable equipment is limited primarily to chemical analyzers or sensors which measure a single physicochemical property such as pH, temperature, or UV/VIS absorbance, although more sophisticated instruments such as X-ray fluorescence analyzers, mass spectrometers, and Fourier transform IR systems have recently been developed[1]. Bringing samples collected in the fields back to the laboratory for analysis results in a time lag that can compromise sample integrity as well as delay any needed response prompted by the analytical result.

Analysis in the field often requires the separation of multiple analyte species before detection and quantitation. For the environmental analyst, liquid chromatography (LC), including ion chromatography (IC), and gas chromatography (GC) remain the primary techniques of choice. Although field portable GC systems have been commercially available for some time, field portable LC systems are virtually non-existent. If used in the field, LC systems typically have to be located in a mobile laboratory, making them at best only moderately portable.

The practice of capillary LC has undergone extensive development since its introduction twenty years ago[2]. The primary advantages of moving from conventional size columns (≥ 4 mm i.d.) into the capillary domain include

higher efficiencies, higher mass sensitivities, low eluent consumption, and a very small sample requirement. LC hardware components other than the absorbance detector have been miniaturized with the development of capillary chromatography. Fully automatable injection valves are available down to 20 nL; small, compact, and inexpensive syringe pumps with very low power requirements have been developed.

Recently, we described a capillary IC with suppressed conductometric detection for anion analysis[3]. The miniaturization of LC hardware components in combination with the excellent performance of this bench-top capillary IC, led us to investigate the feasibility of a field portable capillary IC/LC system.

In this paper, we present a fully computer controlled, stand-alone field portable capillary IC. Further, we describe a dual syringe pump capillary LC system that is in the process of being prepared for field use. The construction and performance of each of these capillary systems is reported.

EXPERIMENTAL

The layout of the capillary IC and capillary HPLC systems are shown in Figure 1a and 1b, respectively. The pumps used were fully computer controlled 48 000 step, motor driven syringe-type dispensers (Model 50300, Kloehn Inc., Reno, NV) equipped with syringes of appropriate size. A 500 µL glass syringe was used for capillary IC; stainless steel syringes (constructed in-house) were used for capillary HPLC because operating pressures are well above 1000 psi. A stainless steel block was machined in-house with appropriately sized ports to accommodate the appropriate syringe head, a low leak dual ball and seat inlet check valve (P/N 44541, Dionex Corp., Sunnyvale, CA), and a liquid output port, A small volume eluent reservoir was affixed next to the syringe dispenser and was connected to the check valve with PEEK tubing to avoid CO_2 intrusion. A pressure sensor (Model SP70-A3000, Senso-Metrics, Simi Valley, CA) was connected to the liquid output port of the stainless steel block using 0.25 min i.d. PEEK tubing. The column backpressure was continuously monitored to insure proper system performance.

Capillary IC System

Water pumped by the syringe was passed through a mixed bed ion exchange resin to remove any impurities leached from glass and metal parts in the upstream components. A previously described microscale electrodialytic sodium hydroxide generator[3] (EDG) was used for eluent production. A mildly pressurized reservoir of 25 mM sodium hydroxide was used as the donor solution for the EDG. A 10 cm long polystyrene capillary, ~80 µm i.d., 250 µm o.d., was placed at the exit of the EDG to remove the H_2 gas in the eluent stream by permeation through this tube. The polystyrene capillary was able to perform gas removal at pressures > 900 psi at NaOH concentrations > 40 mM.

A hollow fiber suppressor, which has been previously described,[3] was deployed prior to the detector. A H_2SO_4 regenerant reservoir, mildly pressurized (< 1 psi), was connected to the suppressor using Tygon tubing. The suppressor was able to suppress NaOH concentrations ranging from 0.5 to 40 mM to a background of $\leq$ 2 µS/cm with eluent flow rates of 1.5-2.2 µL/min. A conductivity cell was connected at the suppressor exit. A bipolar pulse conductivity detection system[4] was used for the IC system. A laptop computer in combination with an executable program, written in C, provided a user interface for the data acquisition system.[5]

Capillary HPLC System

The dual syringe pump capillary HPLC system is shown in Figure 1b. The syringe pumps were coupled to a mixing chamber, having an internal volume of 2 µL, for isocratic or gradient eluent production in the capillary HPLC system. To produce a constant flow rate while operating in the gradient mode, this setup required a custom control program to be written. An executable program written in Microsoft Visual Basic® provided a user interface for instrument control. A typical gradient program utilizes a six step gradient, although more steps can easily be added. The program calculates the appropriate delay between steps for each pump, given the total flow rate, in terms of the percentage of flow necessary from each pump. The program then creates a command string with the appropriate delays for each pump and downloads this into the resident memory of the pump hardware via an RS-232 serial communication port. A Linear model UVIS 200 absorbance detector (Spectra-Physics/Thermoseparation systems), designed for on-column detection with capillaries, was used for HPLC detection. A smaller detector will be developed in the future.

An electrically actuated injection valve equipped with 20-100 nL internal sample loops (Valco Instruments, Houston, TX) was used for sample introduction.

Analytical columns, ~50 cm long, 180 µm i.d. fused silica capillaries (Polymicro Technologies), were packed in-house. The IC columns were packed with the same packing as commercially available Dionex AS-11 columns. The reverse phase HPLC columns were packed with 5 µm PRP-1 and 5 µm HSC-18 particles, respectively. A frit was made at the exit end of the column by placing several short pieces of glass wool into 0.3 mm i.d. PTFE tubing and push fitting the end of the column and a 75 µm i.d., 365 µm o.d. fused silica capillary on either side of the glass wool. No frit was needed at the front of the column. This configuration allowed the front of the column to be easily trimmed when compression of packing material at the head of a column led to a void over a period of time.

For IC experiments using sample preconcentration, the preconcentration column consisted of an ~1.5 cm long piece of 250 µm i.d. fused silica capillary packed with AS-11 packing. The exit frit was constructed by first pushing a small piece of glass fiber filter (Whatman type GF/A, Maidstone, England) into this capillary ~1 cm from the end of the packing. A 50 µm i.d., 150 µm o.d. fused silica capillary was then pushed inside the larger capillary against the glass fiber filter and epoxied into place. The total length of the preconcentrator column was ~8 cm. The electrically actuated sample injector was equipped with a six port valve (Cheminert Model C3-1006-EH, Valco Instruments Co. Inc.), having internal dead volumes of 200 nL between each port, to accommodate the preconcentrator column.

A 24 Vdc power supply (Lambda Electronics, Melville, NY) was used to power the pumps and pressure sensor. A 24Vdc-10Vdc converter was built in-house to provide the pressure sensor with 10 Vdc operating voltage. The bipolar pulse conductivity detector (capillary IC system only) used a 5 Vdc power supply for operation.

Atmospheric Sampling

The capillary ion chromatograph was interfaced to a miniaturized parallel plate diffusion denuder (PPDD) to monitor ambient levels of sulfur dioxide. The PPDD construction is shown in Figure 2. The PPDD was constructed from two Plexiglas plates, each measuring 2 x 17 cm. The active area of the PPDD (0.6 x 10 cm) was prepared by thermally pressing silica gel particles (120 mesh or smaller) onto the Plexiglas plates. The two plates were separated by 1.5 mm thick Teflon coated Plexiglas spacers, 0.7 x 17 cm, which completely cover the untreated edges of the plates. Holes were machined in the top and bottom of the silica coating to provide a liquid input and output, respectively. Stainless steel tubing (23 gauge) was push fit into these holes and epoxied to the plates to provide rigid liquid input/output ports. The two plates were clamped together along their edges. Tubing for the air inlet and air outlet was fixed by epoxy adhesive at the bottom and top of the PPDD, respectively. Hydrogen peroxide (0.5 mM, 30 µL/min flow rate) was used as the denuder liquid. The denuder effluent was loaded onto a preconcentration column at a flow rate of 18 µL/min for 10 minutes for analysis. The PPDD displayed ~100 % collection efficiency up to an air sampling rate of 0.5 standard liters per minute (SLPM). Data presented here was obtained using this sampling rate.

RESULTS AND DISCUSSION

Portable Capillary IC

System Performance

The day to day reproducibility of the portable IC is shown in Figure 3 for repeated injections of fluoride, chloride, sulfate, and phthalate. The chromatograms were obtained under isocratic conditions using an ~20 mM NaOH eluent at a flow rate of 1.5 µL/min. The relative standard deviation of retention times ranged from 0.1% to 0.7% within one day and 0.3% to 0.8% day-to-day. Peak efficiencies for chloride, sulfate, and phthalate were 27 133, 21 018, and 15 422 plates/m, respectively.

Response linearity was studied under the same chromatographic conditions as above. A sample solution containing chloride, sulfate, and phthalate over a concentration range of 10-200 µM was used; fluoride eluted near an impurity and therefore was not used for evaluating response linearity. Linear r^2 values for peak area response vs. injected concentration for chloride, sulfate, and phthalate were 0.9959, 0.9988, and 0.9974, respectively. Above a concentration of 200 µM, peak broadening resulted from column overloading.

The three constituent mixture was also evaluated in terms of attainable limits of detection (LOD) under the same isocratic conditions. The intrinsic electronic noise of the bipolar pulse detector electronics was 0.3-0.4 nS. The noise increased to 2-3 nS/cm during chromatography, regardless of NaOH concentration or flow rate employed. Based on the performance at an injection concentration near the baseline and the peak-to-peak noise level, the S/N = 3 LOD for the three anions are as follows (LOD in µM indicated in parenthesis): chloride (0.03), sulfate (0.12), and phthalate (0.25). This performance is comparable to conventional size IC systems. However, an

increase of >2 orders of magnitude in terms of mass sensitivity is realized in the present system compared to the performance of a bench-top IC using conventional size columns.

Gradient Chromatography

Incorporation of the EDG on the high pressure side of the pump also allows gradient chromatography to be performed easily. The lag time, or time required for the produced NaOH to reach the head of the column from the EDG, was measured to be 1.5 minutes using an eluent flow rate of 1.5 µL/min. Therefore, only a short time is needed for a specific programmed NaOH concentration to reach the head of the column. A gradient chromatogram of a sample containing 15 anions is shown in Figure 4. A linear gradient of ~2 mM to 38 mM NaOH from 5 min to 17 min was used for the separation. This corresponded to a current requirement of 5-95 µA using a water flow rate of 1.5 µL/min. The resulting separation was excellent. Peak efficiencies ranged from 10 648 plates/m for acetate to 240 152 plates/m for chromate, with an average of 80 000 plates/m being observed for the separation.

Miniaturized PPDD Coupled Capillary Ion Chromatography System

An air sampling rate of 0.5 SLPM was chosen for evaluation of the PPDD-capillary IC system due to the collection efficiency of the PPDD being ~100% at this sampling rate. The response linearity was studied over an SO_2 concentration range of 23 pptv to 1944 pptv (at an SO_2 concentration $\geq$ 2000 pptv, sample peak height reached the maximum value permitted with the conductivity detection system). The response linearity over this concentration range was excellent. A log-log plot of peak height vs. SO_2 concentration resulted in a linear r^2 value of 0.998. The reproducibility of the data over this concentration range was $\leq$ 3.2% RSD for each point sampled. Figure 5 shows a chromatogram resulting from the sampling of clean air and 80 pptv SO_2. These data lead to a computed limit of detection of 1.6 pptv SO_2.

Ambient Air Studies

The ambient concentration of SO_2 was studied in Lubbock, TX over a period of 48 h. The system operated over this time period without any user intervention. The results are shown in Figure 6. These results correlate well with the ambient SO_2 levels at this location.

Capillary HPLC System

Isocratic Elution

Experiments evaluating retention time reproducibility were performed on the PRP-1 column injecting samples of biological interest. A solution of 100 mM ammonium formate (pH 4.25) was contained in pump A and the same solution containing 10% acetonitrile was contained in pump B. Figure 7 shows system reproducibility for isocratic elution of 8 sample components with a 50:50 A and B mix.

The average RSD in retention times for the 8 component mixture was 0.825%. Using only a single syringe pump and employing the same eluent conditions, the average RSD in retention times was 0.921%. The fact that the dual pump system actually has a lower average RSD indicates that the main source of retention irreproducibility is not from the pumping system but comes from other components.

Gradient Elution

The gradient capabilities of the system were examined by separating a series of benzene derivatives on the HSC-18 column. Pump 1 contained a mixture of acetonitrile and water (50:50); pump 2 contained only acetonitrile. Figure 8 shows a sample chromatogram that also indicates the gradient profile. Figure 9 shows the dual pump gradient reproducibility. The average RSD in retention times under gradient conditions was 0.545%. This corresponds to a variation of 2.05 (±.88) seconds for 10 peaks eluting in under 8.5 minutes.

System performance in terms of peak efficiency for the gradient HPLC system was also evaluated. The maximum peak efficiency was observed for ethylbenzene, which had 320 000 theoretical plates per meter. The average peak efficiency for the 10 components was 220 000 theoretical plates per meter. This correlates to an average of 17 000 plates per minute.

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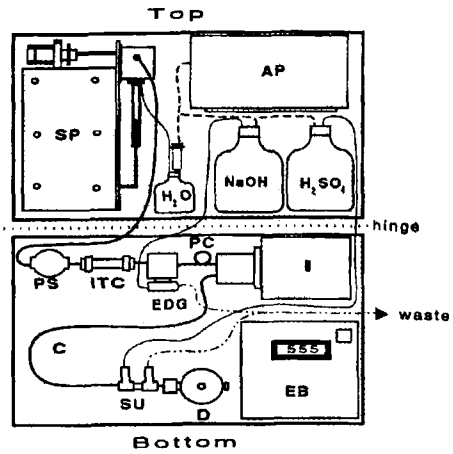


Figure 1a. Schematic layout of portable IC system. Figure designations: SP, syringe pump; AP, air pressure pump; PS, pressure sensor; ITC, ion trap column; EDG, electrodialytic sodium hydroxide generator; PC, polystyrene capillary; I, motorized injector; C, capillary column; SU, chemical suppressor; D, detector; EB, electronics box.

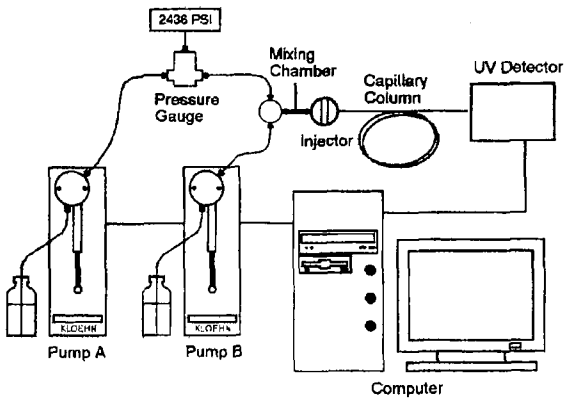
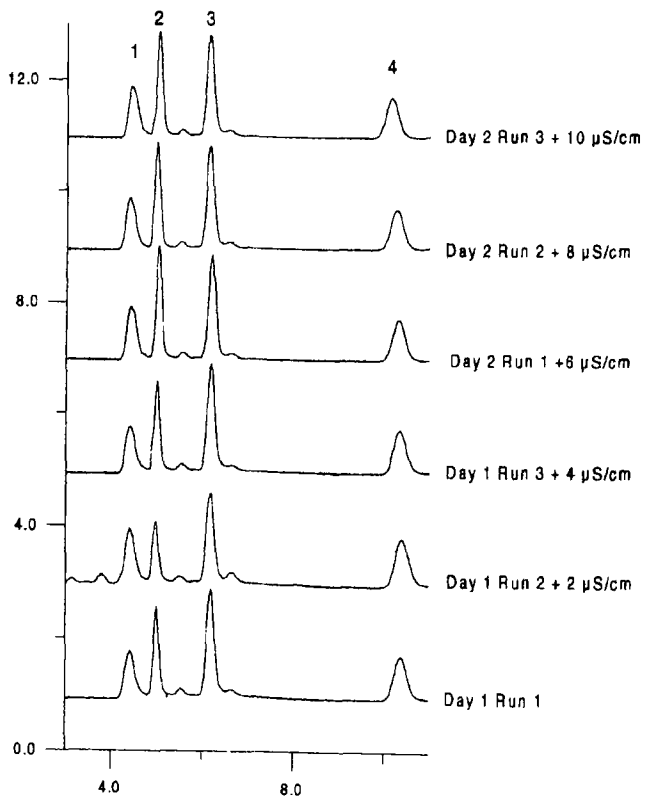


Figure 1b. Schematic layout of capillary HPLC system.



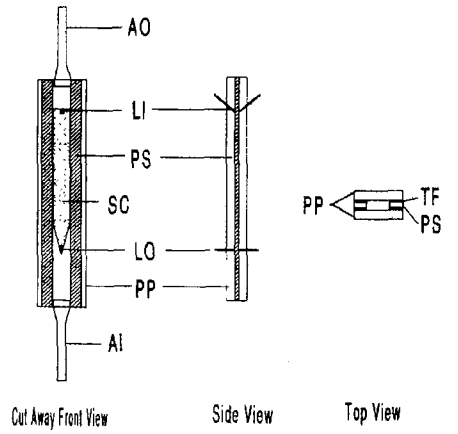


Figure 2. Wet parallel plate diffusion denuder. Figure designations: AO, air outlet; LI, liquid inlets; PS, Teflon coated Plexiglas spacer; SC, silica coating; LO, liquid outlet; PP, Plexiglas plates; AI, air inlet; TF, Teflon film

Figure 3. Day-to-day system reproducibility; repeated 100nL injections with ~20 mM NaOH eluent. Injected concentration was 20 µM for each ion. Peak identities: 1, fluoride; 2, chloride; 3, sulfate; 4, phthalate.

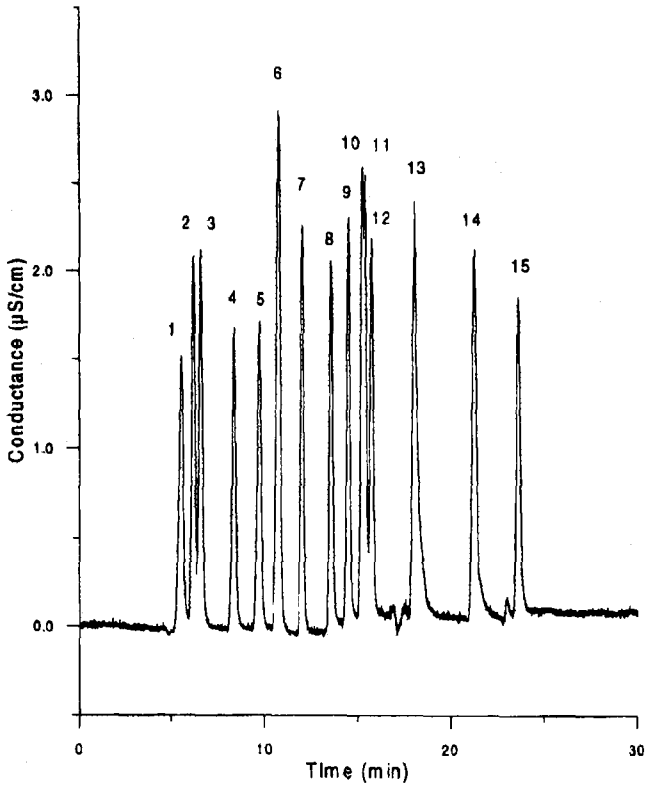


Figure 4. Background subtracted gradient chromatogram. A linear gradient from 2 mM NaOH to 38 mM NaOH from 5 to 17 minutes was used. Peak identities: 1, acetate; 2, formate; 3, methanesulfonate; 4, monochloroacetate; 5, bromate; 6, chloride; 7, nitrite; 8, trifluoroacetate; 9, dichloroacetate; 10, bromide; 11, nitrate; 12, chlorate; 13, sulfate; 14, phthalate; 15, chromate. All ions were 50 µM except dichloroacetate which was 60 µM.

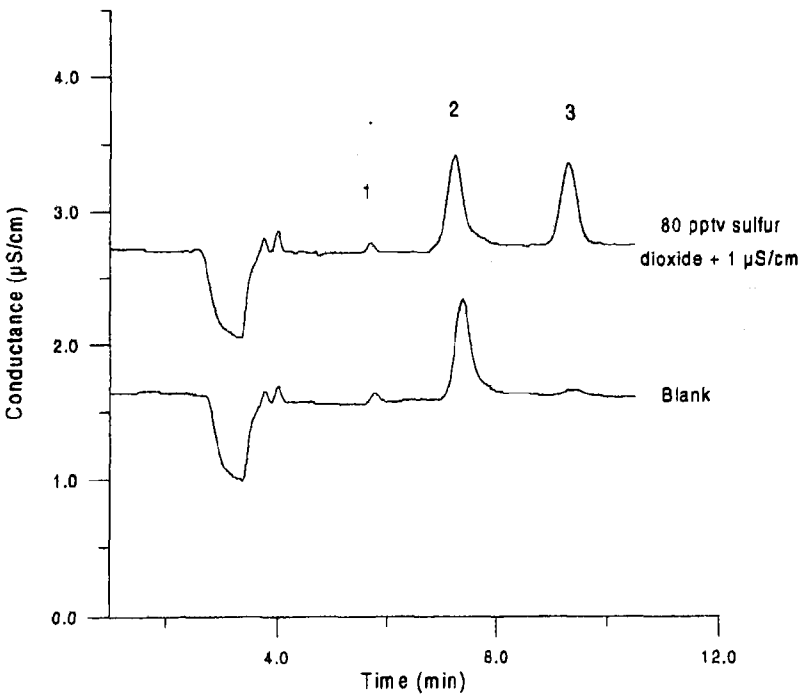


Figure 5. Chromatograms resulting from sampling blank air (lower trace) and 80 pptv SO_2 (upper trace). Peak identities: 1, chloride; 2, carbonate; 3, sulfate.

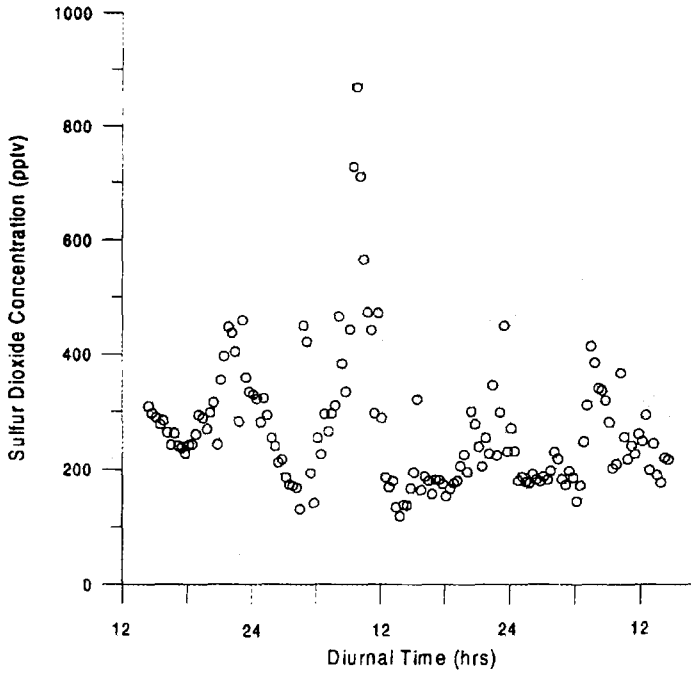


Figure 6. Ambient air levels of SO_2 in Lubbock, TX for a 48-hr period beginning in the afternoon of April 28, 1998.

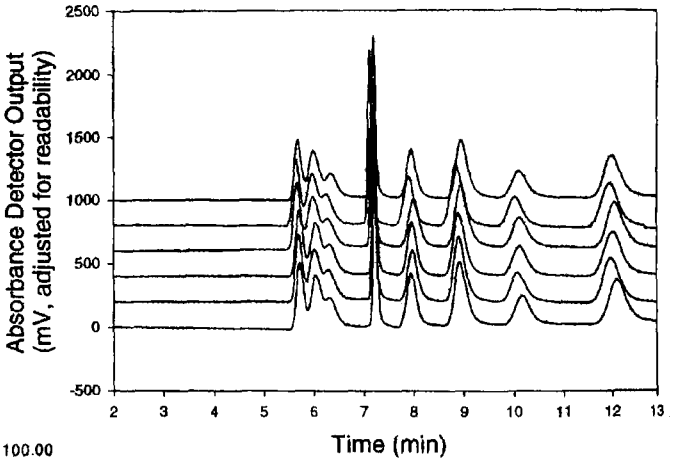


Figure 7. Sample of isocratic system reproducibility. RSD in retention time is < 1%. All samples are 500 µM. Peak identities from left to right: cytosine, uracil, adenine, uridine, thymidine, adenosine, xanthosine, and inosine.

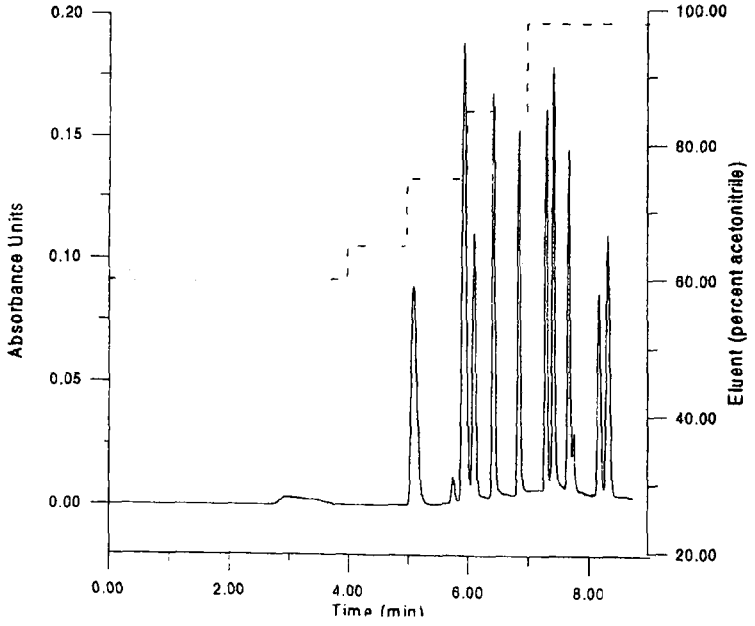


Figure 8. Sample chromatogram with gradient profile using an eluent flow rate of 5.0 µL/min. All samples are 0.5 ml / 100 ml solution in acetonitrile. Peak identities from left to right: phenol, benzaldehyde, benzonitrile, nitrobenzene, benzene, bromobenzene, toluene, ethylbenzene, propylbenzene, and t-butylbenzene.

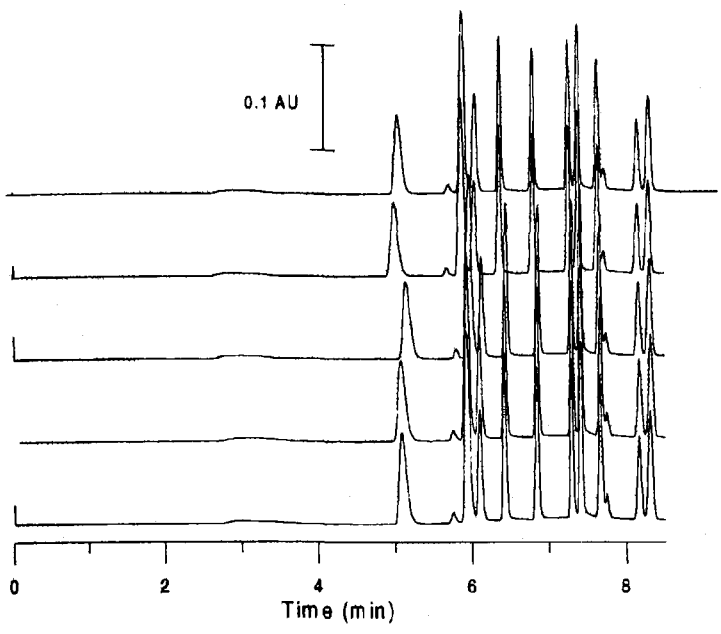


Figure 9. Dual pump gradient reproducibility. Average RSD in peak retention time is 0.545%. Peak identities from left to right: phenol, benzaldehyde, benzonitrile, nitrobenzene, benzene, bromobenzene, toluene, ethylbenzene, propylbenzene, and t-butylbenzene.

RAPID DETERMINATION OF ORGANIC CONTAMINANTS IN WATER BY SOLID PHASE MICROEXTRACTION AND INFRARED SPECTROSCOPY

David C. Tilotta, Danese C. Stahl, Sheila A. Merschman, Daniel L Heglund, and Said H. Lubbad
Department of Chemistry, P.O. Box 9024, The University of North Dakota, Grand Forks, ND 59202

The objectives of this research project are to: identify suitable solid phase films for determining organic contaminants in water by SPME/IR, determine which organic contaminants are amenable to the SPME/IR method, and adapt the basic methodology to field use.

Solid Phases

Of the 15 solid phases examined to date, three polymers have been found to be useful. for SPME/IR: Parafilm M™ (a wax-impregnated polymer/rubber composite), poly(dimethylsiloxane) (PDMS, an important solid phase material of the SPME syringe technology) and Teflon PFA™ (a perfluoroalkoxy teflon polymer).

Analyte Classes

To date, three classes of compounds have been examined for their suitability as analytes for SPME/IR using the three aforementioned films. Table 1 shows formal equilibration times, linear dynamic ranges, detection limits, and precision data (expressed as percent relative standard deviation) for these classes for the appropriate solid phase film(s). Multiple entries in this table for a given analyte imply that more than one film is useful Conversely, the absence of an entry for a given analyte/film combination indicates that that film is not suitable for the analysis.

Volatile organic compounds (VOCs) examined include the BTEX compounds (benzene, toluene, ethylbenzene, xylenes), and halocarbons such as carbon tetrachloride, chlorobenzene, chloroform. and p-chlorotoluene. Parafilm M™ and PDMS both have been useful for the analytical determination of these compounds. SPME/IR analyses using Parafilm, have demonstrated the ability of SPME/IR in distinguishing four of the six alkylbenzenes (benzene, o-xylene, m-mylene, p-xylene) in petroleum industry wastewater samples. Quantitation by simple univariate calibration based on absorbance band heights have provided good agreement with purge and trap GC/MS standard methods. Analytical determinations of ethylbenzene and toluene are, however, complicated by the spectral overlap of other components in gasoline.

Gasoline fuels include the more volatile organics such as the short chain hydrocarbons (e.g., $<C_6$) and, as previously discussed, the BTEX compounds. Teflon PFA™ has been found to successfully extract gasoline-range organics (GROs) from water and to provide a clear spectral region for identification and quantitation. SPME/IR analysis of the C-H stretching region provides a method for determining aggregate hydrocarbons. Whereas Parafilm and PDMS provides a means of identifying individual components of multicomponent mixtures, PFA is more useful for analysis of the mixture itself. The films thus compliment one another in terms of the selectivity they provide.

Analysis of pesticides and herbicides are currently underway using the SPME/IR approach. Poly(dimethylsiloxane) has been identified as the only solid phase that can successfully be used to determine trifluralin in aqueous solutions by SPME/IR.

Future Activities: Future SPME/IR work will involve: 1) continuing the identification of suitable solid phase films, 2) expanding the basic methodology to pesticides and herbicides, and 3) demonstrating the approach in field environments (summer, 1998).

INTRINSIC STABLE ISOTOPIC TRACERS OF ENVIRONMENTAL CONTAMINANTS

Stephen A. Macko, Peter J. Yanik, Nicole A. Cortese
Department of Environmental, Sciences, University of Virginia, Charlottesville, VA 22903
Mahlon C. Kennicutt II, Yaorong Qian
Geochemical and Environmental Research Group, Texas A&M University,
833 Graham Road, College Station, TX 77845

Abstract
The stable isotopic composition of a contaminant in the environment is the end result of a complex chain of events. Chemicals produced from disparate sources by fundamentally different processes would be expected to exhibit intrinsic isotopic compositions that could be used to identify sources. Compound specific isotope analysis (CSIA) based on gas chromatography/isotope ratio mass spectrometry (GC/C/IRMS) is being used to uniquely identify naturally occurring pollutants, such as PAH in petroleum, and synthetic or manufactured pollutants, such as pesticides and PCBs. The expected benefit to be derived from the application of CSIA to environmental questions is to be able to more accurately define the sources, fate, and transformation of pollutant mixtures in the environment. Effective environmental regulation can only be accomplished if contaminant distributions can be unambiguously linked to known processes or sources. As concerns about the quality of the environment have increased it has become clear that our ability to inventory, trace and provide a mass balance of pollutants in the environment is poor. The study presented here includes development of purification techniques, optimization of instrumental conditions, development of models based on study results, and field testing of the concepts developed. Selected polycyclic aromatic hydrocarbons, pesticides, and PCBs have been the analytes of interest. Fused silica capillary columns have been used to provide resolution of complex mixtures, minimize co-elution and background interferences, and limit column bleed during GC/C/IRMS analysis. The resolution and accuracy of the method is being determined by analyzing authentic standards, primary sources of contaminants, extracts of effluents and well-characterized pollutant occurrences. The study has had four primary objectives: (1) development of isolation techniques that produce high purity, unaltered concentrates that maintain the stable isotopic integrity of the analytes; (2) determine the stable isotopic composition of target analytes in primary sources of contaminants; (3) determine the stable isotopic composition of priority pollutants in selected processes that introduce contaminants to the environment; and (4) verify the techniques and models developed with well-characterized sites of pollutant occurrences.

Introduction
In recent years, there has been increased attention concerning the contamination of global soil, water and air. As the human population continues to increase, there is an ever-increasing strain placed on these life-sustaining reservoirs. This added strain is reflected in the quantities of and manner in which waste and potential contaminant sources are dealt with. It is inevitable that there are occasional occurrences when products,

produced or processed for human use, are released into the environment. Upon reaching the environment, the contaminants can be transported in a variety of ways until they reach a depositional end point, possibly in soils, waters or in biological tissues. Depending on the reactivity and toxicity of the contaminants, there is a multitude of possible implications for both the environment and human populations. It is necessary, therefore, to understand the nature of the contaminants, where they came from, and how they reached their depositional location. With this understanding, cleaning contaminated sites and preventing further contamination become more manageable endeavors.

There are many compound classes that have been contributors of contaminants into the environment. Of growing interest in recent decades are polycyclic aromatic hydrocarbons (PAH), organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs). PAH are of interest because they can be indicative of a variety of contaminant sources, such as petroleum spills or combustion processes and are known to be carcinogenic (LaFlemme and Hiles, 1978 and Hites *et al.,* 1980). Although some organisms, such as fish, are able to metabolize PAH, other organisms such as mollusks and crustaceans are unable to do so (Law and Biscaya, 1994; Hickey *et al.,* 1995; Roper *et al.,* 1997). Thus, PAH tend to accumulate in the tissue of these organisms. Pesticides, such as DDT, and PCBs are of interest because they not only can reside in soil and water reservoirs, but due to their lipophilic nature, they can accumulate in tissues and are known to be toxic (Killops and Killops, 1993 and Hickey *et al.,* 1995). The storage of such contaminants in tissue results in heightened concentrations in organisms residing at higher trophic levels, thus enhancing the risk to many predatory species.

In many earlier attempts at deciphering the sources of contaminants such as PAH and PCBs, the approach has been to look at absolute concentration levels and relate a concentration gradient to a point source. Another approach was to determine the concentrations of compound classes relative to one another and compare these relationships to possible source relationships. One difficulty with the first approach is that although measurable amounts of a contaminant may be located near a source known to produce such compounds, there is no absolute proof that the contaminant came from that source. Furthermore, owing to the off-site acquisition of pesticides, there is rarely a point source nearby which can serve as a possible answer to contaminant apportioning scenarios. A problem with the second approach is that chemical or biological activities such as evaporation, water washing or biodegradation could alter the concentration of one compound relative to the others. This chemical or biological alteration could change the original "signature" of the compound class that could lead to an incorrect assignment of a source (O'Malley *et al.,* 1994). In the past, traditional analytical methods using gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) have been used to characterize contamination sites. As the above arguments show however, these techniques may yield ambiguous results (Mansuy *et al.,* 1997).

A Different Technique

In recent years another approach has developed which is based on the stable isotopic composition of the compounds of interest. Carbon, for instance, has two naturally occurring stable isotopes, ^{13}C and ^{12}C. It is reasonable to assume that the ratio of the amounts of these two isotopes is unique for each compound derived from a different source. If two chemical companies were to produce the chemically identical PCBs, for instance, it is probable that the identical compounds will have isotope ratios characteristic of different feedstocks or different manufacturing processes. Upon entering the environment, therefore, a contaminant should be able to be linked to a source by its isotopic composition.

The technique for compound specific isotopic analysis (CSIA) involves coupling a gas chromatograph (GC) to a combustion furnace, which is then attached to an isotope ratio mass spectrometer (GC/C/IRMS). The effluent of the gas chromatograph is introduced into a microcombustion/CO_2 purification interface. Within the GC, fused silica columns have been found to be most effective because carrier gas flows are low (a few ml/min. of He), resolving power is excellent (30 to 60 meter column lengths are routine), and column bleed is minimal (bonded phase columns). The column effluent is combusted to CO_2 in the interface in the presence of CuO and water is removed by a cryogenic trap. Ion current intensities of masses 44, 45 and 46, which represent the major isotopic forms of CO_2, are recorded simultaneously using a high speed on-line acquisition system. A schematic of the system is shown below (Figure 1).

The ratio of the ion current intensities of mass 45 to mass 44 is a measure of the ratio of $^{13}C/^{12}C$ and is compared to the reference value of $^{13}Cl/^{12}C$. The reference and sample ion current intensities are measured in an alternating manner, which ensures a reliable comparison between the reference and sample isotope ratios. A computer interfaced to the instrument is used to calculate in the "per mil" (‰) notation. Isotope compositions are

reported as δ (delta) values, using the following formula:

$$R = {}^{13}C/{}^{12}C$$

$$\delta\ {}^{13}C = (R_{sample}/R_{reference} - 1) \times 1000$$

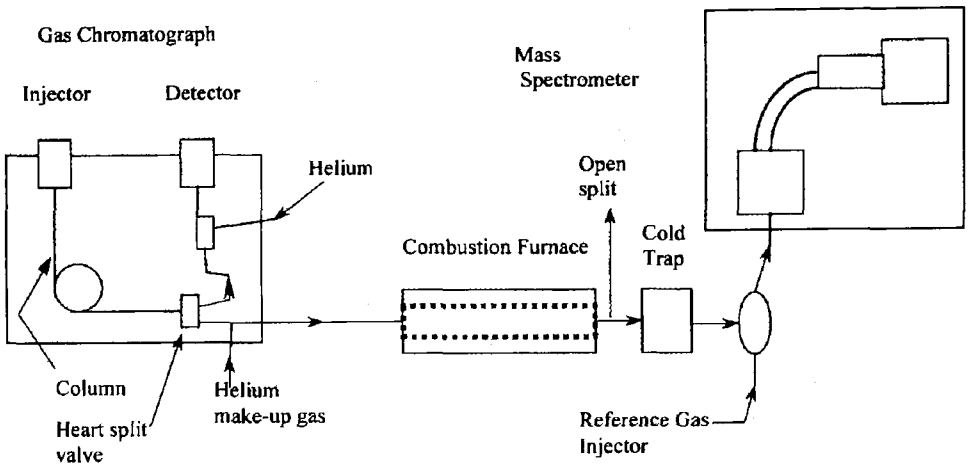


Figure 1. Schematic showing the basic structure of a GC/C/IRMS system (adapted from Freedman *et al.*, 1988).

Isotopic compositions are measured as ratios owing to the normally low absolute abundances of each chemical species of interest. Samples with more ^{13}C than the reference compound will have positive $\delta\ ^{13}C$ values, and are said to be enriched in ^{13}C. Samples with less ^{13}C than the reference compound are said to be depleted. It should be noted that currently, while there are many elements with multiple stable isotopes, the most commonly used in analyses are carbon, nitrogen, oxygen, sulfur and hydrogen. Like carbon, each of the other elements are analyzed in a similar way, with deviations occurring in the combustion and subsequent gas purification processes occurring just before mass abundances are measured. In every case, a sample with more of the heavy stable isotope is said to be enriched for that element under investigation. For instance, with respect to nitrogen, using new modifications of the combustion system, it is now possible to perform CSIA on nitrogenous compounds (Macko *et al.*, 1997). In this case, the heavy isotope is ^{15}N and the mass spectrometer measures the ion current intensities of masses 29 and 28, representingthe two most common forms of molecular nitrogen.

With a state-of-the-art instrument, reproducibility is quite good, with standard deviations on replicate measurements typically better than 0.5 ‰ (Tables 1-3).

Table 1. Average $\delta\ ^{13}C$ values (relative to PDB reference) with associated standard deviations for five PAH standards.

Compound	Average $\delta\ ^{13}C$ value	Standard Deviation (+/-)
Naphthalene	-26.2	0.4
Phenanthrene	-24.4	0.45
Anthracene	-23.7	0.44
Chrysene	-23.9	0.58
2,3,6 - Trimethylnapthalene	-22.6	0.20

Table 2. Average $\delta\ ^{13}C$ values (relative to PDB reference) with associated standard deviations for four alkane standards.

Compound	Average $\delta\ ^{13}C$ value	Standard Deviation
Decane	-29.0	0.30
Undecare	-27.1	0.30
Dodecane	-33.3	0.30
Tridecane	-32.6	0.40

Also, with a state-of-the-art instrument, performing CSIA with a GC/C/IRMS system has many advantages over other techniques for determining contaminant identities and sources. Because a GC is coupled to the mass spectrometer, there is the capability of resolving complex mixtures. Also, with such a system, there is very high

sensitivity, which can be a very important consideration when dealing with trace contaminants. With a GC/C/IRMS system, detection is possible in the sub nM region.

Table 3. Average $\delta\ ^{15}N$ values (relative to atmospheric N_2 reference) with associated standard deviations for four nitrogen-containing compounds.

Compound	Average $\delta\ ^{15}N$ value	Standard Deviation
Pyrazine	0.7	0.12
Tripropylamine	9.5	0.55
Quinoxaline	-0.6	0.16
Nicotine	-1.7	0.41

The Approach

In applying CSIA to the problem of tracing environmental contaminants, measures must be taken to determine whether the techniques are viable under natural conditions. As was mentioned above, using GC/IRMS to measure isotopic compositions for the purpose of tracing contaminants seems to be an exciting alternative to traditional methods. The first steps taken toward application of the technique must be field tests, however. This can be stated in a series of objectives:

1) Establish extraction, isolation, and purification techniques for the contaminants of interest. Of particular importance is obtaining high purity samples that have not been altered in isotopic composition.

2) Determine the stable isotopic composition of the compounds of interest obtained from primary sources, such as manufacturers, petroleum suppliers and chemical storage locations.

3) Determine the stable isotopic composition of the contaminants at locations where they are introduced into the environment. Possible locations include combustion areas (automobile exhaust and industrial exhaust), industrial emission, agricultural runoff, urban runoff and sewage effluent.

Once the first three objectives are fulfilled, the next step is to apply them to well-characterized sites where pollution sources and times of occurrence are well known. In this initial phase, carbon isotopes have been the focus, and within this framework, early efforts have concentrated on the most common PAH, OC pesticides and PCBs (Table 4). The reasons for first analyzing the most common contaminants are two-fold. First, in trying to determine the validity and applicability of this technique, it is undesirable to be sample-limited. From a sample extraction and purification standpoint, it is necessary to deal with sufficient sample quantities. Once the method proves successful, samples of lower of concentration can be addressed. The second reason for focusing on the most common contaminants is time constraints. This approach is fairly time consuming, and thus only a limited number of samples can be analyzed during the study. Choosing the most abundant contaminants for analysis should allow for the greatest chance of success.

Methods

In this study, the matrices of interest are soil and biological tissue. Typically, the first step is the extraction process. Soil samples are Soxhlet extracted with methylene chloride and then separated based on compound class with an alumina/silica column. Aliphatic hydrocarbons are eluted from the column with 50 ml of pentane. Aromatic hydrocarbons, PCBs and OC pesticides are eluted with 150 ml of pentane/methylene chloride (1:1). The second fraction is further separated on a silica column. PCBs are eluted with an additional 90 ml of pentane. High performance liquid chromatography (HPLC) using a cyano/amino bonded phase column as per Killops and Readman (1985) is used to purify the PCBs from fraction 2. Pentane is used as the eluting solvent. Purity is then checked with gas chromatography/electron capture detector (GC/ECD) and GC/MS systems. Fraction two from the silica column is separated into several subfractions, with the aromatic compounds being separated based on the number of double bonds they contain (Killops and Readman, 1985). A pentane and methylene chloride gradient is used for the elution. It should be noted that others have shown that aromatic species can also be separated with molecular sieves based on the arrangement of any alkyl substitutions present (Ellis *et al.,* 1992; 1994). If need be, this is another viable alternative.

For the tissue samples, 20-30 grams of wet tissue are mixed with approximately 50 g of anhydrous sodium sulfate. The extraction is performed with three 100 ml methylene chloride aliquots while macerating with a homogenizer. The combined extract is then separated as described above except there is not an aliphatic hydrocarbon component to contend with. Before analyzing by GC/C/IRMS, if the samples still are not pure

enough, thin layer chromatography (TLC) can be utilized for further purification.

Table 4. List of contaminants that are initially being investigated.

Contaminant	
PAH	Naphthalenes
	Fluorenes
	Phenanthrenes/Anthracenes
	Dibenzothiophenes
	Fluoranthenes/Pyrenes
	Benzanthracenes
	Benzofluoroanthenes
	Benzopyrenes, Dibenzanthracenes
	Perylene
Pesticides	Aldrin, Heptachlor, Endrin, Mirex
	DDT, Dieldrin, Transnonachlor
PCBs	Dichlorobiphenyls
	Trichlorobiphenyls
	Tetrachlorobiphenyls
	Pentachlorobiphenyls
	Hexachlorobiphenyls
	Heptachlorobiphenyls
	Octachlorobiphenyls
	Nenachlorobiphenyls

Upon final separation and purification, the analytes of interest are taken up in an appropriate solvent (pentane and methylene chloride, for example) to a concentration in the 5-100 ng/µl range, depending on the sensitivity of the instrument for a particular compound class. Samples are then analyzed for isotopic composition by the GC/C/IRMS system as described above.

Other Considerations

The stable isotopic composition of a contaminant in the environment is the end-result of a complex chain of events. Naturally occurring pollutants such as spilled crude oil are most easily traced in the environment because the starting material is usually readily available for analysis. Furthermore, intrinsic tracers in spilled crude oil would also be directly reflected in environmental samples since few complicating processes would intervene. Many synthetic materials are produced from petrochemical precursors through manufacturing processes such as distillation, catalytic cracking, chlorination and polymerization to name a few. A change in isotopic composition might occur during the manufacturing process if catalysis or high temperature is involved. Next the product is applied for its intended purpose which could include combustion (gasoline), lubrication (lube oils), pesticide application (DDT), or use as a transformer oil (PCBs) for example. These applications may cause an additional shift in isotopic and molecular composition. During the application, either intentionally or indirectly, some portion of the contaminant is released to the environment (such as soot from combustion or the disposal of waste materials). Once released to the environment, the contaminant is then subjected to redistribution throughout various matrices including air, water, sediments, and biological tissue depending on its chemical properties and stability. The partitioning of the chemical among various phases might be accompanied by a shift in isotopic composition as well as chemical transformation. Environmental transformations are brought about by physical, chemical and microbiological processes. Each process defines an independent set of isotopic and compositional changes. The complex history of a pollutant suggests that a combination of compositional and stable isotopes can be linked to a specific series of events and processes (Figure 2). Chemicals of identical structure may have different isotopic composition if they have witnessed different histories from manufacture to environmental deposition. By analyzing contaminant samples at different stages of transport it should be possible to understand the dominant processes acting on them and to elucidate the complex chain of events which led to the isotopic composition of the contaminants at their environmental end point.

The issue of complex mixtures

As was mentioned above, compound specific isotopic analysis using GC/C/IRMS has the potential to handle complex mixtures. It is inevitable, however, that during some analyses, there are two or more chemical species present in a mixture that are similar chemically and therefore coelute. Perhaps in some of the separated fractions there could be additional compounds present other than the desired analytes of interest that are similar to the desired compounds. If there is only one other compound present, temperature programs for the GC could be altered, columns could be changed, either in length or composition, or additional separation steps could be added to alleviate this problem. When there is a high amount of background, however, owing to more than one additional chemical species being present, the problem is more difficult to handle. The coelution will lead to erroneous isotopic results because what was thought to be the composition of one compound is actually the combined isotopic composition of two or more compounds. This issue is complicated further by the fact that isotope fractionation occurs during elution, with portions of the peak varying dramatically in isotopic composition

(Figure 3). Although the isotope values can be averaged across a peak, with coelution, the modifying effect of the additional species can also vary across the peak if the analyte of interest and the additional species do not elute at exactly the same time. Some researchers have used internal standards in their analyses to monitor the degree to which unresolved complex mixtures (UCM) or other coelution problems affect the results of the isotopic analyses. By knowing how much the isotopic values of compounds of known composition have shifted, corrections can be made for the unknowns (Mansuy *et al.*, 1997). Other researchers have relied on certain separation techniques to try to keep the problem to a minimum (Ellis *et al.*, 1994). Also, within some software packages, monitoring of the background is possible, along with the subsequent subtraction of unwanted contributions to a peak. Based on the above discussion, it is obvious that this issue will require careful monitoring in order to insure results are as accurate as possible.

Initial Applications

Extraction, purification, and analysis on some of the analytes of interest has already been performed (Table 5). PAH mixtures from two sediment sites as well as a sample of creosote were analyzed by GC/C/IRMS yielding variable carbon isotope values. This variability could indicate different sources of the PAH influence into the various reservoirs.

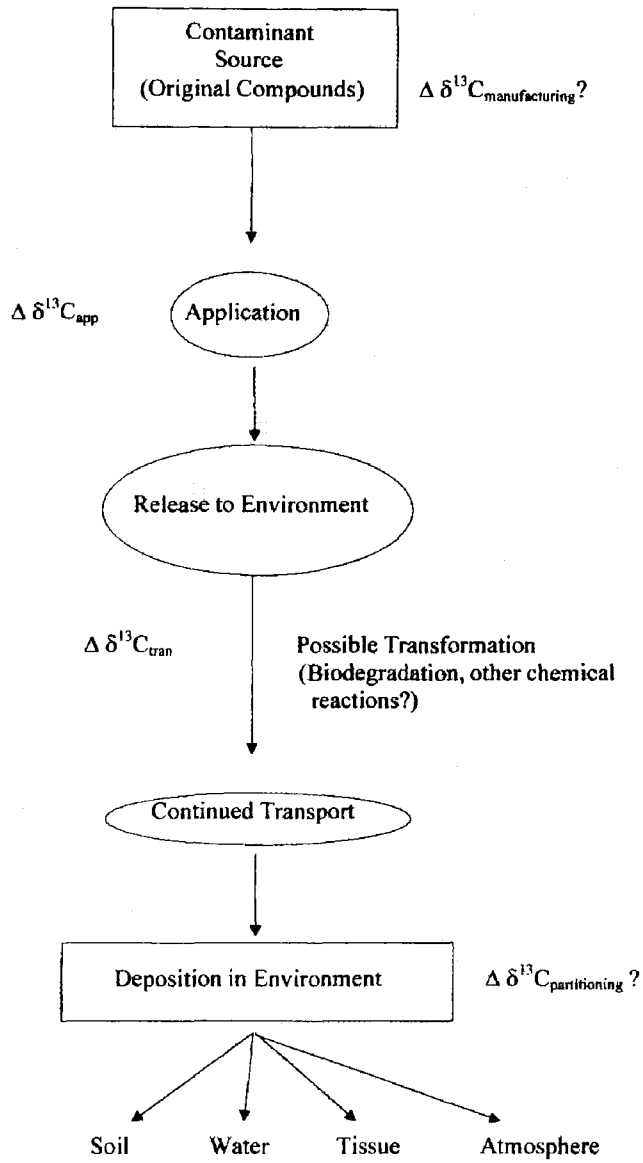


Figure 2. Schematic representing possible pathways for contaminants that enter the environment.

Table 5. $\delta\,^{13}C$ values (relative to PDB reference) for PAH mixtures derived from three different sources.

Compound	Oregon Inlet Sediment	Creosote	Casco Bay Sediment
Naphthalene	-27.1	-23.5	
2-Methylnaphthalene	-27.8	-23.1	-27.9
1-Methylnaphthalene	-28.2	-21.2	-29.5
Biphenyl	-28	-21.4	-26.4
2,6-Dimethylnaphthalne	-28.8		
Acenaphthalene	-27.4		
Fluorene	-27.7	-18.4	
Phenanthrene	-25.6	-24.3	
1-Methylphenanthrene	-25.8		
Fluoranthene	-24.6	-25.2	
Pyrene	-23.0	-25.2	
Chrysene	-23.0		

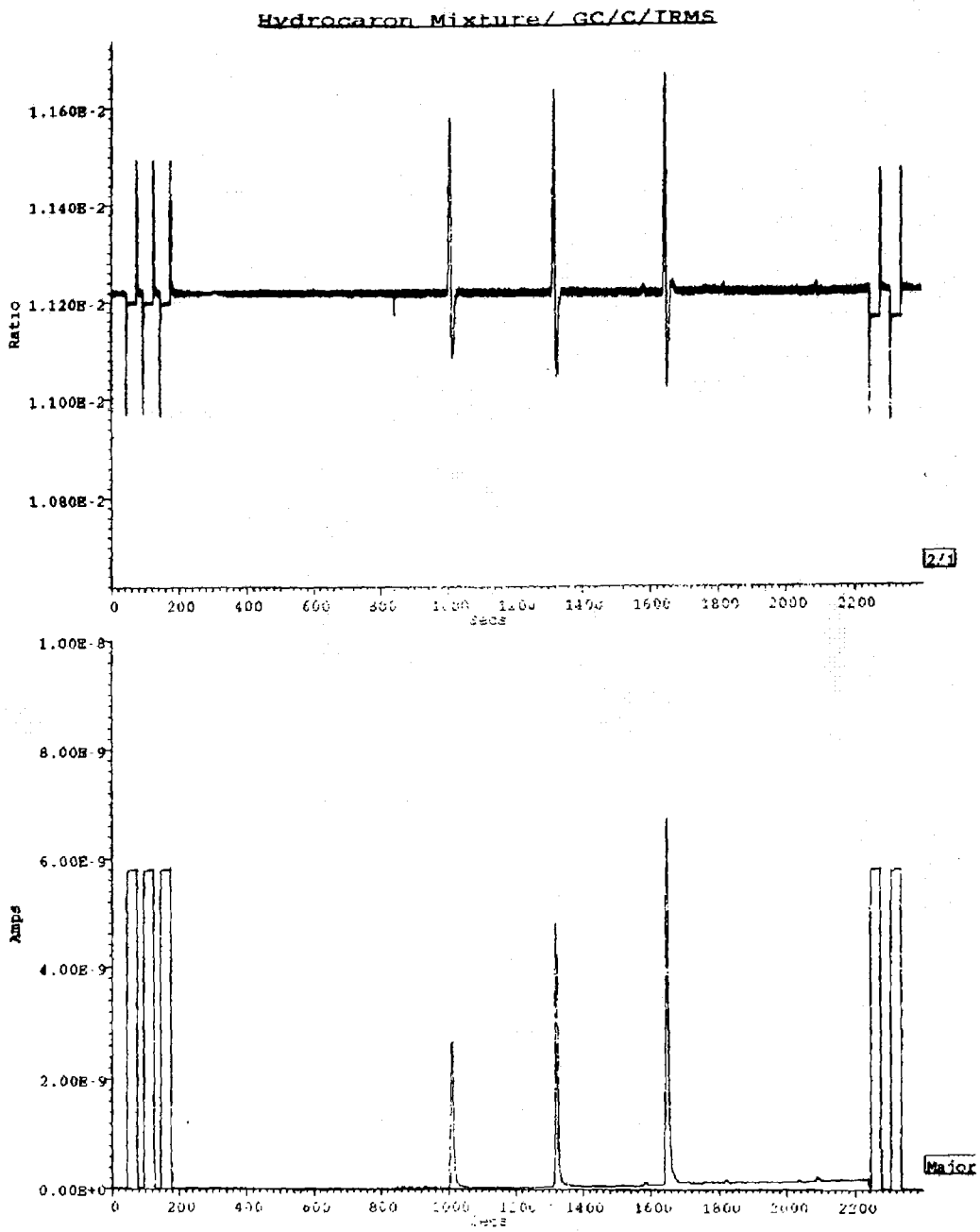


Figure 3. Plot of the carbon isotope signal of three hydrocarbon species. The upper trace is the ratio of ion current intensities of masses 45 and 44. The lower trace is the ion current intensity of mass 44. Note the changing isotope ratio across the peak.

Stable Isotopic Analysis as a Versatile Tool

In recent years, more attention has been focused on stable isotopic analysis, and in recent years, on compound specific isotopic analysis. While traditional molecular approaches are still in active use today, stable isotope analysis has gained popularity as a complement to other techniques or a stand-alone technique when other approaches are ineffective or too time consuming. Furthermore, as more attention is paid to stable isotopic analysis, the versatility of the technique has become more evident. As was mentioned in the above discussion, stable isotope analysis can be used as an effective tracer or method to apportion sources of compounds to a site. GC/C/IRMS has been used to distinguish oils based on the isotopic composition of alkane and isoprenoid constituents present in the oil (Bjoroy *et al.*, 1991). This technique has been applied to oil spills as well; even under conditions where some of the oils have been weathered (Mansuy *et al.*, 1997). With respect to the analytes

of interest in this study, CSIA has been used to not only trace the transport of PAH in aerosols (Ballentine *et al.,* 1995) but to distinguish between biomass burning and fossil fuel burning sources of PAH (Ballentine *et al.,* 1996). Also, sources of PAH have been identified along with the relative amount of influence of each in marine soils. (O'Malley *el al.,* 1994). With respect to PCBs, it was discovered that individual compounds tend to be more depleted in ^{13}C the more chlorine atoms there are present in the structure (Jarman *et al.,* 1998). Stable isotopic analyses have also been used in groundwater studies, both as a source apportioning tool (Kelley *et al.,* 1997) and also as a means of tracing compounds during groundwater flow (Dempster *et al.,* 1997). Perhaps one of the most unique characteristics of stable isotope analysis is that is has been applied to many different scientific areas. Two areas that are utilizing this approach more and more are biology and ecology. Characteristics of food webs, from trophic structure to influences on the diet on individual organisms have found application in stable isotope analysis (Fang *et al.,* 1993 and Jarman *et al.,* 1996). As has been shown, beyond the realm of just contaminant studies, compound specific stable isotope analyses has a wide range of applicability. This should prove very beneficial as the call for more interdisciplinary science continues.

Conclusions

With the current heightened awareness of the need to understand and control contamination sites and sources, the demand for powerful and accurate analytical tools to answer these questions is very high. Compound specific isotopic analysis has been suggested as a new tool to be used to answer these questions. Upon purifying contaminant fractions, GC/C/IRMS can be used to determine the isotopic composition of the individual components in these fractions. These stable isotope compositions can compared to the isotopic compositions of different source materials and contaminants entering the environment through various pathways. With this information, the analyst can begin decipher together the history of the contaminants, linking the source and the process of introduction to the contaminants of interest. Whereas first only being applied to well characterized sites, upon finding that the techniques are valid, the methodology can be applied to sites of unknown composition and influence. Compound specific isotopic analysis could then be used to complement other analytical methods or as a stand-alone technique where the other methods prove to be ineffective.

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RECENT DEVELOPMENTS IN IMMUNOBIOSENSORS & RELATED TECHNIQUES FOR THE DETECTION OF ENVIRONMENTAL POLLUTANTS

M. Masila, H. Xu, E. Lee, O.A. Sadik*
Department of Chemistry, State University of New York at Binghamton,
P.O. Box 6016, Binghamton, New York 13902
Fax: (607)777-4478
E-mail: osadik@binghamton.edu

ABSTRACT
This paper describes inimunobiosensors and other related multianalyte detection methods of identification and quantitation of various environmental compounds and metabolites. It presents the synthesis and characterization of polymers, biological conjugates and metabolites for the detection of a range of toxic chemicals, including chlorinated phenols, s-triazine herbicides, polychlorinated biphenyls, and heavy metals. A new multi-analyte detection technique utilizing polypyrrole derivatives was developed for the detection of chlorinated phenols and other organics. The detection of polychlorinated biphenyls (PCBs), volatile and semivolatile, halogenated organic compounds of environmental interest was conducted using the new polymer sensors. A new promising approach for heavy metal detection is described that utilizes *o*-hydroxypyridylazo metal-protein conjugates which may also be used in the development of nonradioactive immunosensor labels for environmental compliance monitoring and clinical applications.

INTRODUCTION
Very few analytical methods for environmental monitoring that are fast, low-cost and continuous are currently available. The monitoring of residue or contamination in soil, water and air can be classified into two main categories. These are: (i) screening or diagnostic techniques in which only a yes-or-no (qualitative) answer is required, and (ii) semi-quantitative or quantitative techniques in which the detection of unwanted chemicals, and the testing of whether or not the residues of the contaminants are within permissible levels are required. It is possible for the former methods to generate false positive or negative results if the sensitivities are insufficient for the detection of the threshold levels.

The successful coupling of suitable transducers (e.g. electrochemical, optical or mass) with biomolecular systems is of great importance in the search for novel sensing technologies that are inexpensive, highly selective and capable of generating early warning signals in the presence of toxic environmental chemicals. The emergence of on-site chemical and immunochemical biosensors for environmental pollutant monitoring has tremendous potentials due to their small size, low costs and the case of analytical signal generation in real time. These sensors represent a step forward over the conventional laboratory analytical methods.

In recent years, biosensors; that can detect a range of analytes in environmental samples have been developed[1,2] Basically, a sensor consists of a chemically selective layer, a transducer, and a signal processor. If the selective layer utilizes a biological or biochemical species, then it can be classified as a biosensor. Thus, an immunosensor is a subset of biosensor since it comprises either an antibody or an antigen. Each sensor has a number of desirable characteristics depending on its applications. Essentially, a practical biosensor for the monitoring of environmental pollutants must be specific, reversible, able to provide fast response time, and capable of direct detection of an immunoreaction with minimal sequential addition of immunoreagents. Also, the sensor should be capable of continuous flow measurements and capable of determining multiple analytes in complex samples with little or no need for sample preparation steps. Finally, the sensor must be able to process signals, or capable of being integrated into other devices that can exercise real-time feedback as required for pollution monitoring or surveillance studies. Although, a number of pollutant measurement techniques have been reported, only few possess these specific requirements.

One of the major objectives of our research is to develop field-portable sensors that meet or exceed the above sensor requirements for use in the assessment of toxic chemical residues in various environmental media. This paper discusses sensors developed in our laboratory for the identification and quantitation of environmental contaminants.

MATERIALS AND METHODS

Instrumentation

The following instruments were used to conduct the experiments described in this paper: A Hewlett-Packard Diode-array UV/Vis spectrophotometer was used for the characterization of all protein conjugates. ELX 800 UV Plate Reader (from Bio-Tek Instruments) was used for all of the enzyme-linked immunosorbent assay (ELISA) experiments. EG&G PAR potentiostat/galvanostat Model 263A and EG&G 270 software were employed for the electrochemical experiments with silver/silver chloride reference electrode, platinum wire counter electrode and gold (A = 0.2 cm^2) as working electrode. Quartz crystal microbalance (QCM) measurements were carried out using EG&G quartz crystal analyzer (Model QCA917). A 9MHz EG&G At-cut quartz crystals was sandwiched between two gold electrodes (A = 0.186 cm^2). AromaScanner Model A32S (from AromaScan, Inc., NH) was used for the multiarray electronic nose experiments.

Sensor Preparation and Characterization

Immobilization on Quartz: The Au-coated quartz crystal was initially pretreated by cycling the potential between 1.4 and 0.0V for a minimum of 15 minutes in 0.2M perchloric acid. The cell was then rinsed with copious amount of water, and one surface of the crystal was soaked in a 0.02 M cystamine solution. The Au surface was thoroughly rinsed with water to remove any physically adsorbed cystamine before being soaked in 3mM cyanazine hapten solution containing 0.01M HEPES (N-[2-Hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid) buffer solution (pH = 7.3) using 10mM 1-ethyl-3-(3-dimethylamino-propyl) cabodimide EDC coupling reagent.

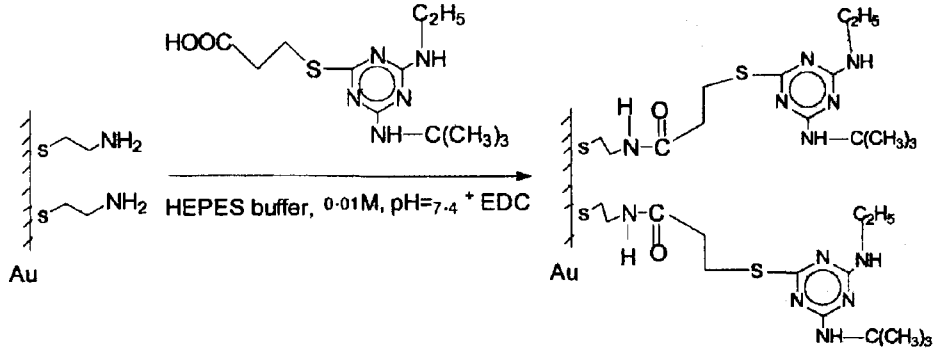
Electrochemical Immobilization: The Au electrode was pretreated as described above before being modified with the cyanazine hapten using EDC as the coupling reagent. The modified electrode was used in the electrochemical analysis, first without soaking in an antibody solution. Later the electrode was incubated in an anti-cyanazine antibody solution at 35°C using a thermostated water-bath. All cyclic voltammetry experiments were conducted at the same temperature. The other electrochemical immobilization procedures were as recently reported[3,4]

Polymer Synthesis: Various pyrrole derivatives were polymerized by electrochemical oxidation to enable the conducting polymer films to be used for conductivity, electrochemical, and mass measurements. Some selective electrodes for phenols, PCBs and *s*-triazines were prepared by the electropolymerization of pyrrole onto platinum electrodes in the presence of tetrabutyl ammonium perchlorate. The selectivities were comparable to a range of structurally similar organic compounds, including 2,3,5,6-tetra chloroanisole, 2,3,4-trichloroanisole, 2-chloroanisole, 2,4,5-trichlorophenol, simazine, cyanazine, and substituted benzenes.

Antibody Production: The design and preparation of analyte analogs and immunogens are essential steps in the development of low molecular weight immunosensors. Triazine analogs were obtained from Dr. J.R. Fleeker's laboratory. These were prepared from active esters of the carboxylic acid analog of the triazine haptens using N-hydroxysuccinamide[5]. The triazines were coupled to a high molecular weight carrier, bovine serum albumin (BSA), or keyhole limpet hemocyanin (KLH) which were used for the production of the antibodies. The antibodies were purified by gel filtration and protein-A immunoaffinity columns, and were subsequently characterized using ELISA and nuclear magnetic resonance (NMR) techniques. By using these antibodies, sensors for *s*-triazine were developed based on the antibody inhibition of the current generated by the ferricyanide mediator on antigen-immobilized gold electrodes.

Pesticide Immunosensors

Several pesticides and herbicides are routinely used to improve crop harvesting and pest-control. Due to the growing concern about health effects, several investigations have been conducted in order to understand how pesticides and herbicides degrade in the environment[6,7] Current methods of monitoring pesticides include liquid chromatography and gas chromatography with mass spectrometry. The high costs and labor involved in the chromatographic methods have led to the search for low-cost alternatives capable of providing rapid analysis. In this paper, we report on the development of immunosensors for atrazine, cyanazine, simazine and their metabolites. The sensor chemistries are shown in Scheme 1 below:



Scheme 1. The assembly of a cyanazine hapten monolayer on Au electrode.

The hapten monolayer electrode sensor assembly was used in the detection of cyanazine in a flow injection analysis mode. The interaction of the electrode with different antibody concentrations resulted in the formation of an antibody-antigen (*Ab-Ag*) complex which insulated the electrode towards the $[Fe(CN)_6]^{4-}/Fe(CN)_6]^{3-}$ redox probe, hence resulting in no charge transfer. The extent of the insulation depended on the antibody concentration and the time of exposure to the antibody solution. The decrease in the amperometric response of the antigenic monolayer to corresponding antibody solution for a fixed time produced a quantitative measurement of the antibody concentration (Figure 1). Typical voltammetric responses obtained for the cyanazine hapten monolayer electrode to different antibody concentrations are shown in Figure 2. The lowest detection limit achieved for the cyanazine sensor was 4.0 µg/ml with a response time of a few minutes and a less-than 2% cross-reactivity to atrazine, simazine and other metabolites.

Multianalyte Sensors

The presence of halogenated organic compounds in the environment has posed a great concern due to their persistent toxicity and the ability to bioaccumulate. Of all the 19 known chlorinated phenols, the most important congeners include the 2,4-Dinitrophenol (2,4-D), 2,4,5-trichlorophenol, (2,4,5-TCP) and pentachlorophenol. While these compounds can be determined using mass spectrometry and gas chromatographic techniques, the structural similarities of substituted phenols and their derivatives enable the development of a rapid, multianalyte method rather than for one or two analytes. The combination of gas sensor arrays and pattern recognition techniques has resulted in a fast and objective method for the simultaneous measurement of a wide range of volative and semi-volative organics.

A 32-array conducting polymer sensor was used for the rapid measurement of volatile and semivolatile halogenated organic compounds of environmental interest. The mathematical expressions for the microscopic polymer network model was described in a recent article[4]. A classical, nonparametric, and unsupervised technique of cluster analysis was used to discriminate between the polychlorinated organic phenol vapor

response vectors in a 2-dimensional space, and to identify clusters, or groups, to which unknown vectors were likely to belong. Consequently, the characteristic pattern for each sample was generated. The pattern was used to generate the database employed in the determination of the Euclidean distances between two given patterns and the normalized sensor response. Also, this was used to develop the 2-dimensional mapping from a multi-dimensional space to quantify the distinctions of the samples.

The resulting sensor arrays were found to recognize small molecules on the basis of their chemical structures which were related to the nature of the chemical class, the type and the position of the functional groups. Each sensor responded in varying degrees to chlorinated organic molecules with standard deviation of less than 0.05. The time averages for the sensor response databases, datamaps, response patterns, and the intensity profiles were obtained for different phenols. Tables 2 and 3 showed the representative databases obtained for 2,4,6-trichlorophenol and 2-CP created from the raw sample data files by selecting sample data between 60 and 120 sec. The limit of detection obtained for 2,4,6-trichlorophenol and 2-chlorophenols using the conducting polymer sensor array were 0.1 and 0.25 ng/mL respectively. This results demonstrated the viability of conducting polymer sensor arrays for the identification and quantitation of chlorinated organic phenols based on the differences in their Euclidean distances. The qualitative differences as defined by the Euclidean distance measurements were most clearly visible when the nature and the type of the functional groups were considered.

Direct Electrochemical Sensors for Polychlorinated Biphenyls (PCBs)
A direct electrochemical immunosensor has been developed for the determination of PCBs in water. The assay was based on the measurement of the current due to the specific binding between PCB and anti-PCB antibody-immobilized conducting polymer matrix. The linear dynamic range of the immunosensor was between 0.3-100 ng/mL with a correlation coefficient of 0.997 for Aroclor 1242. A typical flow injection analysis signal obtained for Aroclor 1254 is shown in Figure 3. Well defined responses were recorded for all aroclors. The method detection limits for Aroclors 1242, 1248, 1254 and 1016 were 3.3, 1.56, 0.39, and 1.66 ng/mL respectively, and a signal-to-noise (S/N) ratio of 3. The immunosensor exhibited high selectivity for PCBs in the presence of potential interference such as chlorinated anisoles, benzenes and phenols. The highest cross-reactivity measured for chlorinated phenolic compounds relative to Aroclor 1248 was less than 3%. The recoveries of spiked Aroclors 1242 and 1254 from industrial effluent water, rolling mill and seafood plant pretreated water at 0.5 and 50 ng/mL ranged from 103-106%. The effect of ionic compounds on the detection indicated that no significant change in immunosensor signal was observed within the uncertainty of the assay procedure. The detection method can be used for continuous monitoring of effluent such as waste streams and ground water.

Rational Design of Immunosensors: Sensors for Heavy Metals
In order to increase the sensitivity of immunosensing methods, a rational design of sensors using *o*-hydroxypyridylazo compounds was explored. The two most important of these compounds employed were 1-(2-pyridylazo)-2-naphthol (PAN) and 4-2-pyridylazo resorcinol (PAR). Both PAR and PAN have been used extensively for the analysis of metals, and they posses lots of useful spectroscopic and luminescence properties.

The use of 2-pyridylazo compounds as precursors for the preparation of protein conjugate by coupling the ligand to BSA, KLH, and ovalbumin was considered. It was anticipated that using these conjugates would lead to the development of new biosensing chemistries and transduction principles. Ultimately, any protein conjugate developed may become useful in developing novel non-radioactive molecular labels for immunoassay, molecular labeling and environmental compliance monitoring applications. The metal-chelate conjugates were tested to determine if the system was simpler and rapid for the identification and quantitation of lead and other heavy metals.

Finally, the PAR-lead-BSA, PAR-lead-Ovalbumin, and PAR-lead-alkaline phosphatase enzymes were successfully designed and synthesized[8]. These conjugates were characterized using UV/Vis, intra-red spectroscopy, NMR, and electrochemical techniques. Figure 3 shows the absorption spectrum obtained for the coupling of PAR (510 nm) and BSA (280 mn) conjugate. A preliminary test of the PAR-conjugates and the detection of lead and mercury were conducted using optical, differential pulse voltammetry and anodic stripping voltammetry techniques. The binding strategies employed include a sandwich configuration using the synthesized PAR-protein conjugates.

Pb^{2+} binding was monitored by recording the change in the cathodic reduction of the ion and the absorbance of the lead-PAR chelate. The binding affinity was controlled by an electro-optical technique which influenced the

PAR-chelate's geometry. However, it is our understanding that no published literature exists on protein that utilizes PAR metal-ion binding and the chromophoric PAR-protein conjugates. Using the electro-optical techniques, it became possible to quantitatively determine mercury and lead at approximately $3x10^{-7}$ and $1x10^{-8}$M respectively. Thus, a good knowledge of the selective interaction of the conjugates with biological macromolecules may result in new applications of metal-ion immunoselective adsorbents.

CONCLUSIONS

We have developed various sensors for the detection of pesticides, PCBs and heavy metals for environmental monitoring. Other sensors developed and their analytical characteristics are summarized in Table 3. The new metal-chelate protein conjugates reported in this manuscript could lead to the development of new immunoassay formats and instrumentation capable of providing rapid and selective environmental monitoring. Details of the design, synthesis and characterization of the conjugates and their analytical applications for metal detection are being compiled for journal publication. This work demonstrates that new and promising applications of the chemical and immunobiosensors and the emerging immunoassay labels will continue to make immunochemical methods more valuable to environmental monitoring.

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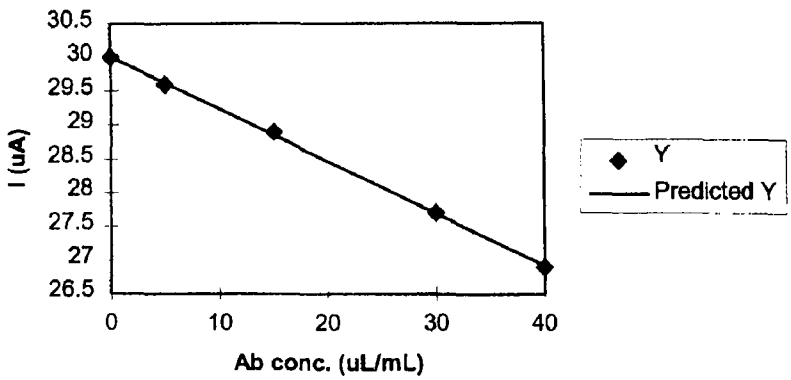

Figure 1. Cathodic peak current versus antibody concentration at constant incubation time of 5 minutes.

Table 1. Representative database obtained for 2,4,6-Trichlorophenol at conducting polymer sensor arrays

Sensor	Intensity	Pattern	SD
1	-2.560	-3.219	0.038
2	-2.450	-3.079	0.003
3	-2.710	-3.407	0.021
4	-2.700	-3.392	0.024
5	-2.540	-3.198	0.037
6	-2.460	-3.096	0.033
7	-2.730	-3.428	0.009
8	-2.600	-3.269	0.013
9	-2.490	-3.132	0.005
10	-2.700	-3.393	0.004
11	-2.320	-2.920	0.014
12	-2.450	-3.080	0.008
13	-2.310	-2.905	0.017
14	-2.720	-3.426	0.007
15	-2.310	-2.902	0.041
16	-2.260	-2.839	0.036
17	-2.150	-2.709	0.070
18	-2.500	-3.145	0.013
19	-2.720	-3.424	0.030
20	-2.790	-3.508	0.006
21	-2.570	-3.238	0.056
22	-2.170	-2.728	0.110
23	-2.300	-2.892	0.109
24	-2.120	-2.659	0.194
25	-2.070	-2.602	0.010
26	-2.440	-3.068	0.012
27	-2.520	-8.175	0.028
28	-2.350	-2.957	0.009
29	-2.430	-3.053	0.039
30	-2.700	-3.398	0.037
31	-2.810	-3.530	0.029
32	-2.570	-3.229	0.054

SD = Standard deviation, experimental conditions. relative humidity 50%, temperature 25°C, equilibration time 30 min.

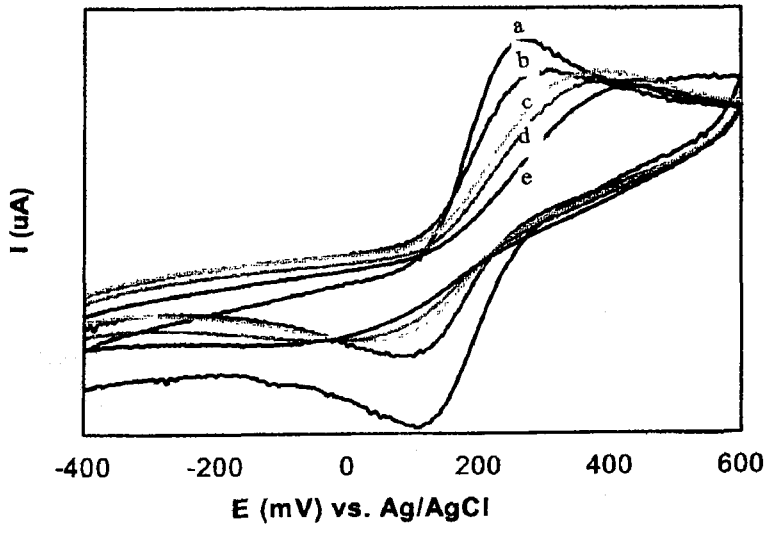

Figure 2. Voltammetric responses obtained for 1.1 mM $K_4Fe(CN)_6$ with cyanazine hapten monolayer electrode using different concentrations of anti-cyanazine antibody at 5-minute incubation time interval. (a) Blank (phosphate buffer), (b) 5µL/ml; (c) 15 µL/ml; (d) 30gL/ml; (e) 40µL/ml.

Table 2. Representative database obtained for 2-Chlorophenol at conducting polymer sensor arrays

Sensor	Intensity	Pattern	SD
1	-0.21	-3.63	1.11
2	-0.08	1.26	0.51
3	-0.15	-2.58	0.85
4	-0.15	-2.59	0.8
5	-0.17	-2.94	0.86
6	-0.18	-3.1	0.99
7	-0.08	-1.56	0.58
8	-0.12	-2.06	0.59
9	0.11	-1.66	0.66
10	-0.05	-0.97	0.62
11	-0.08	-1.36	0.37
12	-0.09	-1.56	0.5
13	0	0.1	0:090
14	-0.09	-1.62	0.55
15	-0.17	-3.09	1.03
16	-0.18	-3.16	1.04
17	0.32	4.77	1.03
18	0.46	6.05	4.58
19	0.02	0.43	0.1
20	0.36	5.44	1.51
21	-0.24	-4.31	1.49
22	0.6	8.45	3.39
23	0.73	10.09	4.38
24	0.81	11.67	3.26
25	-0.04	-0.59	0.16
26	-0.03	-0.64	0.42
27	-0.11	-1.96	0.61
28	-0.01	-0.15	0.14
29	-0.17	-3	0.9
30	-0.11	-2.07	0.72
31	-0.09	-1.65	0.47
32	-0.24	-4.22	1.45

SD = Standard deviation, experimental conditions: relative humidity 50%, temperature 25°C, equilibration time 30 min.

Table 3. Immunobiosensors & Chemical Sensors Developed

Compound	MDL	Detection TechniquelRemarks	Ref.
Chlorinated Phenols	0.25 µg/ml	ΔR	2
PCBs	0.05 ng/ml	FIA mode	1-3
Cyanazine	4.0 µg/ml	Δ[Ab]	b
Heavy metals		absorbance measurement	b
Cyanide	low ppt	Fluorescence	b
Anions	3×10^{-8}M	Current	12
Atrazine	4.0 ng/ml	Δ[Ab]	b
HSA	3×10^{-7}M	*Regenerable*	*9*
P-Cresol	0.5 mg/l	Dynamic range 3 orgers of magnitude, reusable	7
P-Athau	0.01 mg/ml	Regenerable	10

* MDL = Method Detection Limit. The MDL was computed using MDL = $t_{(n-1*1-\alpha=0.99)}$ * S, where t = the students t value, S = standard deviation of the replicate analyses.

[b] Currently under investigation.

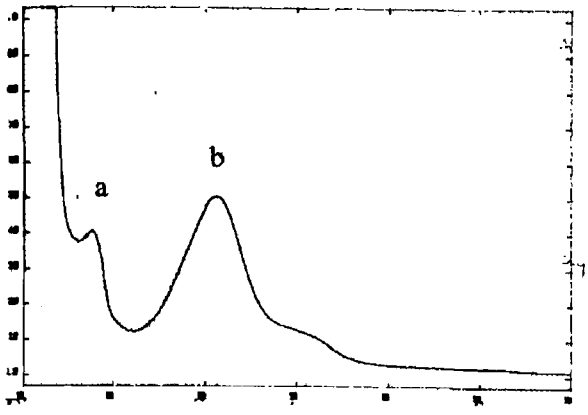

Figure 3. UV/Vis Spectrum recorded for the coupling of BSA (labeled A at 280 nm) and PAR (labeled B at 510 nm) conjugate.

MULTIPLEXED DIODE LASER GAS SENSOR SYSTEM FOR IN-SITU MULTI-SPECIES EMISIONS MEASUREMENTS

R. Hanson

NO ABSTRACT AVAILABLE

OVERVIEW/FUTURE OF NCERQA RESEARCH PROGRAM

Bala Krishnan
US EPA, Office of Research and Development, 401 M St, SW, Washington, DC

NO ABSTRACT AVAILABLE

ADVANCED ANALYTICAL METHODS FOR THE DIRECT QUANTIFICATION AND CHARACTERIZATION OF AMBIENT METAL SPECIES IN NATURAL WATERS

Janet G. Hering and Joon H. Min
California Institute of Technology, Environmental Engineering Science,
1200 E. California Blvd. (138-78), Pasadena, CA 91125

Neither the biogeochemical cycling of trace metals nor their ecotoxicological effects can be fully understood without careful consideration of metal speciation. Investigations of metal speciation in natural waters have demonstrated that, for many metals (particularly Cu, Zn, and Fe), the predominant ambient metal species are nonreactive in chemical and/or biological assays. However, the methods commonly used to monitor metal speciation cannot provide definitive information on the nature of ambient metal species.

Electrospray-mass spectrometry (ESMS) offers a powerful tool for the investigation of ambient metal species. Unlike more common GC-MS techniques, ESMS can be applied to non-volatilizable species and the comparatively gentle ionization in ESMS allows compounds to be analyzed with minimal fragmentation thus

preserving the molecular ion signature.

Preliminary studies with model compounds have been performed to investigate the application of ESMS for analysis of metal-organic complexes. Work to date with the strong organic complexing agent EDTA (ethylenediaminetetraacetic acid) has demonstrated that both uncomplexed EDTA and metal-EDTA complexes can be detected in the positive ion mode as protonated species with a single positive charge. Despite the extreme conditions imposed by the electrospray interface, protonation (and, in the case of uncomplexed EDTA, formation of the Na+ adduct) appears to be the only perturbation of the initial distribution of EDTA species. Molecular ions were detected for EDTA and its complexes with Cu, Pb, Cd, Al, and Fe(III). In the case of the Pb-EDTA complex, the isotopic signature of Pb was also observed. Based on this work, the application of ESMS for the detection of ambient metal species in natural waters appears promising but is limited by the sensitivity of the technique and by variable response to different compounds. Detection limits for EDTA and its metal complexes are approximately micromolar though better sensitivity has been reported for other metal-organic complexes.

Work is in progress to characterize the ESMS response to organic ligands of varying structures (and their metal complexes) and to improve the sensitivity of the technique. The instrument currently in use is a Hewlett Packard Series 1100 LC/MSD; adjustable instrumental parameters include drying gas flow rate and temperature, capillary and fragmentor voltages, gain and nebulizer pressure. The effects of the sample matrix (e.g., pH and methanol concentration) on sensitivity will also be tested for selected model compounds. Model compounds have been selected to include a range structural characteristics including: type of heteroatom(s) and complexing functionalities, metal-ligand stoichiometry, and ligand charge and hydrophobicity. Preliminary, screening studies will be performed to examine ESMS response to reference humic and fulvic acids.

RADICAL BALANCE IN URBAN AIR

Robert J. O'Brien
Chemistry Department
Linda A. George
Center for Science Education
Thomas M. Hard
Chemistry Department, Portland State University, PO Box 751, Portland, Oregon 97207

Atmospheric free radicals hydroxyl and hydroperoxyl (OH and HO_2, collectively HO_x) are the catalysts which cause secondary or photochemical air pollution. Chemical mechanisms for oxidant and acid formation, on which expensive air pollution control strategies are based, must accurately predict these radical concentrations. We used the FAGE technique to carry out the first simultaneous, in-situ, measurements of these two radicals in highly polluted air at downwind sites in the Los Angeles airshed.

To compare the measured OH and HO_2 concentrations with photochemical models, a complete suite of simultaneous ancillary measurements was necessary, and was obtained during each measurement campaign. The suite included speciated hydrocarbons, carbonyl compounds, carbon monoxide, nitric oxide, nitrogen dioxide, ozone, and meteorological parameters. With this suite as input, we tested the ability of a lumped chemical mechanism to accurately predict the measured OH and HO_2 radical concentrations.

Due to the short photochemical lifetime of HO_x (less than 1 minute), this test of radical balance in urban air depends directly and quantitatively on the measured parents and reaction partners of the radicals, and only indirectly on the upstream history of the sample.

Results of the measurements, and of the radical balance tests, will be presented, with acknowledgments to the organizations and scientists who provided assistance.

ENVIRONMENTAL APPLICATIONS OF NOVEL INSTRUMENTATION FOR MEASUREMENT OF LEAD ISOTOPE RATIOS IN ATMOSPHERIC POLLUTION SOURCE APPORTIONMENT RESULTS

Keeler

NO ABSTRACT AVAILABLE

REMOTE SAMPLING PROBE WITH FAST GC/MS ANALYSIS: SUBSURFACE DETECTION OF ENVIRONMENTAL CONTAMINANTS

Albert Robbat, Jr.
Center for Field Analytical Studies & Technology, Chemistry Department,
Tufts University, Medford, Massachusetts 02155

ABSTRACT
This paper describes the results of an in situ sampling probe that is capable of thermally extracting volatile and semivolatile organics bound to soil from depths of 30 ft. The organic vapor is swept to the surface by an inert carrier gas and trapped (volatiles) or condensed (semivolatiles) in appropriate sampling tubes. The organics are subsequently thermally desorbed into a gas chromatograph/mass spectrometer and analyzed in under 5 minutes.

INTRODUCTION
The EPA estimates that the cost for hazardous waste site cleanups will exceed $300 billion over the next 10 years,[1] with the cost for Superfund alone exceeding $26 billion since 1980, The following questions can be posed: Do inadequate site investigations and, therefore, a lack of understanding with respect to the chemical and physical dynamics affecting the cleanup contribute to these costs? Can field-based analytical instrumentation and methods give on-site project engineers the kind of data needed that will lead to faster, better, and cheaper cleanups?

Toward this end, research is leading to the development technology and methods that can produce quantitative analysis of environmental contaminants in minutes by thermal desorption gas chromatography/mass spectrometry (TDGC/MS). The analysis is based on a ballistically heated thermal desorber to achieve large volume sample introduction *and* mass spectral data analysis algorithms that can "look through" complex matrix signals to identify and quantify target compounds.[2] The TDGC/MS when used in a dynamic workplan framework can provide data fast enough to influence the on-site decision making process.[3] We have shown that on-site chemical analyses employing dynamic workplans can reduce the time and cost of hazardous waste site investigations.[4]

Cone Penetrometer (CP) systems can collect samples at much faster rates than can traditional drilling rigs. Figure 1 depicts the sampling probe used to collect subsurface soil and water samples. Typically, 5 cm o.d. pipes are threaded together and pushed underground by truck weights of up to 40 tons. The challenge therefore, is to design 1) a flexible heated, 300 °C, transfer line that can be woven through each pipe section and 2) a programmable thermal extraction sample collection probe that can heat the soil to at least 350 °C. These target temperatures are based an past studies aimed at developing direct measuring thermal desorption gas chromatography (TDGC) sample introduction system.[5,6,7,8,9] The design of a thermal extraction cone penetrometer (TECP) system for subsurface sampling of soil-bound organics from depths of up to 25 m is described in this paper as well as a new data analysis system that provides unique compound identification and quantification capabilities under fast TDGC/MS conditions.

MATERIALS
Heated Transfer Line
The materials used to fabricate the heated transfer line include: deactivated fused silica lined stainless steel tubing 30 in x 1 mm, i.d. 0.76 mm Silcosteel® (Restec Corp., Bellefonte, PA); Nextel 312 thermal insulation sleeving and Viton shrinkable tubing (Omega, Stamford, CT), heat shrinkable Teflon tubing (Patriot Plastics,

Woburn, MA); aluminum foil with silicon adhesive backing (COMCO), polyimid moisture insulation tape (Newark Electronics, Chicago, IL); thermal insulated fiber glass cloth tape (Fisher Scientific, Pittsburgh, PA). The heated transfer line is heated by connecting high temperature power lead wires (Newark Electronics) to both ends of the Silcosteel® tube. Temperature was measured using Thermocouples C01-K and C02-K (Omega).

Heated Probe

The probe was made from a 1 m x 4.5 cm, 2.5 cm i.d., threaded steel pipe. A 20 mm i.d. hole was cut in the pipe at one-third the distance from the bottom. The heat was supplied by inserting an aluminum casing into the pipe, which contained a 10 cm x 1.5 cm heating cartridge L4A712, 240V/1000W. The same model Thermocouples used to measure the transfer line temperature were used in the Probe.

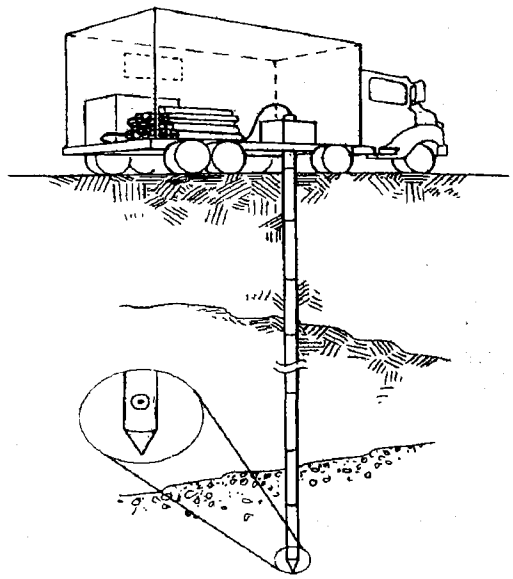

Figure 1. Cone penetrometer and thermal extraction sampling probe.

Equipment

The Silcosteel® was heated by passing current through the tube using an electrical isolation step-up transformer (Grainger, Haverhill, MA) with power and temperature controllers model DCIP-50245-F00 and model 988A-10FD-AARG, respectively (Watlow, St. Loius, MO). A Hewlett Packard (Palo Alto, CA) model 5972 mass spectrometer was ruggedized for the field and used in combination with a Tufts University (Medford, MA) designed thermal desorption gas chromatograph. All GC/MS total ion current chromatograms (TIC) were acquired by HP's data acquisition system. A new mass spectrometry data analysis software developed at Tufts was used to identify and quantify polycyclic aromatic hydrocarbons (PAHs). The Ion Fingerprint Detection™ software is available from Ion Signature Technology (Cambridge, MA).

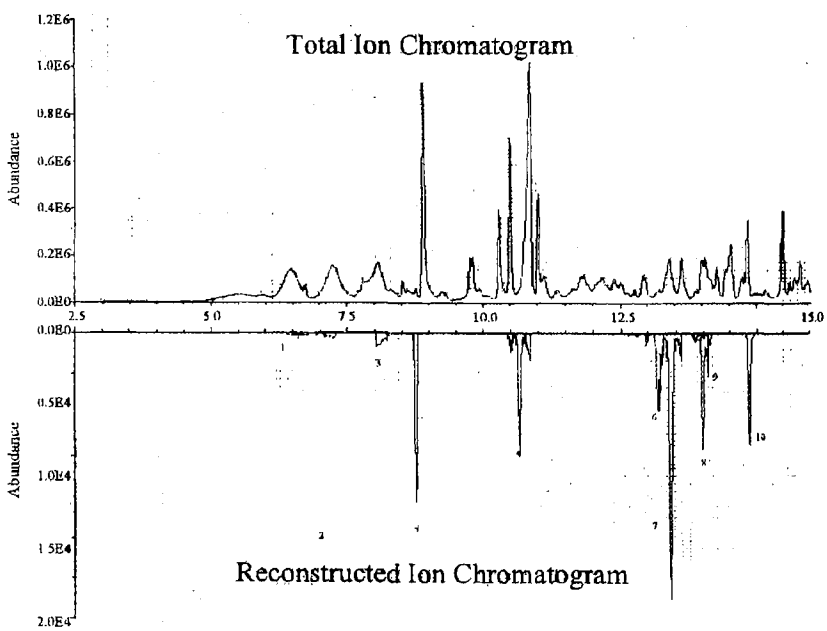

Figure 2. GC/MS analysis of a soil sample collected from Hanscom Air Force Base (Bedford, MA); compounds found: 1) 1,1,1-trichloroethene, 2) methylene chloride, 3) 1,1-dichloroethene, 4) 1,4-difluorobenzene (surrogate), 5) toluene-d_8 (internal standard), 6) ethylbenzene, 7) m/p-xylene, 8) o-xylene, 9) styrene, 10) 4-bromofluorobenzene (surrogate).

RESULTS

Two key breakthrough technologies have been developed that meet the EPA data quality measurement objectives and EPA Soil Screening Level quantitation levels under fast GC/MS conditions. First is the mass spectral data analysis software. The software extracts between three and ten characteristic fragment ions for each targeted organic and then, based on a patented set of algorithms, compound identity and concentration are determined. Algorithmic details can be found elsewhere.[2] Although all MS systems can extract ions, they cannot handle the amount of extracted ion information and determine compound presence using current statistical or

library matching routines when high levels of interferents are present in the sample. For example, the software can provide compound identification in complex environmental samples without the need for extensive sample cleanup. The second technology breakthrough is the thermal desorber. Unlike other commercially available units, the TD can be ballistically heated from subambient temperatures to 320 °C in 8-sec. The TD uses a standard Tenax tube for trapping VOCs and an empty glass sleeve for semivolatiles that have been swept from depth to the surface by the carrier gas. Direct desorption of organics from solid materials or an organic extract into the GC is made by placing known quantities into an empty glass sleeve.

Figure 2 illustrates a representative total ion current chromatogram (TIC) and a reconstructed ion current (RIC) chromatogram where the data analysis software was able to "see through" the matrix. Note that the internal standard (peak #5) and target compounds 1,1,1-trichloroethene and 1,1-dichloroethene (peaks 1 and 3) are buried within the matrix and that their corresponding signals are 10^2 to 10^4 times smaller than the matrix signal. Typically, analysts would dilute this sample prior to analysis based on visual inspection of the petroleum present in the sample. This practice will result in the loss of low level target compounds such as the chlorinated solvents found in this sample.

Figure 3 shows the TIC and RIC chromatograms produced from a 10-min TDGC/MS analysis of a standard mixture of polychlorinated biphenyls (PCBs, Aroclor 1248), polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and engine oil (25% v/v). A total of 1,000-ng PCBs was thermally desorbed into a 15-m GC column along with 19 chlorinated pesticides (20-ng/compound), 16 PAHs (40-ng/compound), and pyrene-d_{10} (50-ng) added as an internal standard. An expanded view of the RIC chromatogram between 6.7 min and 6.9 min is shown here. Note that there are six compounds that elute within this time domain. Compound identification was made based on a set of algorithms that extracted 3-6 fragment ions per compound from the TIC and computed their match against standard reference spectra in seconds. Each compound's RIC signal, based upon preselected quantitation ions, are then used to produce the RIC chromatogram and to quantify compound concentration. The algorithms and results will be presented documenting measurement accuracy, precision, and sensitivity.

Figure 4 depicts the schematic of the heated transfer line and the electronic circuitry used to control the power and temperature. The figure shows the various layers including moisture, electrical, and thermal insulation sleeves as well as the fused silica coated stainless steel tube Silcosteel® The goal was to heat the transfer line to 300 °C and achieve a 15 cm bend radius so that the pipes in the truck could be stacked efficiently. This feature is important since cone penetrometer systems can reach subsurface depths of up to 60 m when the geology is amenable. Based on the design shown in the figure a 10 cm bend radius was obtained, with the Silcosteel® temperature programmable from ambient soil temperatures up to 300 °C. To date, a 30 m transfer line has been made, which can be woven through ten 1 m pipe sections to achieve subsurface depths of 10 m. The transfer line is heated by passing direct current through the stainless steel tube. Imbedded in the transfer line are the electrical and thermal couple wires needed to carry current to the probe head and to monitor both the transfer line and probe temperatures.

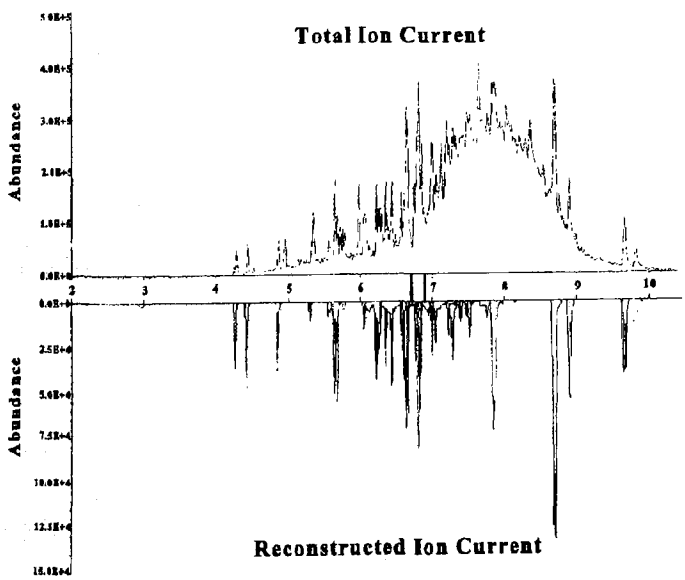

Figure 3. 10-min TDGC/MS analysis of a soil sample fortified with a standard mixture of PCBs, PAHs, pesticides and gasoline/engine oil (1:3 by vol).

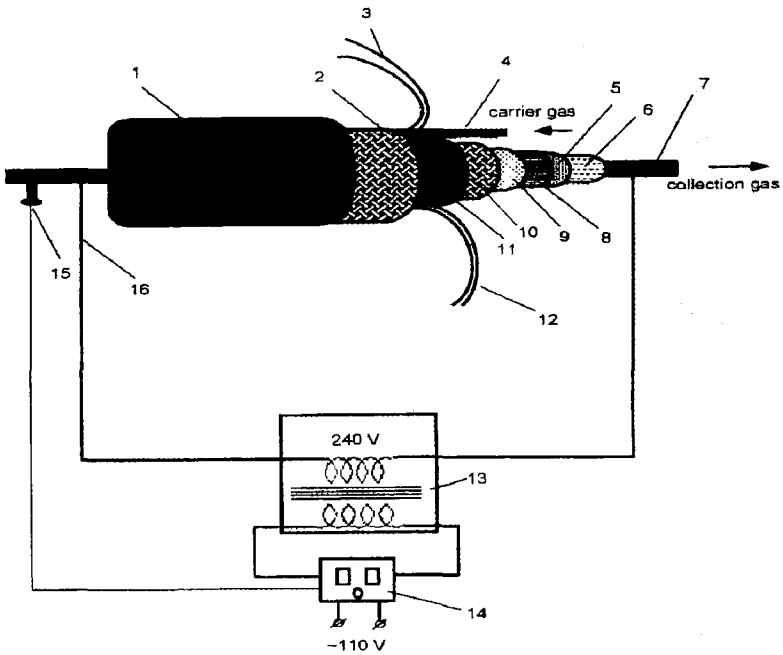

Figure 4. TECP system, which includes 1) heat shrinkable sleeve, 2) fiber glass insulation, 3) high temperature electrical wires, 4) Viton shrinkable tubing, 5) heat shrinkable Teflon tubing, 6) Nextel 312 thermal insulation sleeving, 7) deactivated fused silica lined stainless steel tubing 30 m x 1 mm, i.d. 0.76 mm Silcosteel® 8) aluminum foil with silicon adhesive backing, 9) polyimid moisture insulation tape, 10) thermal insulated fiber glass cloth tape, 11) polyimid moisture insulation tape, 12) thermocouple wire, 13) isolation step-up transformer, 14) temperature and power controllers, 15) transfer line thermocouple, and 16) high temperature electrical wires.

Table 1. Material Balance of Closed Chamber
(Re_m = 5700; V_o = 32; w_g = 0.6 m/s; dry sand)

	250 °C			300 °C		
	% Rec	% Soil	% Ads	% Rec	% Soil	% Ads
Naphthalene	5	ND	ND	15	ND	ND
Acenaphthylene	61	ND	ND	63	ND	ND
Acenaphthene	74	ND	3	78	ND	ND
Fluorene	72	ND	2	75	3	0.6
Phenanthrene	76	5	2	83	5	2
Anthracene	75	6	3	78	6	2
Fluoranthene	79	5	3	80	4	3
Pyrene	86	9	2	83	6	1
Benzo(a)anthracene	56	42	2	67	30	1
Chrysene	50	40	2	61	31	1
Benzo(b)fluoranthene	41	53	6	55	40	4
Benzo(k)fluorarthene	41	53	6	55	40	4
Benzo(a)pyrene	65	31	4	65	23	3
Dibenz(a,h)anthracene	NA	NA	NA	37	59	2
Indeno(1,2,3-ed)pyrene	NA	NA	NA	37	59	2
Benzo (g,h,i)perylene	NA	NA	NA	23	67	4

ND - not detected; NA - not analyzed

Little degradation of the silica lining is observed as long as air is purged from the system. Air is flushed from the transfer line by nitrogen prior to transfer line heating. After the Silcosteel® has been conditioned the gas valve is switched to re-direct nitrogen into the carrier gas line. At this point, a vacuum pump is turned on to collect the soil/organic vapor at the collection window and to transport the organics to the surface through the Silcosteel® tube. The valve can then be re-positioned to cleanse the transfer line tube when high levels of sample are collected. This step is intended to eliminate sample carry over from one sample location to the next. Work is in progress to automate the TECP system to control the probe and transfer line temperatures as well as the carrier, flush, and collection gas lines.

Material balance experiments were conducted to determine the thermal extraction efficiency for PAHs at 250°C and 300°C, see Table 1. At optimum conditions, i.e., soil temperature, carrier gas flow rate, collection volume, and under closed cell conditions, greater than 55% recovery was obtained. Closed cell conditions represent the maximum amount that can be extracted, as opposed to the TECP, since none of the organic vapor produced is

lost to the environment and all soil is uniformly heated. The organic vapor is efficiently flushed from the cell into Tenax for VOCs or the cold trap for semi-VOCs. Note that less than 4% of the collected organics remained in the transfer line after collection. Research is in progress to chemically modify the surface to minimize (eliminate) organic absorption. Nonetheless, back-flushing for 5-min reduced the percent adsorbed to non detectable levels.

Table 2. Comparison of TECP vs. Closed System
T_{pipe} = 450 °C; T_{soil} = 280 °C; Re_m = 6000; w_g = 1.2 m/s; L/d = 15

	TECP % Recovery						Closed Chamber % Recovery	% Diff
	50-ppm	25-ppm	15-ppm	5-ppm	Ave Rec	% RSD		
Naphthalene	20	37	26	37	30	23	18	68
Acenaphthylene	34	36	36	33	35	5	62	44
Acenaphthene	41	39	33	30	36	18	77	53
Fluorene	49	36	38	37	40	17	73	46
Phenanthrene	37	32	35	34	35	7	80	57
Anthracene	37	32	34	34	34	7	77	56
Fluoranthene	65	53	48	36	50	34	80	37
Pyrene	64	53	45	68	47	15	85	32
Chrysene	27	37	31	41	34	16	57	40
Benzo(a)anthracene	49	37	36	41	40	12	62	36
Benzo(b&k)fluoranthene	29	27	29	23	27	12	48	44
Benzo(a)pyrene	25	23	36	24	27	26	65	58
Indeno(1,2,3-ed)pyrene	26	19	20	23	22	14	65	31
Dibenz(a,b) anthracene	26	19	19	23	22	14	62	32
Benzo(g,h,i)perylene	17	16	16	16	10	4	20	19

Note: % Difference is between Average TECP Recovery and Closed Chamber Recovery

The TECP and closed cell data comparison study is shown in Table 2. Recall that the closed system represents maximum recovery of analyte while the TECP is what one should expect to achieve in the field. The TECP measurement precision determined over an order of magnitude for PAHs is excellent. The results are remarkable and are as good or better than what is achievable through soil/solvent extraction. The accuracy for the TECP approximates one-half that of the closed (ideal) system. Results will be presented illustrating collection efficiency as a function of soil type, probe depth and moisture content.

Table 3. TECP Field Study, Berlin Vermont
T_{pipe} = 450 °C; T_{soil} = 280 °C; $T_{tr\ line}$ = 280 °C; Re_m = 6000; w_g = 1.6 m/s

	TECP Measured PAH/Soil Concentration				
	Boring 1		Boring 2		
	97-cm	142-cm	130-cm	155-cm	190-cm
Naphthalene	2	2	4	ND	ND
Acenaphthylene	9	6	14	ND	5
Acenaphthene	2	2	3	2	3
Fluorene	7	3	10	4	3
Phenanthrene	11	5	5	2	4
Anthracene	11	5	7	2	4
Fluoranthene	44	3	6	2	3
Pyrene	29	4	6	5	4
Benzo(a)anthracene	45	11	6	3	2
Chrysene	45	11	6	3	2
Benzo(b)fluoranthene	5	0.4	0.5	ND	ND
Benzo(k)fluoranthene	6	0.3	0.5	ND	ND
Benzo(a)pyrene	12	0.6	ND	ND	ND
Dibenz(a,h)anthracene	2	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	3	ND	ND	ND	ND
Benzo(g,h,i)perylene	6	ND	ND	ND	ND

The TECP and heated transfer line was tested in the field employing ARA's CPT in Berlin, Vermont. The location was a Vermont state central maintenance facility known to contain petroleum hydrocarbon contamination. The

TECP was tested for mechanical ruggedness and its ability to collect subsurface bound organics. The vertical profile of two borings are shown in Table 3. PAHs were found at depths of 97-cm and 142-cm at boring one and 130-cm. The hot organic vapor was cooled by dry ice and collected in an empty glass sleeve attached to the transfer line. Total collection and analysis time required at each depth location was approximately 15-min per sample inclusive of sample collection, transfer line back flushing, and analysis time. Unfortunately, comparison measurements between the TECP measured concentrations and actual soils collected at depth and analyzed by standard GC/MS methods were not possible since ARA was unable to re-enter the hole with a soil sample collection probe without breaking the CP rod. The results produced to date are promising suggesting that direct on-line chemical measurements of subsurface contaminants may be possible within a couple years.

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AN INTEGRATED NEAR INFRARED SPECTROSCOPY SENSOR FOR *IN-SITU* ENVIRONMENTAL MONITORING

Roland A. Levy and John F. Federici
New Jersey Institute of Technology, University Heights, Newark, NJ 07102
Tel. (973)-596-3561

The monitoring of environmental organic contaminants currently involves off-site methods which prohibit optimal usage. This study explores the possibility of combining the principles of interferometry with that of near infrared evanescent wave absorption spectroscopy to produce a novel integrated sensor technology capable of monitoring and determining *in-situ* the concentration of numerous organic analyte species simultaneously. This novel sensor promises to be non-intrusive and to provide accurate, rapid, and cost effective data. The overall instrument is envisioned to be compact, portable, rugged, and suitable for real time monitoring of organics. The sensor consists of a symmetric, single mode Mach-Zehnder interferometer with one arm (sampling) that is either exposed directly to the analyte or coated with a thin hydrophobic layer that enhances the binding of pollutant molecules onto its surface. A glass buffer layer protects the second arm (reference) from the influence of pollutants. Light is coupled into the waveguide and split between the sampling and reference arms using a Y-splitter configuration. Changes in the refractive index caused by the presence of organic contaminants result in a measurable phase difference between the sampling and reference arm. Selectivity of the sensor is achievable by utilizing evanescent wave absorption spectroscopy in the near infrared, a technique which measures wavelength dependent refractive index changes. The waveguide structures used in this study are fabricated on 10 cm silicon wafers. V-grooves are first formed in the silicon substrate to hold the fibers which couple to the ends of the Mach-Zehnder interferometer. A 10 μm thick SiO_2 film is synthesized by low pressure chemical vapor deposition (LPCVD) to act as cladding material for the waveguide and prevent light from coupling with the underlying silicon. A 4 μm thick phosphorus-doped (7.5 wt% P) LPCVD SiO_2 film is then deposited to act as core material for the waveguide. This layer is patterned using standard lithographic exposure and plasma etching techniques and subjected to a 1050 °C anneal to cause viscous flow and round off the edges. This rounding-off procedure is necessary to minimize coupling losses between fiber and waveguide. The refractive index of the doped glass is near 1.48, thus, producing with the underlying SiO_2 (n=1.46) substrate a single mode waveguide

device. Deposition of a 0.5 μm thick LPCVD undoped SiO_2 buffer layer over the entire wafer and a subsequent lithographic step results in selective removal of that layer over the sampling arm of the interferometer. This configuration allows for exposure of the sampling arm (uncoated or coated) to various contaminants in the environment which cause a change in the effective refractive index of that arm. The arm coated with the SiO_2 buffer layer sees a constant refractive index of n=1.46. A lithographic mask is used to produce the required patterns. Five micron wide waveguides form the two interferometer paths using a splitting angle of 2°. The sampling and reference arms are at a fixed separation of 50 μm and variable lengths (4, 6, 8, and 10 mm). A detailed analysis of these processing steps together with the principles of operation of the sensor will be discussed.

A NITRIC OXIDE AND AMMONIA SENSOR ARRAY FOR FOSSIL FUEL COMBUSTION CONTROL

B.T. Marquis, J.F Vetelino and T.D. Kenny
Laboratory for Surface Science & Tech. and Department of Electrical and Computer Engineering,
University of Maine, Orono, Maine 04469

ABSTRACT

In fossil fuel combustion processes, nitric oxide (NO) emissions are minimized by a selective catalytic reduction (SCR) technique where ammonia (NH_3) is injected into the flue gas stream to react with NO to form environmentally safe gases such as nitrogen and water vapor. Unfortunately, this process is usually incomplete, resulting in either NO emissions or excess NH_3 (NH_3 slip). Therefore, a critical need exists for an *in situ* sensor array to continuously monitor the NO and NH_3 levels at the output of the SCR system near the stack to provide real time control of the NH_3 injection and hence minimize the NO emissions to the environment. Chemiresistive sensor technology is being used to develop a small, portable, sensitive and selective sensor array that has potential to continuously measure NO and NH3 emissions. The sensor array utilizes a tungsten trioxide (WO_3) film as the sensing element to simultaneously identify NO and NH_3 concentrations present in the fossil fuel gas exhaust. Several film parameters such as thickness, dopant (gold vs. ruthenium), doping method (post-sputter vs. co-sputter), doping amount, deposition temperature, annealment procedure and operating temperature were varied to determine their effect on the film's sensing properties. As a result, a 500Å WO_3:16Å Au film post-sputtered at 200°C demonstrated high sensitivity and selectivity to NH_3 whereas a 1000Å WO_3 undoped film sputtered at 200°C exhibited greater sensitivity to NO.

INTRODUCTION

The detection and measurement of flue gases are critical not only for achieving real time process control of new clean combustion systems, but also to minimize their emissions of dangerous air pollutants. Among the most dangerous of these air pollutants are nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NO_x. Currently about one half of all NO_x emissions into the environment are due to power plants and industrial boilers. NO_x gas which is the precursor to nitric and nitrous acid, causes acid rain and photochemical smog and is a critical factor in the formation of ozone in the troposphere. Ground level ozone is a severe irritant, responsible for the choking, coughing and burning eyes associated with smog. Ozone often damages lungs, aggravates respiratory disorders, increases susceptibility to respiratory infections and is particularly harmful to children. Elevated ozone levels can also inhibit plant growth and cause widespread damage to trees and crops. Therefore, exceeding critical NO_x levels poses immediate health and environmental problems.

In fossil fuel combustion NO_x is formed by high temperature chemical processes from both nitrogen present in the fuel and oxidation of nitrogen in air. Typically, the NO_x emissions consist of 90-95% NO with the remainder being N_2O and NO_2.[1]

Several methods have been examined as potential control systems for the reduction of NO emissions in combustion processes including combustion control and flue gas treatment techniques such as selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR)[2,3]. SCR technology achieves the highest overall control efficiency of 60-80% NO reduction. In this process, NH_3 is uniformly injected into the flue gas stream that passes through a catalyst bed to enhance the kinetics of the NO/NH_3 reaction. This can be further improved with air staging to provide a longer residence time allowing more NO to react with the NH_3 , thus

increasing NO reduction and decreasing NH_3 emissions (commonly called NH_3 slip). Although there are several chemical reactions that may take place in the catalyst bed, the most common reactions are as follows,

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O, \quad (1)$$
$$4\ NH_3 + 6\ NO \rightarrow 5\ N_2 + 6\ H_2O, \quad (2)$$
$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O \quad (3)$$

and

$$4\ NH_3 + 5O_2 \rightarrow NO + 6\ H_2O. \quad (4)$$

Reaction (1) is the predominant reaction[1] and reduces NO into harmless nitrogen and water vapor. The reaction given in equation (3) neutralizes some of the excess NH_3 that did not fully react with the NO in equations (1) and (2) and hence decreases the NH_3 slip. An unwanted side reaction given by equation (4) oxidizes NH_3 to form water vapor and NO. This harmful oxidation process however usually takes place at elevated temperatures, and can be minimized by temperature control. If a judicious choice of NH_3 injection levels is made, NO emissions in SCR systems, as well as NH_3 slip into the atmosphere can be reduced significantly.

In order to control the precise levels of NH_3 injection, a critical need exists for an NO/NH_3 sensor system in the flue gas exhaust prior to the stack emission. The output from the sensor would be fed back to the SCR system via a real time control system to adjust NH_3 injection levels thereby maximizing NO reduction with minimal NH_3 slip into the atmosphere. Current NO and NH_3 measurement techniques, such as chromatography, chemiluminescence and infrared adsorption are very expensive and too bulky for *in situ* operation. Chemiresistive semiconducting metal oxide (SMO) films offer the technology to develop a small, inexpensive and reliable *in situ* sensor array for the simultaneous identification of NO and NH_3 present in a flue gas exhaust.

The first report on chemiresistive SMO films for gas sensing appeared in 1962[4] Since that time, considerable efforts have been made[5] to study SMO films for the detection of a variety of gases. Investigators have examined SMO films such as SnO_2 [6-15], TiO_2 [15,16], indium tin oxide (ITO) [17], ZnO [15,17,18] and WO_3 [19-22] for detecting NO, as well as ZnO [23-28], MoO_3/TiO_2 [29] and WO_3 [30-34] for detecting NH_3. WO_3 films can operate at elevated temperatures for long periods of time and selectively detect NO and NH_3 in the presence of interferent gases such as H_2, CO, CO_2, CH_4 and various other hydrocarbons. These films are also electrically and structurally stable at elevated temperatures.

The electrical conductivity of thin WO_3 films doped with metals such as gold (Au) and ruthenium (Ru), change upon exposure to NO and NH_3. The sensitivity of WO_3 to NO and NH_3 depends significantly upon film parameters such as thickness, dopant type, doping method, deposition temperature, annealing procedure and operating temperature. Furthermore, the functional relationship between sensitivity and each of these parameters is different for both gases.

THEORY

The WO_3 film conductivity changes as a function of NO and NH_3 gas concentrations. These films exhibit very fast response and recovery times and, after initial film conditioning, show no appreciable aging effects after repeated gas exposures. The basic chemical sensing mechanism involves the dissociative chemisorption of the target molecules and the formation of transitory concentrations of chemisorbed atoms on the WO_3 film surface. The rate of dissociation of the target molecules on the surface can be greatly enhanced by the addition of catalytic metals such as gold or ruthenium. Although the overall chemistry of the possible interactions of NO and NH_3 with WO_3 is complex and not well defined, certain primary interactions dominate.

In the case of NH_3 , which acts as a reducing agent (an oxygen scavenger), the carrier concentration in the film rises as a result of a decrease in adsorbed surface oxygen, as follows,

$$2\ NH_3 + 3O^-(ad) \rightarrow N_2 + 3\ H_2O + 3\ e^- \quad (5)$$

This rise in carrier concentration within the film is then manifested as a decrease in resistivity.

Unlike NH_3, NO acts as an oxidizing agent (oxygen donor) at the temperatures of interest. Thus, reactions with NO result in an increase in chemisorbed oxygen in the film, decreasing the free carrier concentration, as follows,

$$2\ NO + 2\ e^- \rightarrow N_2 + 2\ O^-(ad). \quad (6)$$

This decrease in carrier concentration causes the film resistivity to rise. This behavior is completely opposite to that observed with NH_3.

EXPERIMENTAL SETUP

The WO_3 sensing films were deposited on alumina and sapphire substrates by reactively sputtering a pure tungsten target in an 80/20 argon-oxygen atmosphere using an RF magnetron sputtering system. Alumina and sapphire substrates were used because they are good electrical insulators and thermodynamically stable. A DC magnetron gun was used to precisely dope the WO_3 film with gold or ruthenium to selectively catalyze the reaction with NO or NH_3. After the films were sputtered, they were subjected to an annealing process which transformed the as-deposited amorphous film into a polycrystalline film. This results in a more stable film that is chemically and conductiometrically inert to moisture and many potential interferent gases. Microheaters which controlled the temperature of the sensing film were fabricated by depositing a thin chrome serpentine structure on alumina.

The chemiresistive sensing element is placed on the surface of the serpentine microheater with silicone heat sink grease. The heater and a thermocouple are used to control the film's operating temperature. The entire apparatus is suspended on two wires attached to the sensor package to provide thermal isolation from other nearby sensors and electronics. Electrical connections to both the sensing film and microheater are made with 100µm aluminum bond wire to the sensor package. The chemiresistive sensing element and microbeater is shown in Figure 1.

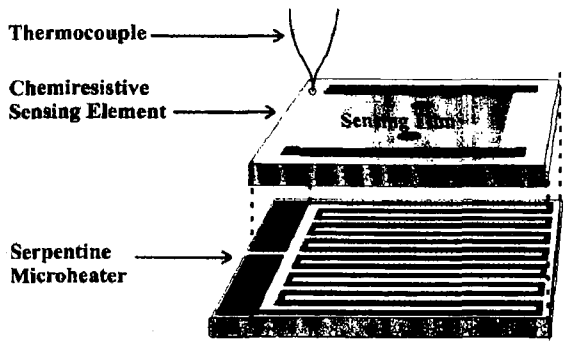


Figure 1. Chemiresistive sensing element and microheater.

In order to determine the electrical conductivity of a large number of WO_3 films exposed to a wide range of gas concentrations, a system capable of simultaneously testing and controlling up to eight sensors was designed and built. This system improved testing efficiency and insured that all films were subjected to the same gas environment during each test. A block diagram of this system is shown in Figure 2.

The sensing elements shown in Figure 1 reside inside the sealed teflon gas chamber. Two-point conductivity measurements of each sensing film are performed with an electrometer and read into the computer via a HPIB interface. The computer outputs an analog voltage to the microheater that is determined by feeding the measured film temperature through a proportional integral differential (PID) temperature control algorithm. The support electronics include power stages to supply the necessary current to all the microheaters and amplifiers that linearize the thermocouples' temperature measurements into a 10mV/°C analog signal for the computer's temperature control algorithm.

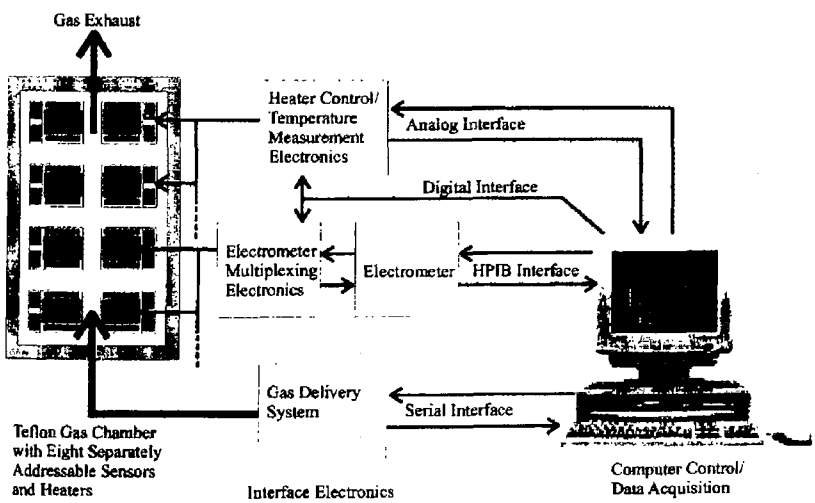


Figure 2. Block diagram of the experimental testing system.

The delivery of the NO and NH_3 gases to the sensor is achieved with the system shown in Figure 3. The apparatus consists of a bottle of the dilution gas (simulated flue gas, in this case), bottles of each test gas (NO and NH_3), an electronic three-way solenoid valve (Y-valve) and a system of mass flow controllers and plumbing. The entire system is computer controlled and is capable of delivering precise concentrations of NO and NH_3 in an atmosphere of controlled humidity for precise lengths of time. It is fully programmable and capable of running

multiple tests and collecting data without user input or intervention.

RESULTS

In order to engineer the film to respond to NH_3 and NO in a fashion unique to each gas, a large number of experiments were performed to determine the film parameters that would result in responses to NH_3 and NO that were clearly different. In particular, relationships between film thickness, gold doping, annealing environment, operating temperature and electrical conductivity when the film is exposed to NH_3 and NO gas were determined. A few of these experiments are discussed below in order to demonstrate the feasibility of using WO_3 films in a sensor array to selectively detect NH_3 and NO.

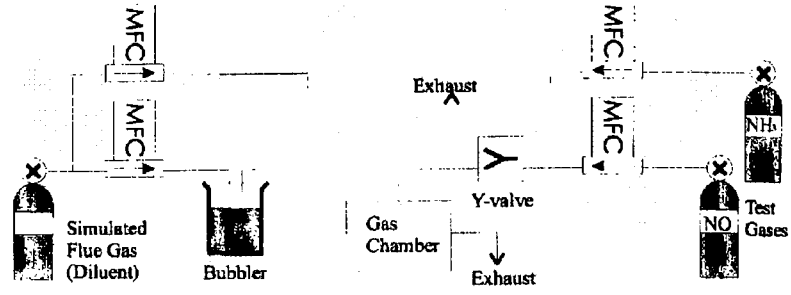
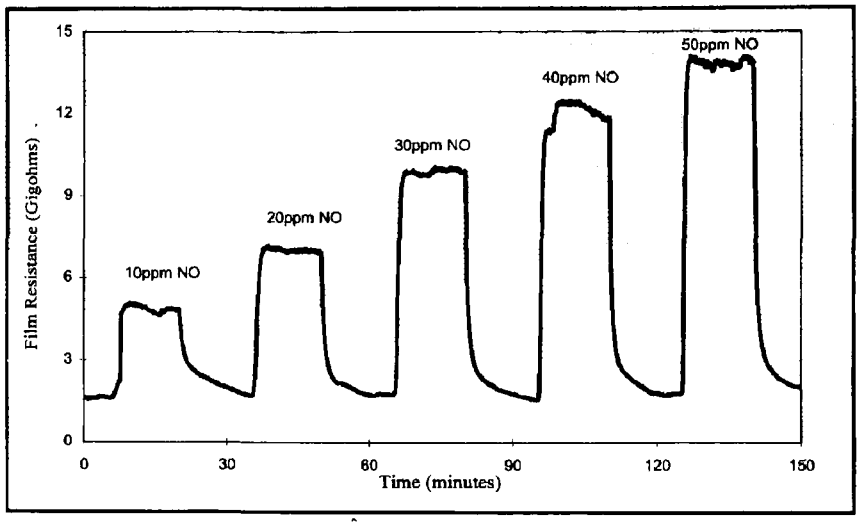


Figure 3. Gas Delivery System



A 1000Å WO_3 undoped film was sputtered at 500°C on a sapphire substrate and annealed in dry air at 300°C for 10 hours and exposed to concentrations of NO ranging from 0-50ppm at a temperature of 300°C in an environment of dry CO_2. As can be seen in Figure 4, the film demonstrated a very fast linear response to 0-50ppm NO. It also recovered to the baseline resistance when the gas was taken away which allows the sensor to measure absolute NO concentrations in real time.

Figure 4. Response of a 1000Å WO_3 film to 0-50 ppm NO at 300°C in dry CO_2

Likewise, Figure 5 shows the same 1000Å WO_3 film responding to a 50ppm pulse of NH_3 in 50% humid air. It is important to note that the response to NO is manifested as an increase in resistivity, while NH_3 results in an increase in conductivity (i.e. a *decrease* in resistivity), as predicted by equations (5) and (6) above. The film's change in resistivity is 6 times greater to 50ppm NO than to 50ppm NH_3. In fact, the film's response to only 10ppm NO was still greater than the response to 50ppm NH_3. The typical NH_3 and NO concentration ranges found in the fossil fuel combustion exhaust are 0-5ppm and 5-75ppm, respectively. Therefore, this film could selectively measure up to 10-50ppm NO in the presence of up to 50ppm NH_3.

A 500Å WO_3:16Å Au film post-sputtered at 200°C on alumina and annealed in dry air at 350°C for 5 hours was exposed to 3 pulses of 10ppm NH_3 and 3 pulses of 50ppm NO in dry air at 350 °C. Figure 6 shows the film's high sensitivity and reproducibility to 10ppm NH_3 and relatively low sensitivity to 50ppm NO. Again, the response to NH_3 is manifested as an decrease in resistivity, while NO results in an increase in resistivity. The film demonstrates adequate resolution to potentially measure NH_3 concentrations between 0-10ppm in the presence of up to 5-75ppm of NO.

SUMMARY

As a result of the tests described above, it can be deduced that the film parameters, such as thickness, doping, annealing procedure, and operating temperature significantly effect the film's sensitivity and selectivity to NH_3 and NO gas concentrations. Both, the 1000Å WO_3 undoped film operated at 300°C and the 500Å WO_3:16A An post-sputtered film operated at 350°C show potential as a two sensor array capable of simultaneously identifying concentrations of NO and NH_3. Eventually, a neural network could be trained and integrated with the

chemiresistive sensor array to improve real time process control and correlate the sensors' responses to the NO and NH_3 concentrations present in a flue gas exhaust. In future work, this technology could be extended to include other combustion gases such as SO_x and H_2S

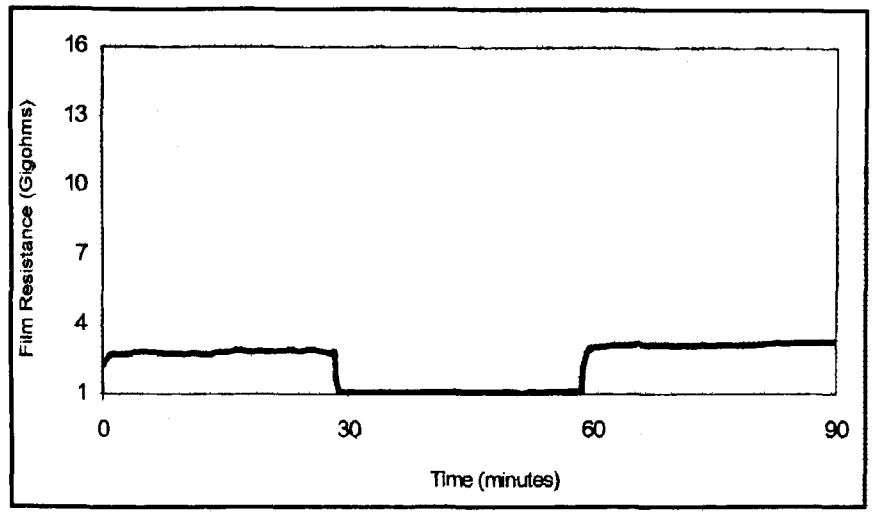
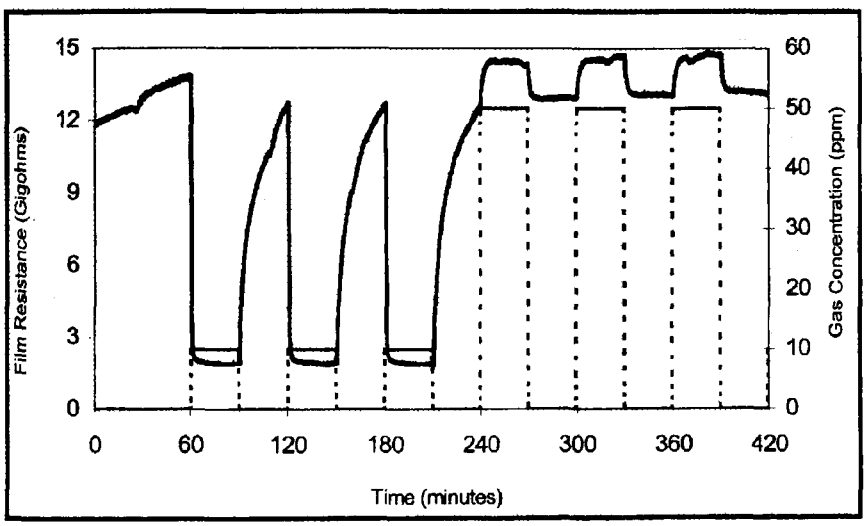


Figure 5. Response of 1000Å WO_3 film to 50ppm NH_3 at 300°C in humid air.



ACKNOWLEDGMENTS

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Figure 6. Response of a 500Å WO_3:16Å Au film to (3) 10ppm pulses of NH_3 and (3) 50ppm pulses of NO at 350°C in humid air, respectively.

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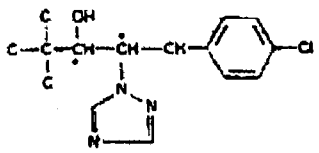
RELEVANCE OF ENANTIOMERIC SEPARATIONS IN ENVIRONMENTAL SCIENCE

Daniel W. Armstrong
Department of Chemistry, University of Missouri-Rolla, Rolla, MO

A significant number of all organic chemicals that are released into the environment are racemic mixtures. Most environmental regulations and scientific environmental studies treat racemic mixtures as though they were single, pure compounds. This can lead to incorrect toxicological, distribution, degradation and other data. A series of new enantioselective analytical techniques have been developed that allow the facile separation and quantitation of chiral compounds of environmental importance.[1] Table 1 shows a typical example of the disparate biological activities of paclobutrazol stereoisomers.[2]

Table 1. Biological activity of paclobutrazol diastereoisomers and enantiomers.



Compound	Fungicidal activity (cereal mildews and rust)	Plant growth regulatory activity (apple seedlings)
2RS,3RS	High	High
2R,3R (+)	High	Low
2S,3S(-)	Low	High

Note: The 2R,3R(+) enantiomer has a high fungicidal but a low plant growth regulatory activity. For the 2S,3S (-) enantiomer the reverse situation holds true. Separation of the enantiomers implies separation of the desired and the undesired action

We have examined the enantioselective biodegradation of chlorinated pesticides and the herbicides dichlorprop and mecoprop. While it is known that the herbicidally active enantiomer is the (+) enantiomer for both herbicides, and fate of each enantiomer in broadleaf weeds and grass has not previously been reported. Both dichlorprop and mecoprop are sold as racemic mixtures and are among the most commonly used herbicides for the control of broadleaf weeds in grass. This presentation compares the biodegradation of each enantiomer of dichlorprop and mecoprop in several types of broadleaf weeds and common grasses. The results indicate that one enantiomer is degraded faster in weeds, while both enantiomers degrade at equal rates in grass.

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DEVELOPMENT OF AEROSOL MASS SPECTROMETER FOR REAL TIME ANALYSIS OF PAH BOUND TO SUBMICRON PARTICLES

J.T. Jayne, D.R. Worsnop and C.E. Kolb
Aerodyne Research, Inc. 45 Manning Road Billerica, MA 01821
Tel: 978-663-9500, Fax: 978-663-4918
X. Zhang and K.A. Smith
Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, MA 01239
Tel: 617-253-1973, Fax: 617-253-2701

Polycyclic aromatic hydrocarbon (PAH) are mutagenic pollutants formed as by-products of combustion. Measurements of the distribution of PAH species with different aerosol particles of different sizes are critical for a complete understanding of the environmental fate of the human exposure to PAH. We present here an aerosol mass spectrometer (AMS) designed to simultaneously measure particle size, particle number density and size-resolved particle composition for volatile and semi-volatile compounds. The instrument combines a unique aerodynamic sampling inlet which focuses the particles into a narrow beam and efficiently transports them from

atmospheric pressure into a vacuum chamber where particle mass/size is determined by time-of-flight (TOF) measurement. Size-resolved single particles are flash vaporized on a heated filament and ionized by resonance enhanced multi-photon ionization (REMPI) using an excimer laser (248 nm). The PAH ions are detected by a molecular TOF mass spectrometer. The ionization process is highly selective for aromatic PAH.

The AMS described here provides size-resolved single particle composition detection down to 50 nm. Molecular mass spectra for a number of PAH aerosols have been measured. The sampling efficiency and the size resolution of the instrument have been investigated using a differential mobility analyzer (DMA) and condensation nucleus counter. Size resolution defined as $\Delta Dp/Dp = 4$ (where Dp = particle diameter) has been measured for tenth micron size particles with sampling efficiencies approaching unity, and found to be about 25%.

REAL-TIME TRACE DETECTION OF ELEMENTAL MERCURY AND ITS COMPOUNDS

Robert B. Barat
New Jersey Institute of Technology, Dep't. of Chemical Engineering,
Chemistry, and Environmental Science Newark, NJ 07102

Introduction

Emission of elemental mercury [Hg] vapor and volatile mercury compounds [e.g. $HgCl_2$, $Hg(CH_3)_2$] from combustion and other processes is an important environmental issue [Von Burg and Greenwood, 1991]. The present research addresses the need to develop real time stack monitoring of emissions of Hg and its compounds. Such continuous emission monitor (CEM) technology would enable identification of peak emission events and the possibility of corrective action. Realistic emission inventory will enable regulatory agencies to better assess health risks associated with future siting of emission sources, such as waste incinerators.

To be useful to a wide range of applications, the CEM should be capable of detection in the range of 1-5000 $\mu g/m^3$, with an ultimate sensitivity limit on the order of 0.1 $\mu g/m^3$ (ca. 10 pptv). Current best technology for Hg detection uses cold vapor trap resonant atomic fluorescence [Tekran, 1998]. However, this technology provides no information on mercury compounds.

In this work, detection of mercury compounds is based on photo-fragment fluorescence (PFF) excited by deep ultraviolet (UV) light. The fluorescence spectra can facilitate identification of the original mercury compounds. Photo-fragment fluorescence has been successfully applied for the gas-phase analysis of $HgCl_2$, $Hg(CH_3)Cl$, and HgI_2 (Barat and Poulos, 1998).

The detection for Hg uses Doppler-shifted resonant atomic fluorescence excited by a UV laser or a low pressure mercury lamp. The Doppler-shifted fluorescence will be separated from the unshifted background signal by use of an optically dense Hg vapor filter precisely matched to the spectral linewidth of the source. An alternative to the vapor filter is precise use of time gating to distinguish the nearly instantaneous background scattering from the relatively long fluorescence signal.

The experimental program involves three stages. In the first, a static cell (no flow) containing mercury (elemental or compound) vapor is probed with a deep UV laser to generate spectra. An atmospheric pressure flow cell is used in the second stage. The third stage utilizes the expanding jet.

Compounded Mercury

In general, mercury compounds absorb light strongly below 250 nm [Gowenlock and Trotman, 1955], and these absorption bands are generally dissociative. In PFF, a photolyzing UV photon dissociates the target molecule into fragments, some of which are imparted with excess energy. The energy might then be lost by fluorescence:

$$A\text{-}B \xrightarrow{h\nu} A + B^* \quad (1a)$$

$$B^* \longrightarrow B + h\nu' \quad (1b)$$

where A and B can be atoms or polyatomic species. The fragment identities and distributions, as revealed in the fluorescence spectrum, can, in principle, provide information on the parent species, in a manner analogous to mass spectrometry and other fragmentation spectroscopies.

For example, Figure 2 shows the PFF spectrum from 193 nm excimer laser excitation of $Hg(CH_3)Cl$ vapor in a static cell (Figure 1). Two features are evident: atomic Hg emission lines at 546 and 579 nm; and a broad continuum assigned to the B-->X system of HgCl** excited state (Mandl and Parks, 1978; Whitehurst and King, 1987). Likely photochemical processes resulting in these observations are:

$$Hg(CH_3)Cl \xrightarrow{h\nu} HgCl^{**} + CH_3 \quad (2)$$

$$HgCl^{**} \longrightarrow HgCl + h\nu' \quad (2a)$$

$$\longrightarrow Hg + Cl \quad (2b)$$

Steps (2a) and (2b) are clearly implicated, but the origin of the Hg atomic emission lines is open to question. Focussing the laser beam increases the emission from Hg, and generates the blue emission at 431 nm from CH*.

The lowest concentration of mercury compound [$Hg(CH_3)Cl$] measured in the static cell was approximately 50 $\mu g/m^3$. Using reasonable improvements in optics and electronics, it is estimated that the limit-of-detection can be lowered by at least a factor of 500.

The concentration of the target compound is related to the fluorescence intensity from a hot fragment. Excitation laser energy of about 2 mj/pulse at a repetition rate of 10 Hz at 222 nm was applied to $HgBr_2$ vapor (in Argon) in an atmospheric pressure flow cell (Figure 3). The PFF was monitored using a photomultiplier tube and narrow interference filters centered at 254 nm - a strong Hg* emission line - (see Figure 4). Excellent linearity was obtained over a wide concentration range. Similar results were obtained using a compact monochromator + CCD system.

The supersonic jet spectroscopy (to be discussed in the next section) is expected to further improve sensitivity of PFF detection. Spectra will be sharpened, leading to better discrimination of fragment vibrational structure. Quenching by O_2 will be reduced due to the low pressure.

Elemental Mercury

Atomic Fluorescence Spectroscopy (AFS) is a highly sensitive spectroscopic marker for elemental Hg detection. Current AFS instruments (e.g. Tekran, 1998) use a cold vapor trap for collection + concentration of the air sample, purging (to remove O_2), desorption, excitation with an Hg vapor lamp (253.7 mn), and then measurement of the resonant fluorescence (at the same wavelength). Sensitivity is limited by the elastically scattered light from the exciting source.

The technique under study, shown in Figure 5, will expand the Hg-contaminated air stream across a supersonic nozzle into a high vacuum chamber. Light at 253.4 rim will be directed across the jet. Atomic Hg fluorescence will be Doppler-shifted by between 1 and 3 GHz due to the jet motion. Total collected light, comprised of the shifted fluorescence and stray elastic scattering, will be passed out of the vacuum chamber and through (Figure 6) an optically dense, sharp cut-off Hg vapor filter (centered at the excitation wavelength) to reduce elastic scattering while transmitting the fluorescence signal (Miles, 1991; Finkelstein, et al., 1994).

The expansion reduces the collision rate of Hg* with O_2, so collisional quenching and collisional broadening are both substantially reduced. The low temperature associated with this expansion further reduces the fluorescence linewidth, enhancing the performance of the Hg vapor filter.

In the absence (or in conjunction with) the atomic filter, time gating of the collected signal offers an alternative means to extract the fluorescence signal from the scattering background. It has been observed in the atmospheric pressure flow cell experiments with $HgBr_2$ that scattering is essentially instantaneous, lasting for the duration of the laser pulse (i.e. 10 nanoseconds). The relatively long lifetime for Hg* (117 nanoseconds at 253.7 nm - Dodd et. al., 1970) results in the fluorescence signal appearing as a long-tailed shoulder on the scattering signal. Prudent placement of the signal detection gate, as well as subtraction of the background signal measured in the absence of Hg vapor, should allow for extraction of the desired fluorescence signal.

Quality Assurance / Performance Assessment

For comparison of time-averaged test concentrations, the mercurycontaining sample stream will be diverted to a reference method, such as optical absorption. Testing of the research technology will consist of obtaining data on five performance measures:

Relative Accuracy: the absolute mean difference between the metals concentration determined by the monitor and that determined by the reference method, plus a 2.5 percent uncertainty confidence coefficient based on a test series.

Calibration Drift: the difference in the monitor output reading from the established reference value after a stated period of operation. The reference value is established by a calibration standard which has a concentration nominally 80 percent or greater of the full scale reading capability of the monitor.

Zero Drift: calibration drift when the reference value is zero.

Response Time: the time interval between the start of a step change in the concentration of the monitored gas stream and the time when the output signal reaches 95 percent of the final value.

Detection Limit: three times the standard deviation of nine repeated measurements of a low-level (near blank) sample.

Acknowledgement

The author thanks Dr. Arthur T. Poulos, President of Poulos Technical Services, Inc., for his significant contributions to this research. The author would also like to thank the U.S. Environmental Protection Agency - National Center for Environmental Research and Quality Assurance for its financial support of this work (Grant # R-825380-01-0), and grant project officer Mr. William Stelz for his administrative guidance.

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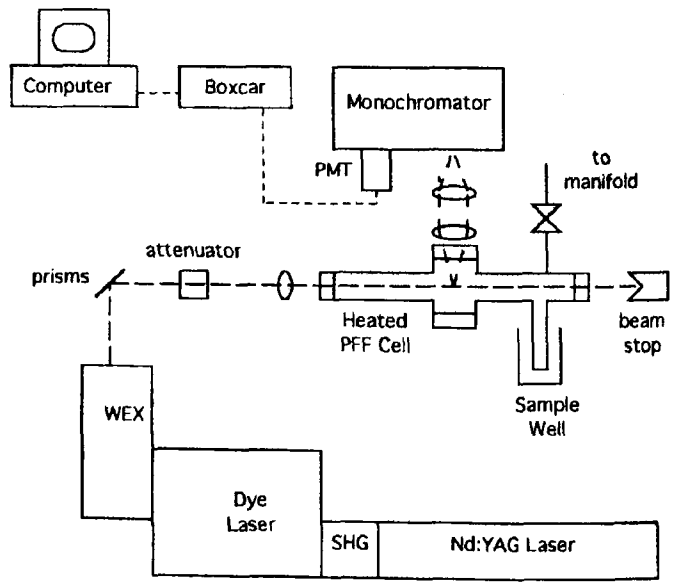


Figure 1. Research Apparatus #1: Static Cell for Atomic and Photo fragment Fluorescence

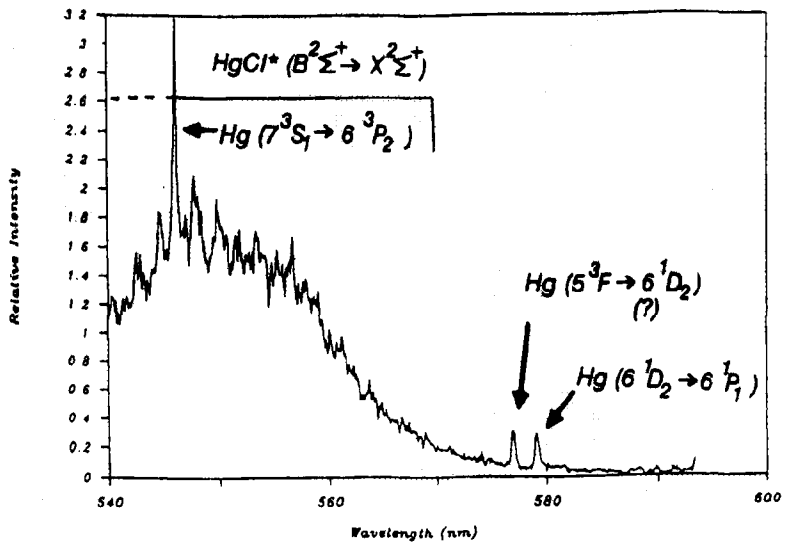


Figure 2a. PFFS of $Hg(CH_3)Cl$ 193 nm excitation - not focused

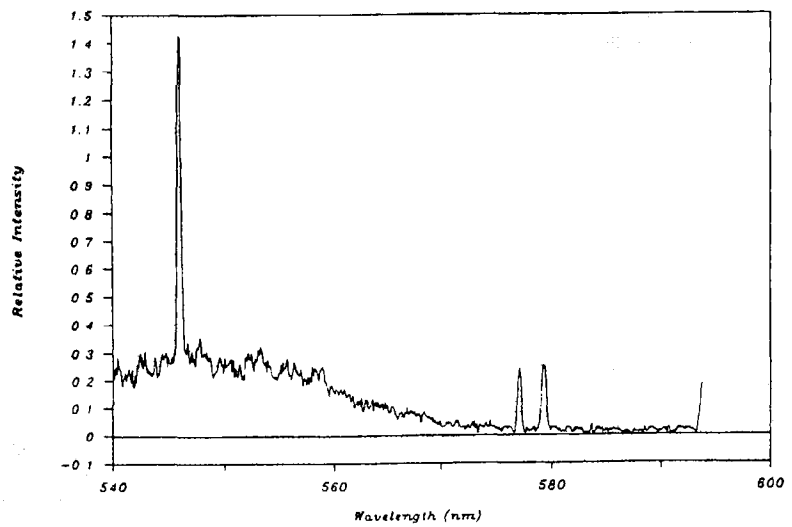


Figure 2b. PFFS of $Hg(CH_3)Cl$ 193 nm excitation - focused

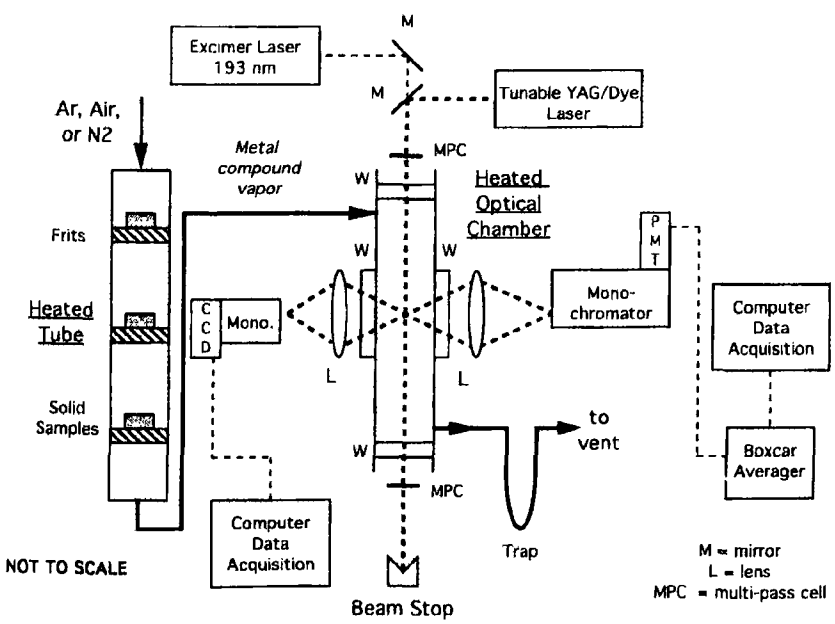


Figure 3. Research Apparatus #2: Flow Cell for PFF

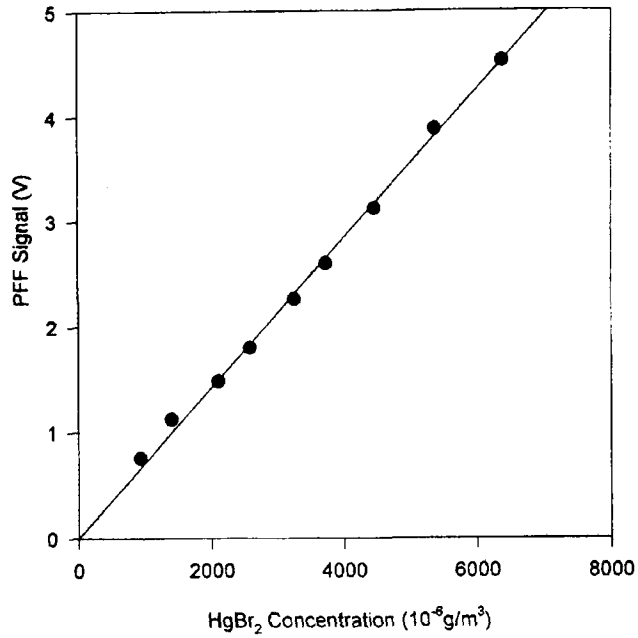


Figure 4. Photofragment Fluorescence (PFF) Signal vs. $HgBr_2$ Concentration

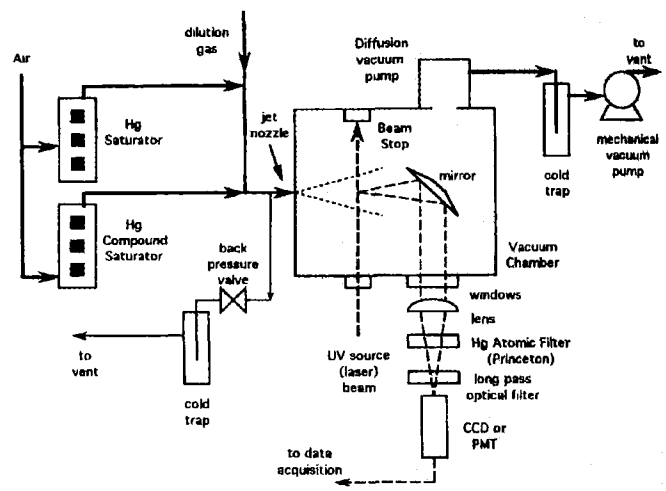


Figure 5. Apparatus #3: Atomic Fluorescence and Compound PFF in Vacuum

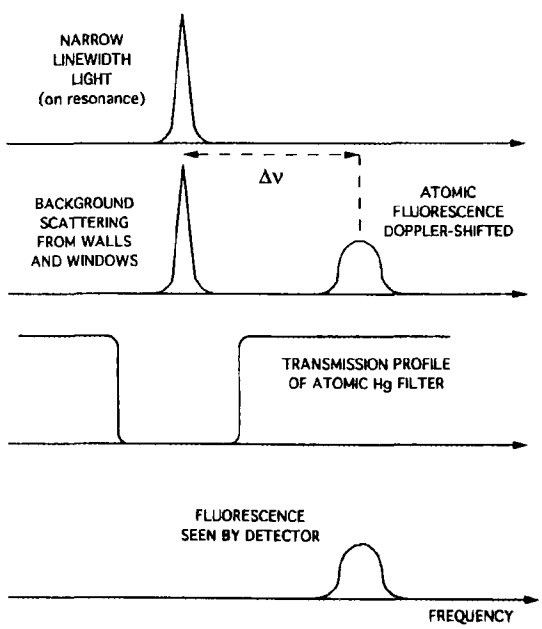


Figure 6. Doppler-shifted Resonant Fluorescence

ORTHOGONAL BACKGROUND SUPPRESSION TECHNIQUE FOR EPA'S FIELD INFRARED DATA PROCESSING

Blaterwick

NO ABSTRACT AVAILABLE

DEVELOPMENT OF A CONTINUOUS MONITORING SYSTEM FOR PM_{10} AND COMPONENTS OF $PM_{2.5}$

Morton Lippmann, Judy Q. Xiong and Wei Li
New York University Medical Center, Nelson Institute of Environmental Medicine,
57 Old Forge Road, Tuxedo, New York 10987

ABSTRACT

While particulate matter with aerodynamic diameters below 10 and 2.5 μm (PM_{10} and $PM_{2.5}$) correlate with excess mortality and morbidity, there is evidence for still closer epidemiological associations with sulfate ion, and experimental exposure-response studies suggest that the hydrogen ion and ultrafine ($PM_{0.15}$) concentrations may be important risk factors. Also, there are measurement artifacts in current methods used to measure ambient PM_{10} and $PM_{2.5}$, including negative artifacts because of losses of sampled semivolatile components (ammonium nitrate and some organics) and positive artifacts due to particle-bound water. In order to study such issues, we are developing a semi-continuous monitoring system for PM_{10}, $PM_{2.5}$, semivolatiles (organic compounds and NH_4NO_3), particle bound water, and other $PM_{2.5}$ constituents that may be causal factors. PM_{10} is aerodynamically sorted into three size-fractions: 1) coarse (PM_{10}-$PM_{2.5}$); 2) accumulation mode ($PM_{2.5}$-$PM_{0.15}$); and 3) ultrafine ($PM_{0.15}$). The mass concentration of each fraction is measured in terms of the linear relation between accumulated mass and pressure drop on polycarbonate pore filters. The $PM_{0.15}$ mass, being highly correlated with the ultrafine number concentration, provides a good index of the total number concentration in ambient air. For the accumulation mode ($PM_{2.5}$-$PM_{0.15}$), which contains nearly all of the semivolatiles and particle-bound water by mass, aliquots of the aerosol stream flow into system components that continuously monitor sulfur (by flame photometry), ammonium and nitrate (by chemiluminescence following catalytic transformations to NO), organics (by thermal-optical analysis) and particlebound water (by electrolytic hygrometer after vacuum evaporation of sampled particles). The concentration of H^+ can be calculated (by ion balance using the monitoring data on NO_3^-, NH_4^+, and $SO_4^=$).

OBJECTIVES

Background

Particulate matter (PM) is an ambient air criteria pollutant that does not, as listed, have any specific compositional definition. When initially defined (in 1971) as total suspended particulate matter (TSP), it had no specific particle size distinction either. The TSP inlet cut-size was determined by the inlet aspiration efficiency, whose upper 50% cut-size (20-50 gm) varied with ambient wind speed and direction. The 1987 PM_{10} National Ambient Air Quality Standard (NAAQS) revision was defined in terms of the mass concentration of PM aspirated by a non-directional and wind speed insensitive inlet with a 50% sampling efficiency at ~10 μm aerodynamic diameter. The PM_{10} cut approximates that of the normal human upper respiratory tract during oral inhalation, so that the sampled particles represent those that can penetrate to the thoracic airways (tracheobronchial tree and more distal gas-exchange airways). Particles depositing along the tracheobronchial tree (lung conductive airways) can exacerbate asthma and cause bronchitis and bronchial cancer, while those depositing in the gas-exchange airways can cause lung fibrosis, emphysema and peripheral lung cancers. Particles that are retained in the lung airways can cause persistent local irritation and/or dissolve and be translocated to more distant organs via the bloodstream.[1,2]

Neither the PM_{10} nor the TSP NAAQS made any distinction as to the chemical composition of the particles sampled. In terms of composition, there is a relatively clear distinction between coarse and fine particles in the ambient air, as illustrated in Figure 1.

The coarse mode of the ambient aerosol is generally composed of soil and soil-like dust and ash particles generated and/or dispersed by mechanical forces. It is typically dominated by basic mineral oxides in particles larger than ~1.0 µm. By contrast, the fine mode particles are generally derived from gas-phase precursors, which form in the atmosphere as ultrafine (nuclei mode) particles after chemical transformations. The transient nuclei mode particles rapidly coagulate and coalesce to form larger accumulation mode particles in the light-scattering range (0.1 to 1 pm), are persistent in the air for many days, and contain almost all of the sulfate, ammonium and hydrogen ion, as well as most of the nitrate ion and carbonaceous particles. Size-selective ambient air samplers have been developed to collect the coarse mode and fine mode particles separately, typically with a relatively sharp size-cut at 2.5 µm in aerodynamic diameter ($PM_{2.5}$). When using a 2.5 µm cut, the fine mode includes essentially all of the sulfates and organics, but also includes the lower tail of the coarse mode.

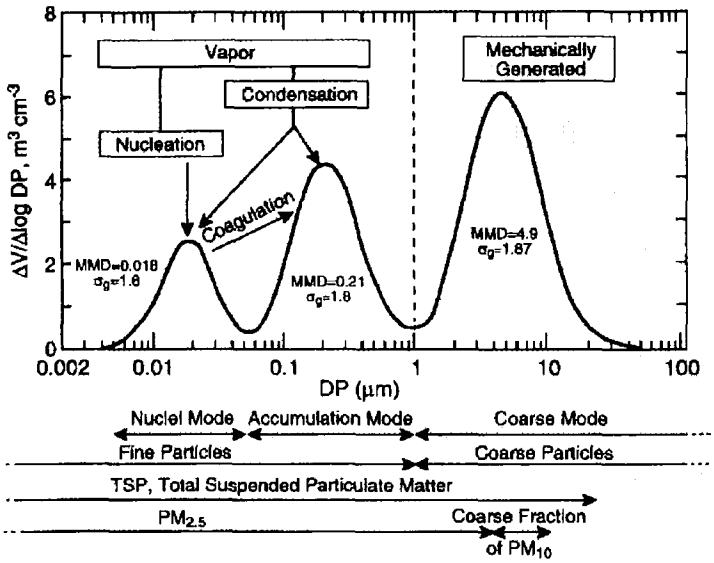


Figure 1. Measured mass size distribution showing particles in nuclei and accumulation modes of fine particles. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation).

From some epidemiological studies, there is suggestive evidence that the excess mortality and morbidity associated with elevated PM was more closely correlated with $PM_{2.5}$ than with PM_{10}.[3] The fine particle mass in the eastern U.S. is dominated by sulfates ($SO_4^=$), and the epidemiological evidence suggests that excess mortality and morbidity are as well or better correlated with ambient $SO_4^=$ than with $PM_{2.5}$.[4] The $SO_4^=$ is, in turn, highly correlated with aerosol acidity (H^+), a more likely causal factor than SOC on the basis of controlled exposure studies in humans and animals.[4]

At this time, the actual causal factor(s) for the excess mortality and morbidity are not clearly established. However, in 1997, the EPA adopted both 24 hr and annual average $PM_{2.5}$ standards on the basis that $PM_{2.5}$ is the best currently available surrogate index for the health effects associated with ambient air PM.[5] At the same time, EPA retained the PM_{10} NAAQS, with some relaxation in stringency, because of residual concerns about the health risks from the coarser particles that deposit on lung conductive airways, and may cause or exacerbate asthma, bronchitis, or bronchial cancer.[5]

Currently available monitoring methods, which are based on filter sampling of ambient PM_{10} or $PM_{2.5}$, with subsequent determination of sampled mass, have significant limitations for the accurate determination of ambient PM mass concentrations. Some of the ambient PM is semi-volatile, especially ammonium nitrate and some of the organic constituents. Sampled PM mass can be lost, especially when the temperature is elevated during the sampling and/or prior to analysis. Nitrate (NO_3^-) can also be lost from the sampling filter after collection of acidic sulfates as the H^+ combines with NO_3^- to form nitric acid vapor (HNO_3) that is carried off by air passing through the filter. There can be positive artifacts as well, most notably due to water of hydration at high ambient humidities. Their associated water may contribute to the measured fine particle mass without adding to the health risk. In view of these considerations, there is a need to be able to determine the concentrations of several key species within the accumulation mode particles that may be either candidate causal factors or likely sources of sampling artifacts. The most important of these aerosol components are $SO_4^=$, NO_3^-, NH_4^+, H^+, semi-volatile organics (SVOC) and water vapor.

There is also some concern about the health effects of ultrafine particles (those less than 0.1 µm diameter). Some animal studies indicate that extremely small mass concentrations of ultrafines 25 µg/m³) can cause excess mortality and pathological changes after brief exposures[6,7] Evidence for an important role for ultrafines is reported by Peters et al.,[8] who found somewhat closer associations between reduced pulmonary function in nonsmoking adult asthmatics with number concentration than with $PM_{2.5}$ mass concentration. Finally, it remains

possible that the effects of $PM_{2.5}$ may really be due to its total mass concentration and not to any of its specific chemical constituents. Thus, it is important to accurately determine the overall mass concentration.

Design Objectives

These considerations lead to our design objectives for the continuous monitoring of PM_{10} and $PM_{2.5}$. The concentrations of components to be measured separately are: 1) coarse mode particle mass (i.e., PM_{10}-$PM_{2.5}$); 2) fine mode sulfate ($SO_4^=$); 3) fine mode nitrate (NO_3^-); 4) fine mode ammonium (NH_4^+); 5) fine mode organic carbon (OC) and elemental carbon (EC); 6) fine mode water (H_2O); 7) fine particle mass ($PM_{2.5}$); and 8) ultrafine mode mass ($PM_{0.15}$).

The sum of mass components 1 and 7 equals PM_{10} mass. H^+, a PM parameter of interest can also be derived from the monitoring data. As shown in Figure 2, the milliequivalent sum of the accumulation mode anions ($SO_4^=$ and NO_3^-) is equal to the sum of the cations (NH_4^+ + H^+). Thus, we can estimate H^+ concentration by net ion difference. For ultrafines, the parameter of interest may be number concentration rather than mass concentration. However, as indicated in Figure 3, the mass and number concentrations for particles below 0.1 µm are highly correlated. Thus, the ultrafine number concentration can be reliably estimated from the corresponding measured mass concentration. Alternatively, the number concentration can be directly measured using a condensation nucleus counter (CNC).

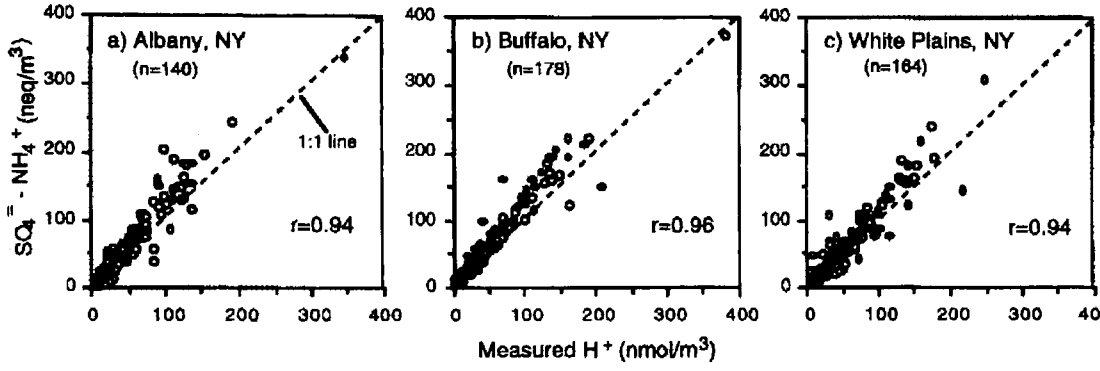


Figure 2. Comparison of estimated H^+ (via ion difference) to directly measured H^+ (via pH) for data collected on Teflon filters at 3 NYDEC sites (June-August, 1988 and 1989). Unpublished data from Dr. G.D. Thurston, NYU.

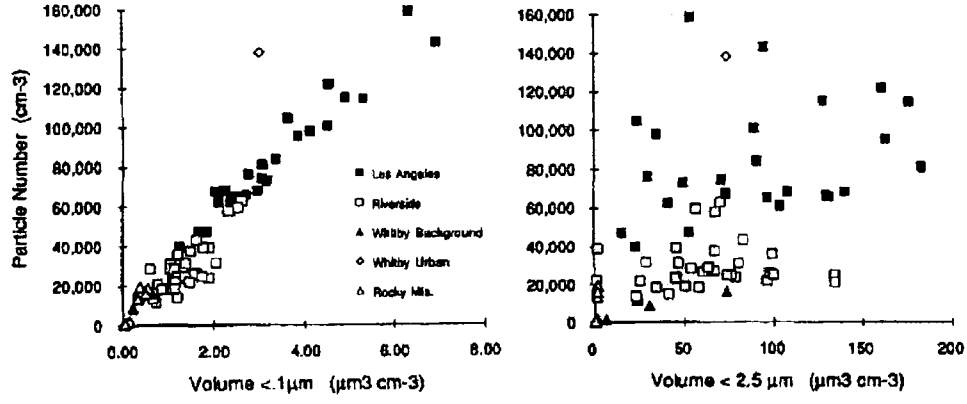


Figure 3. Relationships between particle number and volume concentrations: Left panel for ultrafine particles (smaller than 0.1 µm); right panel for fine particles (smaller than 2.5 M). From: USEPA (1996).

Design Concept

The overall design concept is illustrated schematically in Figure 4.

The PM_{10} inlet limits access to those particles that can penetrate into the human thorax. This is followed by a virtual impactor with a 2.5 µm cut-size. The coarse particle mode is directed onto a spot on a polycarbonate pore ucleporeTM) filter tape using the filter resistance method developed by Koutrakis et al.[9] After a suitable sampling interval and determination of particle mass collected, the tape spot is mechanically advanced for sample storage

and presentation of a fresh filter surface for the next sampling interval. The fine particle fraction (suspended in 29 lpm of the inlet flow) is carried into a second virtual impactor with a 0.15 µm cut-size (lowest practical cut-size). The smaller (ultrafine) particles are collected on a filter spot on a sequential filter sampler for periodic mass concentration analyses in a manner similar to that used to measure the coarse particle fraction. The extension of the method of Koutrakis et al.[9] to ultrafine particles is described in detail later in this paper. The accumulation mode particles (0.15 to 2.5 µm), suspended in 2.9 lpm of the inlet air, are directed into: 1) a stream of 1.8 lpm leading to the aerosol water detector; and 2) a stream of 1.1 lpm leading to the inlets of the continuous detectors for accumulation mode aerosol components of primary interest, i.e., $SO_4^=$, NO_3^-, NH_4^+, OC, and EC. A third filter tape sampler draws off 0.2 lpin of the fine particle ($PM_{2.5}$) stream into a filter tape sampler for the determination of the overall mass concentration of $PM_{2.5}$.

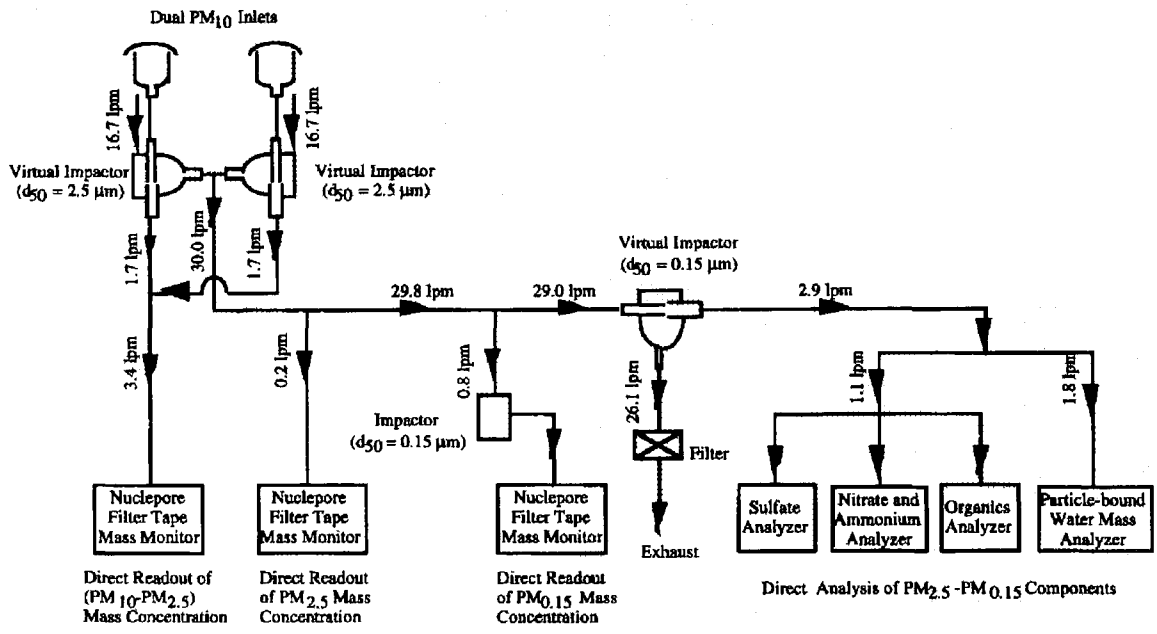


Figure 4. Overview of the system for continuous measurement of PM 10 and components of $PM_{2.5}$.

With the exception of the aerosol water and particulate mass detectors, each of the continuous monitors uses well established detection methods available in widely used commercial instruments. Similarly, the PM_{10} inlet and 2.5 µm virtual impactor are widely used and commercially available. A 0.15 µm virtual impactor was designed and tested by Sioutos et al.[10]

Monitoring System Elements Based on Commercial Available Equipment

1) Flame-Photometric Detector (FPD) for Aerosol Sulfate: The Meloy Model 285 FPD can be used to measure total concentration of sulfur in the aerosol by using PbO diffusion denuders at the inlet to remove ambient vapors, such as SO_2, H_2S, and mercaptans. The sulfur in the aerosol is, with rare exceptions, due to its presence in sulfates (H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$). Thus, the sulfate ion mass concentration is essentially equivalent to three times the measured sulfur concentration. This application of the FPD has been described by Cobourn et al.[11] and Allen et al.[12] The instrument detection limit is 1 ppb (4 µg/m^3 $SO_4^=$) with a sampling flowrate of 180 ml/min. Since the sample is preconcentrated 10 times by means of a 0.15 gm virtual impactor before analysis, the detection limit is ~0.4 µg/m^3 for accumulation mode particulate SO_4 in ambient air.

2) Thermal-Optical Technique for Measurement of Aerosol Organic Carbon (OC) and Elemental Carbon (EC): For measurement of aerosol organic and elemental carbon, we plan to adopt an *in situ* aerosol carbon analysis method developed by Turpin et al.[13] The method combines the sampling function of a two-port parallel filter sampling technique with the analytical function of a thermal-optical carbon analyzer,[14,15] and was employed in the Carbonaceous Species Method Comparison Study (CSMCS) in Glendora, California, in the summer of 1986, for side by side measurement of sub-2.5 gm aerosol carbon concentrations with other conventional sampling and analysis methods.[16] The detection limit of the method was reported to be as low as 0.2 µg carbon with a precision of about 3%.

3) PM_{10} Inlet and $PM_{2.5}$ Virtual Impactor: We use 16.7 liter/min (lpm) inlets and 2.5 µm virtual impactors from Series 241 Graseby-Andersen PM_{10} Manual Dichotomous Samplers. They separate the 16.7 lpm of inlet flow into: 1) a 1.7 lpm stream containing the PM_{10} coarse-mode fraction along with 10% of the fine fraction; and 2) a 15 lpm stream containing 90% of the fine PM fraction.

Monitoring System Elements Under Development and/or Undergoing Evaluation Detail in this Research

1) Particulate Mass Concentration Monitors: We are using the newly developed method of Koutrakis et al.,[9] in which the mass accumulated on a polycarbonate pore (Nuclepore™) filter can be shown to be directly proportional to the pressure drop across that filter. The basis for the method is that the particles are collected at the entries to and within the pores of the Nuclepore™ filter by interception or Brownian diffusion, rather than on the surfaces between the pores by impaction. The flow through the pores is restricted by the presence of the collected particles in proportion to their volume.

For the coarse particles (PM_{10}-$PM_{2.5}$), a Nuclepore™ filter with 10 µm pores is being used, while for the fine mass 2 µm pores are used. In order to measure the mass concentration of ultrafine particles, we use a modified system that uses a filter with 0.2 µm pores. The 0.2 µm pore filter has a relatively high baseline flow resistance, and very small mass increments due to collected ultrafines will markedly increase the resistance, providing a very sensitive measure of the mass concentration of ultrafine particles.

Design and Validation of the Ultrafine Mass Monitors

The ultrafine, mass monitor (CPMM-U) consists of two parallel channels, four capillary pore filters (N1 ... N4), and two HEPA filters (Figure 5). In addition, needle valves and flow meters are used to control and monitor the flow rates in each channel. Two sensitive pressure transducers (T1 and T2) are used to measure the change in pressure drop at two locations along each channel as shown in Figure 5. The measured pressure drops can be related to the mass loading of the first capillary pore filter of the measurement channel. The left channel, which has a capillary pore filter exposed to ambient particles, is the measurement channel. The right channel, with both capilliary pore filters behind the HEPA filter, is the reference channel.

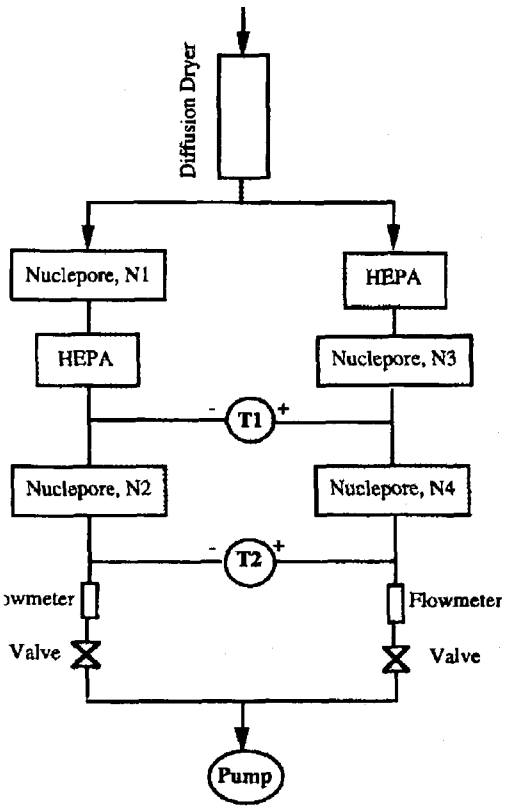


Figure 5. Schematic layout of the basic elements of the system for the measurement of the mass concentration of the ultrafine function of ambient air particulate matter. The increased flow resistance across the N1 Nuclepore filter is proportional to the accumulated mass and number of ultrafine particles.

The pressure drop across a capillary pore filter is affected by relative humidity, temperature, flow rate, and the static pressure at the entrance of the filter. The effect of any one of these factors can exceed the change in pressure drop due to particle loading. While N2 serves as a reference to eliminate the fluctuations in relative humidity, temperature and flowrate, a one-channel design has serious limitations. First, since the range of the change in pressure drop across N1 is very small (<5%) in comparison to the overall pressure drop of the filter, it is difficult to accurately measure the change in pressure drop due to particle loading. Also, it cannot be assumed that N2 operates at the same conditions as N1. This requirement is approximately satisfied for humidity, temperature, and flow rate. However, the pressure at the entrance of N2 may be different if N1 causes a significant pressure drop, as in the case of using a capillary pore filter with a small pore size. A two-channel design greatly improves on these limitations.

To measure the mass of ultrafine particles, a very small pore size is needed in order to match the size of particles of interest and optimize the sensitivity of the instrument. This results in a very high baseline pressure drop. The typical pressure drop in the Koutrakis[9] CPMM design using a 2 µm pore size was ~12 inches of water, while the pressure drop in CPMM-U using a 0.2 µm pore size is ~70 inches. Two problems arise: 1) the difficulty

of balancing both pressure transducers as the sampling time increases (use of a pressure transducer with a broad measurement range limits the sensitivity); 2) the difficulty of maintaining a leak-free system increases (a small leak in the system will cause errors in mass measurement).

Only those particles depositing at the entrances to, or inside of the pores of, a filter can contribute to the increase in pressure drop. Therefore, the flow rate was selected to minimize the impaction of particles on the surface of the filter, and to maximize the diffusion and interception of particles inside of the pores. Other factors important in the selection include: 1) ensuring that the change in pressure drop across N1 can be measured in a reasonably period of time for the typical ambient particle concentration; 2) achieving a pressure drop that is not too high (causing operational problems). A capillary pore filter with 0.2 μm pore size and a face velocity of 5 cm/sec was selected.[18]

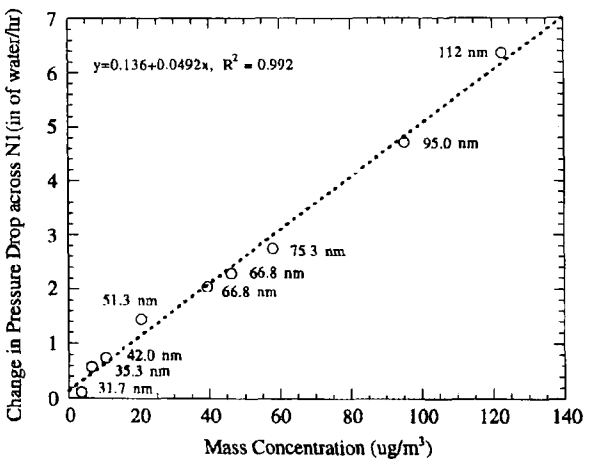
Koutrakis et al.[9] have shown that, for the CPMM, the increase in pressure drop of N1 can be calculated by 2T1-T2. One of the assumptions is that the pressure drop of N2 is the same as that of N1. This condition is satisfied when using capillary pore filter of larger pore size (2.0 μm). However, this condition is not satisfied when 0.2 μm capillary pore filters are used, because the pressure drop across a capillary pore filter depends upon the flow rate and pressure at the filter face. Because of the pressure drop across N1 (~70 in. of water), the pressure drop across N2 is only about 85% of that across N1. Generally, the pressure drop across N1, ΔP, can be expressed as,

$$\Delta P = \frac{(1=\alpha)T1-T2}{\alpha}$$

$$\alpha = \frac{\Delta P_{N2}}{\Delta P_{N1}}$$

where T1 and T2 are the pressure differentials recorded by pressure transducer 1 and 2. ΔP_{N1} and ΔP_{N2} are the pressure drop across N1 and N2 at a given flow rate, respectively. For a face velocity of 5 cm/sec, the α has a value of 0.85.

As aerosol enters the CPMM-U, it is dried by passing through a diffusion dryer. The flow then splits. On the left path, particles deposit on N1 , causing a increase in flow restriction across N1. Any particle that penetrates N1 will be removed completely by the HEPA filter that is located further down the line. Therefore, the flow restriction of N2 will not change due to particle loading during sampling. On the right path, particles are immediately removed by the HEPA filter. The flow restrictions of both the first and second capillary filters will not change due to particle loading during sampling because: 1) the capacity of the HEPA filter is much larger than that of a capillary filter; and 2) the pressure drop across the HEPA filter is less than one hundredth of that across a capillary pore filter under our experimental conditions. Thus, the increase in flow restriction of HEPA filter is negligible in comparison to that of the capillary pore filter.



As particles deposit on N1, the balance of the system is self-adjusted to accommodate the change in flow restriction of N1. Thus, the pressure drop across the N1 increases and the T1 reading increases. Assuming that the flow rates of both lines are not significantly changed during the period of sampling, the T2 reading also increases. For the calibration of the ultrafine particle mass monitor (CPMM-U) we employed a method using an Ultrafine Condensation Particle Counter and monodisperse particles to calibrate the CPMM-U. The system used is described in a separate paper.[19] The results of the calibration tests for various sizes of monodisperse ultrafine particles are shown in Figure 6.

Figure 6. The results of the calibration tests for various sizes of monodisperse ultrafine particles.

Since the pressure drop across the capilliary pore filters in the CPMM-U is 5-7 times higher than that in the CPMM, the filter tape advancement system for CPMM was considered unsuitable for the CPMM-U. Koutrakis et al.[20] have shown that a small leak in the CPMM can cause a significant error in the measurement of mass

concentration. To avoid leakage problems we use a multi-head filter holder that can provide a tight seal for each filter. Instead of a filter advancement system, we use a sequential sampling approach. Figure 7 shows the systematic design of the multi-head filter holder. The multi-head filter holder is machined from an aluminum block. Recessed filter holders (the number depends on the optimization of the CPMM-U) are machined into the block. Each filter holder includes a stainless steel screen backup and a gasket. The solenoid valves, which are controlled by a computer, select one sampling channel at a time. The capilliary pore filters are loaded into the filter holder block in the laboratory, and the multi-head filter holder is replaced as a whole in the field. Since the linear range of the instrument extends to a mass concentration up to 20 $\mu g/m^3$, one filter may be used for long period sampling if the concentration of particles is relatively low. For example, if the mass concentration of the ultrafine fraction is 1 $\mu g/m^3$, the linear response range will not be exceeded until 20 one-hour consecutive samplings are made on one filter. Therefore, a multi-head holder containing 14 filter holders should be sufficient for a one week sampling under almost all ambient conditions in the U.S.

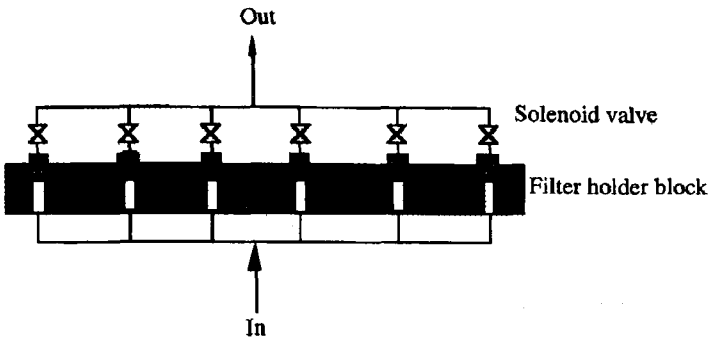
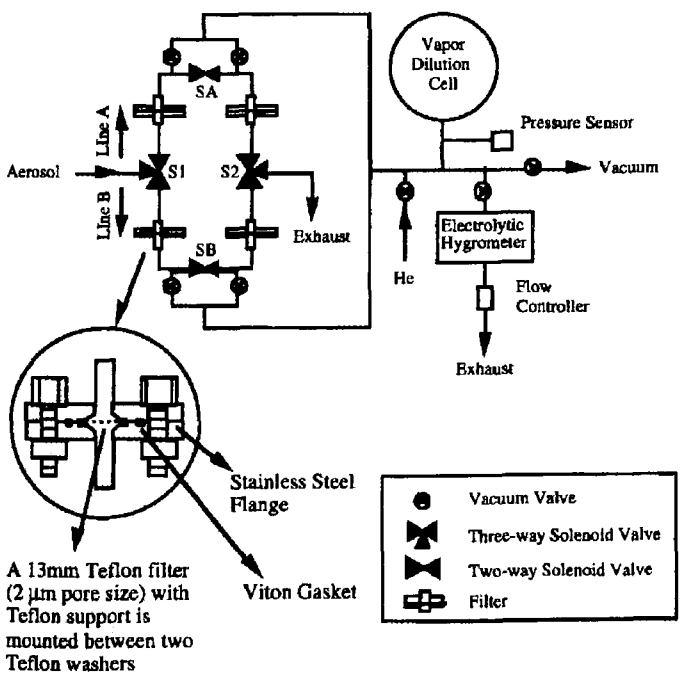


Figure 7. Systematic design of the multi-head filter holder.

2) Particle-Bound Water Detection System: The basic problem that must be overcome is the extremely high background water vapor concentration in the air compared to the water bound by particles at normal environmental conditions. Due to the rapid equilibrium between water vapor and particle surface water (milliseconds time-scale), there is no conventional method for separating the particle-bound water and its coexisting vapor without disturbing the phase equilibrium. The innovative concepts of our method are: 1) to collect particles over a relatively short time period (compared with the time scale of environmental variation); and 2) to collect the particles without disturbing the water equilibrium between the particle and gas phases (by maintaining the sampling system at the condition of the ambient environment); and 3) to minimize the sample cell volume in which the associated air remains. The particle-bound water can then be readily detected above the background in air by means of a highly sensitive moisture detector, such as a P_2O_5-Pt electrolytic hygrometer. The electrolytic hygrometer was chosen as a water detector because: 1) it has the lowest detection limits currently available; 2) it is relatively inexpensive; and 3) it is convenient to operate.



A schematic diagram of our semi-realtime analyzer for particle-bound water in accumulation mode aerosol is illustrated in Figure 8. The basis for the technique is the accretion of $PM_{2.5}$-$PM_{0.15}$ particles by means of a filter over a preset period of time. Two identical sample cells, each one consisting of a 13 mm Teflon membrane filter (2 μm pore size) and a small enclosure, are connected in series. The Teflon membrane filter was selected due to its excellent particle collection efficiency, low moisture uptake, and low trace background. The upstream sample cell collects and preconcentrates the particles in the sampled air from the 0.15 μm virtual impactor, while the second cell analyzes the backgrounds from the air and filter.

Figure 8. Schematic diagram of the system for continuous measurement of particle-bound water within $PM_{2.5}$

A pair of parallel sampling lines are used for alternating the sampling and analysis processes. They are

controlled by 2 three-way solenoid valves, the sample inlet valve (S1) and the exhaust valve (S2). When S1 and S2 switch to line A, the line A starts sampling and the line B starts analysis of the samples collected in the prior sampling period. At the end of the sampling period, both S1 and S2 switch, and the functions are reversed. During Line A sampling, solenoid valve SA opens. When switched to analysis, SA closes, and the two sample cells will be separated and analyzed in order. The air background goes first and the aerosol sample next. All the solenoid valves are controlled by an interfacing computer with a preset program.

The water detector consists of a 1000 cm^3 Vapor Dilution Cell (VDC), an Electrolytic Hygrometer, a flow controller, a pressure sensor, a vacuum line, and a helium gas line. The procedures for analysis of the water contents collected by each sample cell are: 1) evacuate the VDC; 2) close the vacuum line and open the VDC to the cell to be analyzed; 3) extract the water bound in the particles and absorbed on the filter and draw it into the VDC along with the air remaining in the cell by vacuum; 4) fill the system with helium gas to a pressure of about 900 torr (slightly higher than atmosphere); 5) open the system to the hygrometer, and allow a small flow (10 cm^3/min) to pass through the electrolytic sensor; and 6) start one measurement. The output signal is recorded and processed by an interfacing data acquisition system. The particle-bound water is determined from the difference between the measurements of the two cells. The filter of the aerosol sample cell is changed after each run.

A P_2O_5-Pt electrode is used to sense water vapor concentration in the system. It consists of a quartz tube wound with two platinum (Pt) wires. The winding is coated with a phosphorus pentoxide (P_2O_5) film, which has a high affinity for H_2O. A voltage is applied to the platinum winding so that the water molecules adsorbed on the P_2O_5 film are electrolyzed to H_2 and O_2 and a current flow is generated as described below:

Cathode reaction: $2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2$

Anode reaction: $2\ OH^- \rightarrow H_2O + \frac{1}{2}\ O_2 + 2\ e^-$

Since every H_2O molecule electrolyzed produces two electrons (based on Faraday's Law of Electrolysis) the current is directly proportional to the concentration of the H_2O molecules in the gas stream. This correlation is insensitive to gas pressure and mass flowrate. The sensor is commercially available for sampling moisture in gas streams and at normal atmospheric pressure. The working range is 0-1000 ppm with an accuracy of 2%. The lowest reported detection limit is 10 ppb.[21] The sample cell volume is 2 cm^3 (See Figure 8). For a flowrate of 1.8 lpm and a sampling time of 60 minutes, the concentration of particle-bound water is elevated by a factor of 5.4×10^5 in relation to its carrier air stream (including a preconcentration factor of 10 provided by the 0.15 virtual impactor). Therefore, the particle-bound water is measured despite the associated vapor in the air stream. A detection limit of the system for measuring particle-bound water is ~5 $\mu g/m^3$ of total particle mass concentration with a water composition of 15% at RH above 40%, and 5% at RH below 40%, in a sampling period of 60 minutes.

3) Tungstic Acid Technique - Chemiluminescent NO_x Detector (TAT-CLD) System for Measurements of Particulate Nitrate (NO_3^-) and Ammonium (NH_4^+): A system for continuous measurement of particulate NO_3 and NH_4^+ is shown in Figure 9. The system combines a two-channel chemiluminescent NOx Analyzer (Monitor Labs, Model 8840) with the Tungstic Acid Technique (TAT) developed by Braman et al.[22] The TAT was used by Braman et al.[22] for preconcentration and determination of gaseous and particulate nitrate and ammonia, based on the principle that nitrate and ammonia are quantitatively chemisorbed at the tungstic acid-coated surfaces at room temperature, and thermally desorbed at high temperature (350°C).

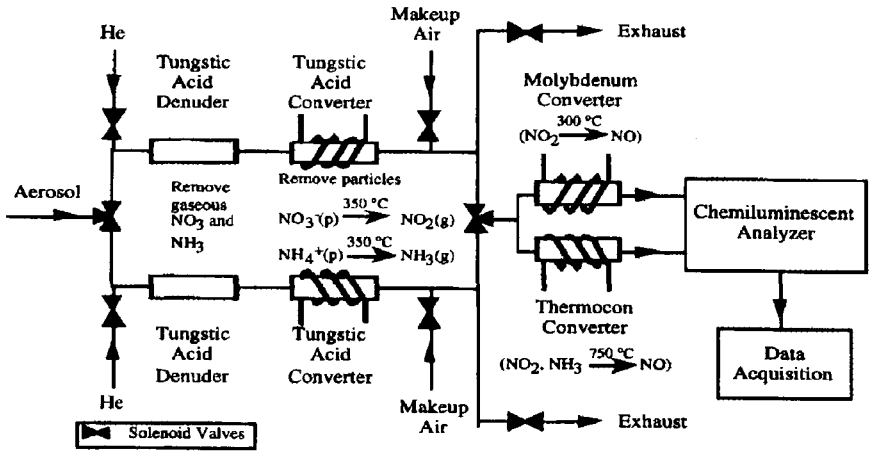


Figure 9. Schematic diagram of tungstic acid denuder and converter-chemiluminescent NO_x detector system for continuous measurement of nitrate and ammonium concentrations in accumulation mode particles.

The advantage of the TAT is that there is essentially no interference of aseous NO_x in either the NO_3^- or NH_4^+ analyses. The weakness of the Braman et al.[22] TAT is the limited particle collection efficiency of the TAF. For a 34 cm long three-section TAF, the particle penetration was as high as 22% at a sampling flowrate of 1 lpM.[22] Large packed tubes can be used to improve efficiency, but this limits the sampling flowrate attainable. In our system, the sample air is preconcentrated 10 times prior to entering the analysis system. The sampling flowrate of the TAT-CLD may be as low as 0.1 - 0.2 lpm without increasing the detection limit of the original TAT. Thus a much higher particle collection efficiency is achieved. A two-channel CLD is used for parallel detection of NO_3^- and NH_4^+ in our system, which simplifies the processes of sample separation. It also minimizes the sampling artifacts reported by Braman et al.[22]

The instrument detection limit of CLD is 2 ppb with a sampling flowrate of 250 ml/min for each channel. The detection limits of TAT-CLD system for ambient accumulation mode particulate NO_3^- and NH_4^+ are below 0.1 $\mu g/m^3$ for a 30-minute sampling period.

4) Data Acquisition and System Control: To automate the detection system and the data acquisition, we use a computer interfaced data acquisition and instrument control system. As shown in Figure 10, it consists of an IBM-PC computer, an Analog-to-Digital Converter Board (ADC), a four-channel Signal Conditioner, a Digital Interface Board, and a Multichannel Relay Board (MRB). The Signal Conditioner converts the signals from sensors to standard signals (0 - ± 5V, or 0 - ± 10V), which can be accepted by ADC. The signals received from ADC are recorded and stored in the computer at specified intervals. To control the solenoid valves, a MRB and a Digital Interface is used.

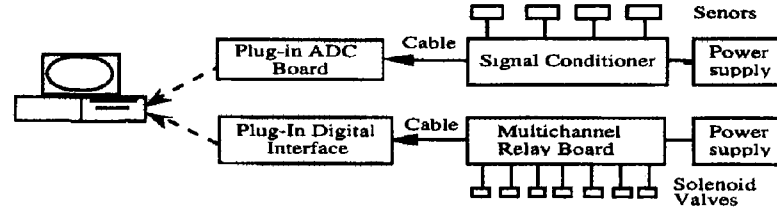


Figure 10. Schematic of the data acquisition and instrument control system.

DISCUSSION

An ambient PM monitoring package (prototype monitor) has been designed to be capable of continuous operation at our laboratories in New York City and in Tuxedo, NY, a location 50 miles north-northwest (NNW) of New York City. It will provide records of concentration data as a fimction of time for PM_{10} and eight of its components, including coarse mode particles (PM_{10}-$PM_{2.5}$), fine particles ($PM_{2.5}$), ultrafine particles ($PM_{0.15}$) and the constituents of the accumulation mode aerosol ($PM_{2.5}$-$PM_{0.15}$) of primary interest, including $SO_4^=$, NO_3^-, NH_4^+, H^+, H_2O, OC, and EC. Using three different pore sizes for the three mass fractions helps insure that interception will be the dominant collection mechanism and that each fraction will be collected within the optimum range for linear response. Using this monitoring system, researchers will be able to measure the mass concentrations of PM_{10} and $PM_{2.5}$ in near real-time, and without sampling artifacts due to sample volatilization and particle-bound water. They will also be able to develop data bases for the concentrations of specific components of $PM_{2.5}$ that may be causal factors for the PM-associated health effects of concern (e.g., H^+, $SO_4^=$, OC, EC, and ultrafines), thereby providing opportunities for more definitive epidemiological studies. Such studies could provide the basis for future NAAQS for specific PM components and thereby more rationale design and implementation of source controls of PM and/or PM precursors.

ACKNOWLEDGMENTS

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The consultation and support of Dr. Petros Koutrakis and his colleagues for our application of the filter resistance method for PM mass concentration measurement developed at the Harvard School of Public Health is also gratefully acknowledged.

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A REAL-TIME SAMPLER RAMS, FOR THE DETERMINATION OF $PM_{2.5}$, INCLUDING SEMI-VOLATILE SPECIES

F Obeidi, E. Patterson and D.J. Eatough
Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602 USA

The RAMS, Figure 1, is a real-time ambient monitor for the determination of fine particulate mass, including the volatile components (Eatough 1998). The RAMS has a particle concentrator, followed by diffusion denuders to remove gas phase compounds which can be absorbed by charcoal, a Nafion dryer to remove water, and a "sandwich filter" containing a Teflon coated filter to collect particles and a charcoal impregnated filter to retain

volatile components which can be lost from the particles during sample collection. Semi-volatile fine particulate material retained on the "sandwich filter" include ammonium nitrate and semi-volatile organic compounds. The "sandwich filter" is located at the tip of the tapered oscillating element of a TEOM monitor and mass retained on the "sandwich filter" is measured as a function of time.

The results obtained with the RAMS have been validated by comparison with results obtained from diffusion denuder integrated samples, to determine the mass of fine particulate material retained on a filter and the semi-volatile organic material and ammonium nitrate lost torn the filter during sampling. This has included comparisons with sampling periods for the denuder samplers as short as 1 hour. Results obtained with RAMS and denuder samplers for samples collected in Riverside CA in the summer and Bakersfield, CA in the winter show that semi-volatile fine particulate species are accurately monitored with the RAMS.

Research is currently underway to validate the measurement of volatile constituents of fine particles with the RAMS in chamber experiments using well characterized particles of ammonium sulfate, ammonium nitrate, glycerol and a carboxylic acid.

ACKNOWLEDGMENTS

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DYNAMIC NUCLEAR POLARIZATION (DNP): A NEW DETECTOR FOR ANALYSIS OF ENVIRONMENTAL TOXICANTS

Harry C. Dorn
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

The objective of this study is the development of a new analytical instrument designed for environmental monitoring applications. Specifically, this will consist of dynamic nuclear polarization detection with either direct-coupling continuous-flow supercritical fluid chromatography (SFC/DNP) or recycled-flow ^{13}C (DNP) analysis of toxicant mixtures. The DNP detector is a variant of the well known nuclear magnetic resonance (NMR) phenomena. A salient feature of NMR is the chemical shift parameter which provides a very sensitive probe of the local electronic environment about a given atom in a molecule. Thus, the DNP detector could have wide ranging applications for specific monitoring of various organic toxicants mixtures (e.g., chlorocarbons, organophosphates, pesticides, petroleum pollutants, etc.). A major limitation of NMR for most environmental monitoring applications has been sensitivity constraints. The DNP approach helps alleviate the sensitivity limitation of NMR by transfer of polarization from an electron spin to the nuclear spin of interest (^{1}H, $_{13}C$, ^{31}P, etc.). The corresponding DNP signal enhancements are proportional to the electron-to-nuclear magnetogyric ratio (γ_B/γ_n) which is on the order of 10^3-10^4 for most nuclides.

In this presentation, LC/DNP and SFC/DNP results for chlorocarbon mixtures will be presented, In addition, the results for continuous monitoring of a mixture of benzene and several chlorocarbons with a recycled-flow ^{13}C DNP instrument will also be presented. Finally, progress towards development of a routine SFC/DNP instrument will be reported.

PARTITIONING TRACERS FOR IN-SITU DETECTION AND MEASUREMENT OF NONAQUEOUS LIQUIDS IN POROUS MEDIA

Brusseau

ABSTRACT NOT AVAILABLE

QUALITY ASSURANCE

CD-R ARCHIVE AND CATALOG OF HEWLETT-PACKARD LOW RESOLUTION FORMAT DATA FROM NETWORKED GC/MS SYSTEMS

Robert G. Briggs and Herman Valente
The Wadsworth Center, New York State Department of Health,
Empire State Plaza, Box 509, Albany, New York 12201-0509
Phone (519)473-4871
robert.briggs@wadsworth.org

ABSTRACT

(1) Taped GC/MS data are not efficiently accessible; (2) Cataloging of archived data with descriptive information requires retyping information entered by the operator at the time of data acquisition. We have addressed these two problems, in our laboratory by archiving all of our data, generated on various Hewlett-Packard GC/MS systems, on CD-R (Compact Disk, Recordable) media. Data are initially sent to a Mylex Level 5 RAID array; then a CD is prepared using the Pinnacle Computing RCD-202 and associated RCD-PC software. A Microsoft Visual Basic program developed in-house (Arch-CD) extracts sample information entered at analysis time from each data file selected for archive and generates a Microsoft Access database (.MDB) file. This MDB file is included with the data files on the CD and also merged with an integrated database. The database along with the CDs on a changer provide instant access to five years of GC/MS data.

INTRODUCTION

Our laboratory applies EPA CLP (Contract Laboratory Protocol) volatilcs and semivolatiles methodology to water and soil samples or their extracts.

- We have four GC/MS systems dedicated to this work, three Hewlett Packard MSD systems and one Varian Saturn Ion Trap system.
- Submission rate for samples of all types averages a modest 750 per year. With daily calibration and other QC, which proceeds irrespective of sample submission, this translates to about 3000 GC/MS runs per year. The average input rate belies the fact that submission is episodic (figure 1) and that samples for a given instrument are received at a rate up to 30 per day, rather than the more prosaic one per day. Turnaround requirements cannot be adjusted to sample submission rate so we must be ready to handle the maximum.
- Prior to 1993, we were limited in disk space, even with a network of PCs, and data was archived on tape. In a major project where non-target analytes are of concern, it is desirable to reevaluate previously processed samples when a new class of substances is detected. The report time is inordinately extended because of the need to move data in and out of storage. Taped GC/MS data are not efficiently viewed or accessed.
- Once data are sent to long-term archive, key information should be put in a database to facilitate future access. A catalog of archived data should contain, at minimum, the descriptive information entered by the operator at the time of data acquisition, but retyping this information into a database is tedious and should be unnecessary.

SUMMARY

We have addressed these two problems of short-term data access and long-term accessibility in our laboratory. For five years we have been archiving all of our data, generated on various Hewlett-Packard GC/MS systems, on CD-R (Compact Disk, Recordable).

- Data are initially sent to a 1.2 Gigabyte partition on a Mylex Level 5 RAID array.
- Then they are mastered using RCD-PC software for the Pinnacle Computing RCD-202 onto a 0.8 Gigabyte partition on the RAID array.
- CD-R disks are prepared and transferred to SCSI chained Pioneer 604X/624X six disk changers.
- CDs beyond the twelve accessible disks are kept in 6-disk cartridges for insertion in the changer and reasonably rapid access.
- A Microsoft Visual Basic program developed in-house (Arch-CD) extracts sample information entered at analysis time from each data file selected for archive and generates a Microsoft Access database (.MDB) file. This is included with the data files on the CD.
- A master database is built up from individual MDB format files.
- The success of this system is illustrated for analysis of volatile organics in water (figure 2). Although the percentage of total time from sample receipt to the analytical report dedicated to data processing has remained a constant 80% - 90%, the total time necessary for analysis and report has fallen significantly since

implementation of this system, from 40 days (or more) to 10 -20 days. During this time, the rate of submission for samples in this category actually increased (figure 1).

- The long report time events of 1995 (figure 2) were due to data glut on our ion trap system, one of the two systems used for water volatiles. This low-level ion-trap system was only recently connected to the network, has limited hard disk storage and has depended on tape backup. We have avoided recurrence of this problem by networking the instrument and archiving its data with those from the HP systems. We have not yet developed information-extraction methodology to incorporate these Saturn data into the database. Hewlett Packard publishes the structure of data files for users whereas Varian does not.

CONCLUSION

Accumulated sample information from a five-year-period is now accessible for HP systems and the data files are readily retrieved for use.

THE USE OF ACCEPTABLE KNOWLEDGE FOR THE CHARACTERIZATION OF TRANSURANIC WASTE IN THE DEPARTMENT OF ENERGY COMPLEX

R. Vann Bynum
Science Applications International Corporation, 2109 Air Park Road S.E., Albuquerque, NM 87109
R. Butch Stroud and R. Denny Brown
Department of Energy, Carlsbad Area Office, 4021 National Parks Highway, Carlsbad, NM 88220
Laurie D. Sparks
Waste Isolation Division, Westinghouse Electric Co., a Division of CBS,
P.O. Box 2078, Carlsbad, NM 88221

ABSTRACT

The Resource Conservation and Recovery Act (RCRA) regulations codified in 40 CFR Parts 260 through 265, 268, and 270, authorize the use of acceptable knowledge as a method which can be used in appropriate circumstances by waste generators, or treatment, storage, or disposal facilities to make hazardous waste determinations. Acceptable knowledge, as an alternative to sampling and analysis, can be used to meet all or part of waste characterization requirements under RCRA.

One example of the use of acceptable knowledge within the U. S. Department of Energy (DOE) complex is the waste characterization requirements for the Waste Isolation Pilot Plant (WIPP), a deep geologic repository for the disposal of transuranic (TRU) waste. The WIPP will be disposing of TRU mixed and non-mixed waste from various generators within the DOE complex in accordance with the provisions of the DOE Carlsbad Area Office (CAO) Quality Assurance Program Plan, the EPA Final Certification Decision, an anticipated RCRA Permit, and the WIPP Waste Acceptance Criteria. Part B of the WIPP RCRA Permit application contains a Waste Analysis Plan which describes the measures that will be taken by the DOE/CAO to assure that mixed wastes received at the WIPP repository are characterized appropriately. To satisfy the characterization requirements, acceptable knowledge is confirmed by radiography, drum headspace gas sampling and analysis, and solidified waste sampling and analysis. Acceptable knowledge is primarily used in TRU waste characterization activities to delineate TRU waste streams, to determine if TRU debris wastes exhibit a toxicity characteristic (40 CFR 261.24), and to determine if TRU wastes are listed (40 CFR 261.31). The physical form and the increased health and safety risks associated with obtaining a representative sample of TRU debris wastes, clearly justify the use of acceptable knowledge in making hazardous waste determinations.

DOE complex waste generators apply knowledge of their waste based on the materials and processes used to generate the waste. Acceptable knowledge includes information regarding the physical form of the waste, the base materials composing the waste, the nature of the radioactivity present, and the process(es) generating the waste.

The DOE/CAO audits the TRU waste generators to grant TRU waste certification authority to the generators. The DOE/CAO conducts audits at least annually thereafter to verify ongoing compliance with approved plans and procedures including those for waste characterization using acceptable knowledge. The information resulting

from DOE/CAO audits is used by the DOE/CAO to help sites across the DOE complex prevent or solve problems associated with the compilation and use of acceptable knowledge for TRU waste characterization. Past and current issues with respect to the compilation, use, and defensibility of acceptable knowledge for TRU waste characterization along with the solutions to those problems and their prevention will be addressed.

INTRODUCTION

Waste Isolation Pilot Plant (WIPP)

The WIPP is a deep geologic repository designed to permanently dispose of transuranic (TRU) radioactive waste generated from the research, development, and production of nuclear weapons in an evaporite salt formation. The mission of the WIPP Project, as authorized by the U.S. Congress in 1979 (Public Law 96-164), is to provide a research and development facility to demonstrate the safe disposal of TRU waste generated as a result of United States defense activities. WIPP is located in Eddy County in southeastern New Mexico about 26 miles east of Carlsbad, New Mexico, in an area known as Los Medanos - a relatively flat, sparsely inhabited plateau with little surface water. WIPP encompasses a 16-square mile area under the jurisdiction of the U.S. Department of Energy (DOE) pursuant to the Land Withdrawal Act.[1] The site boundary was established to ensure that at least 1 mile of intact salt exists laterally between the waste disposal area and the accessible environment and to ensure that no permanent residences will be established in close proximity to the facility.

The DOE's objective is to operate and maintain the WIPP free of both chemical and radiological contamination. Therefore, all waste sampling and analyses will be conducted by the DOE generator/storage sites in accordance with the requirements of the WIPP Waste Analysis Plan (WAP, Chapter C of the RCRA Part B Permit Application)[2] and the WIPP Compliance Certification Application (Chapter 4)[3] as allowed by 20 New Mexico Administrative Code (NMAC) 4.1, Subpart V, Paragraph 264.13, and consistent with joint U.S. Environmental Protection Agency (EPA) and U.S. Nuclear Regulatory Commission guidance.

Transuranic Waste

The transuranic (TRU) elements have atomic numbers greater than that of uranium (92). Examples of transuranic elements include neptunium (Np), plutonium (Pu), americium (Am), curium (Cm), etc. Each element typically has several isotopes and is produced during nuclear reactions. These man-made elements are radioactive and provide the key components for building nuclear weapons.

Transuranic waste consists of clothing, tools, rags, and other items contaminated with trace amounts of radioactive TRU elements - mostly plutonium. TRU waste is defined[1] as "waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, per gram of waste, with half-lives greater than 20 years, except for a) high-level radioactive waste, b) waste that the Secretary has determined, with concurrence of the Administrator, does not need the degree of isolation required by the disposal regulations; or c) waste that the Nuclear Regulatory Commission has approved for disposal on a case-by-case basis in accordance with Part 61 of Title 10, Code of Federal Regulations."

TRU-mixed waste is waste that is commingled with hazardous materials, such as lead or organic solvents. It is regulated by both the Atomic Energy Act and RCRA (as defined in 20 NMAC 4.1, Subpart VIII, Paragraph 268.35(d) and in the Federal Facility Compliance Act.[4] TRU-mixed waste has physical and radiological characteristics similar to TRU waste. The majority of TRU-mixed waste contains relatively small quantities of spent halogenated solvents, which were used in cleaning and degreasing of equipment, glassware, and components. Based on sampling of gases within TRU waste drums, the most common volatile organic hazardous constituents are methylene chloride, carbon tetrachloride, and 1,1,1-trichloroethane.[5] TRU-mixed waste also contains various RCRA-regulated metals. These metals are usually associated with solid materials, such as lead shielding. Lead, chromium, and cadmium are the most prevalent hazardous metals in TRU-mixed waste. TRU-mixed waste constitutes approximately 60 percent of the DOE's TRU waste.[6] The hazardous components of TRU-mixed waste to be managed at the WIPP are designated in Part A of the RCRA Permit application.[2] Henceforth, the term TRU waste used in this paper includes both TRU and TRU-mixed waste.

Transuranic Waste Generator/Storage Sites

TRU waste has accumulated over the past 50 years as a result of weapons development and production at U.S. defense facilities. Since 1970, DOE has segregated TRU waste from other radioactive waste and stored it in a manner that allows it to be retrieved. TRU waste to be emplaced at WIPP has resulted primarily from the following: (1) nuclear weapons development and manufacturing, (2) plutonium recovery, (3) defense research and development, (4) environmental restoration, (5) decontamination and decommissioning, (6) waste

management, and (7) testing at facilities that are under DOE contract.

Table 1 has been reproduced from the National TRU Waste Management Plan.[7] It lists the volumes of TRU waste currently in storage and the volumes of TRU waste projected to be generated by ongoing and new missions during the life of the WIPP. Estimates from environmental restoration, decontamination and decommissioning and future missions are also included. The nuclear weapons complex consists of ten major facilities, including those at large reservations listed in the upper half of Table 1.

Table 1. TRU Waste Storage Locations and Pre-treatment Volumes (cubic meters)[7]

		Contact-Handled TRU Waste		Remote-Handled TRU Waste	
Site	**Location**	**Stored***	**Projected through 2033****	**Stored***	**Projected through 2033****
Argonne National Lab.-East	Argonne,IL	94	109	0	0
Hanford Reservation	Richland, WA	16,127	7,305	200	1,592
Idaho National Engineering and Environmental Lab.	Idaho Falls, ID	64,575	15,009	86	53
Lawrence Livermore National Lab.	Livermore, CA	297	835	0	0
Los Alamos National Lab.	Los Alamos, NM	8,255	8,544	101	128
Mound Plant	Miamisburg, OH	241	6	0	0
Nevada Test Site	Nevada	618	19	0	0
Oak Ridge National Lab.	Oak Ridge, TN	917	180	1,268	100
Rocky Flats Environmental Technology Site	Golden, CO	1,505	6,988	1,268	100
Savannah River Site	Aiken, SC	11,725	17,811	1	21
Small-Quantity Sites					
Ames Laboratory	Ames, IA	0	<1	0	0
ARCO *Medical Products Company*	West Chester, PA	<1	<1	0	0
Babcock & Wilcox-NES	Lynchberg, VA	20	0	0	0
Battelle Columbus Laboratories	Columbus, OH	0	0	0	369
Bettis Atomic Power Laboratory	West Mifflin, PA	0	114	0	2
Energy Technology Engineering Center	Santa Susana, CA	7	0	0	1
General Electric-Vallecitos Nuclear Center	Pleasanton, CA	6	3	8	5
Knolls Atomic Power Lab.	Niskayuna, NY	0	0	<1	5
Lawrence Berkeley Lab.	Berkeley, CA	<1	4	0	0
Missouri University Research Reactor	Columbia, MO	<1	1	0	0
Paducah Gaseous Diffusion Plant	Paducah, KY	2	0	0	0
Sandia National Laboratories	Albuquerque, NM	7	44	1	3
U.S. Army Material Command	Rock Island, IL	2.5	0	0	0
Total Waste Volumes***		104,400	56,972	1,666	2,268

* Volumes Prior to treatment and repackaging.

** Projected volumes include estimates from environmental restoration, decontamination and decommissioning, and future Departmental missions, for example, the disposition of weapons-useable plutonium at the Savannah River Site. Estimates will change based upon future compliance actions under environmental law.

*** Totals reflect rounding of numbers.

Continued temporary storage of TRU waste at these and other sites across the nation poses potential problems. For example, some of the metal drums used to store TRU waste are showing signs of corrosion, and the contents of these drums eventually will have to be repackaged. Not only would additional storage facilities be needed at the generator/storage sites, but also additional worker exposures to penetrating radiation would occur due to

repackaging and inspection of waste containers. New treatment capacity would also be needed because much of the TRU waste is subject to RCRA Land Disposal Restrictions and cannot be placed in or on the land unless it is treated to satisfy those restrictions. Sound environmental practice requires that TRU waste be permanently isolated to prevent human exposure for many generations to come.

TRANSURANIC WASTE CHARACTERIZATION

The process of identifying and classifying the chemical, physical, and radiological constituents of each drum of waste is a critical aspect of waste characterization. TRU waste characterization is a subset of the waste certification process and is based on sampling and analysis combined with acceptable knowledge of each waste stream in accordance with the requirements of the TRU Waste Characterization Quality Assurance Program Plan[8] (QAPP). The QAPP utilizes a performance-based approach to allow individual sites to have the flexibility to employ analytical and examination methods that meet the quality assurance objectives specified in the Waste Analysis Plan (WAP)[2] and implemented by the requirements of the QAPP.

Retrievably stored[i] TRU waste will be characterized by the generator/storage sites as the waste is retrieved. Newly generated[ii] TRU waste will be characterized as it is generated. Waste characterization requirements for retrievably stored and newly generated wastes are slightly different and are discussed in the WAP. Waste characterization activities at the generator/storage sites include the following, although not all of these techniques will be used on each container:

- Acceptable Knowledge: Compilation of documented characterization and/or process knowledge into an auditable record
- Headspace-gas sampling and analysis: Used to determine volatile organic compound (VOC) content of gases in the void volume of the containers
- Sampling and analysis of homogeneous solid waste forms: Used to determine concentrations of hazardous waste constituents and toxicity characteristic contaminants of waste in containers
- Radiography: an x-ray technique used to determine physical contents of containers
- Visual examination: Used to verify radiography results
- Radioassay: Used to identify isotopic inventory and associated activity

The origins of these requirements in the WAP are traceable to applicable regulatory requirements and commitments made to regulatory authorities such as the NMED and the EPA.

NMED Basis for Waste Characterization

The Waste Analysis Plan (WAP), Chapter C of the RCRA Part B Permit Application,[2] describes the measures that will be taken to assure that TRU waste received at the WIPP facility is within the scope of the RCRA permit as established in and with unit-specific requirements of Title 20 of the New Mexico Administrative Code, Chapter 4, Part 1, Subpart V, Paragraph 264.13 (20 NMAC 4.1). The WAP establishes waste characterization requirements that are referenced in the Waste Acceptance Criteria (WAC),[9] the QAPP, and the TRU-waste generator/storage sites Quality Assurance Project Plans (QAPjPs). It includes descriptions of waste parameters, rationale, and characterization methods; waste sampling and analysis strategies; waste shipment screening and verification processes; and a quality assurance (QA)/quality control (QC) program.

The WIPP underground disposal unit is classified as a "miscellaneous unit" subject to regulation under 40 CFR Part 264, Subpart X. Permit applications for miscellaneous units must describe the wastes to be managed and assess the potential environmental impacts associated with the proposed waste management activities. A listing of the EPA Hazardous Waste Numbers that may be associated with the waste to be emplaced in the miscellaneous unit is contained in Part A of the WIPP RCRA Permit Application.[2] This listing was determined by a survey of the generator/storage sites' TRU waste inventories and includes such RCRA-regulated constituents as:

- toxic characteristic contaminants listed in 20 NMAC 4.1, Subpart II, Paragraph 261.24, Table 1 (corresponding to 40 CFR 261, Subpart C, Paragraph 261.24) except for pesticides,

[i] Retrievably stored waste is defined as waste generated after 1970 and before implementation of the QAPP characterization requirements.

[ii] Newly generated waste is defined as waste generated after implementation of QAPP characterization requirements.

- F-listed solvents (F001, F002, F003, F004, F005, F006, F007, and F009) found in 20 NMAC 4.1, Subpart I, Paragraph 262.31 (corresponding to 40 CFR 261, Subpart D, Paragraph 261.3 1), and
- hazardous constituents included in 20 NMAC 4.1, Subpart H, Paragraph 261, Appendix VII (corresponding to 40 CFR 261, Appendix VIII).

Waste is characterized on a waste stream basis. A waste stream is defined as waste material generated from a single process or from an activity that is similar in material, physical form, and hazardous constituents. Wastes are initially categorized into three broad Summary Category Groups that are related to the final physical form of the wastes. These groups include homogeneous solids (Summary Category S3000), soil/gravel (Summary Category S4000), and debris wastes (Summary Category S5000). Waste streams are grouped by Waste Matrix Code Groups related to the physical and chemical properties of the waste. Generator/storage sites must use the characterization techniques described in the WAP to assign appropriate Waste Matrix Code Groups for WIPP disposal. The Waste Matrix Code Groups are solidified inorganics, solidified organics, salt waste, soils, lead/cadmium metal, inorganic nonmetal waste, combustible waste, graphite, filters, heterogeneous debris waste, and uncategorized metal.

A statistically selected portion of waste containers from waste streams of homogeneous solids and soil/gravel will be sampled and analyzed for total volatile organic carbons (VOCs), semi-volatile organic compounds (SVOCs), and metals. TRU waste classified as debris wastes will be characterized based on acceptable knowledge. Acceptable knowledge refers to applying knowledge of the hazardous characteristic of the waste in light of the materials or processes used to generate the waste. The use of acceptable knowledge is outlined in a guidance manual[10] wherein the EPA has specifically referred to the characterization of radioactive mixed waste as a situation where the use of acceptable knowledge is appropriate.

Since waste containers will not be opened to perform confirmatory sampling at the WIPP site, waste characterization data produced at the site is reviewed at three levels to ensure it meets Program needs and objectives. At the data generation level, data are reviewed, validated, and verified. Data packages are submitted to the project level for validation and verification. The third and final level is the CAO level at which data from the project level are verified.

Data review determines if the raw data have been properly collected and ensures raw data are properly reduced. Data validation confirms that the data reported satisfy the requirements defined by the user (e.g., quality assurance objectives and data quality objectives) and is accompanied by signature release. Validation at each level ensures that certain aspects of characterization and quality assurance have been met. Data verification authenticates that data are in fact that which is claimed.

EPA Basis for Waste Characterization

An estimate of each generator/storage site TRU waste inventory was compiled in the TRU Waste Baseline Inventory Report,[11] modeled by the performance assessment,[3] and evaluated using a sensitivity analysis to determine the impact of each waste component on the long term performance of the repository. The results of the sensitivity analysis identified several parameters that must be monitored and tracked to assure the validity of assumptions used in the performance assessment. These parameters are listed in an Appendix to the Compliance Certification Application (CCA)[3] entitled "Waste Component Limits" (WCL). Being that Appendix WCL identifies the radionuclide content of the waste as one of the components to be monitored and tracked, radiological characterization of the waste by radioassay is of concern to the EPA.

ACCEPTABLE KNOWLEDGE

The use of acceptable knowledge is discussed in the EPA document, "Waste Analysis: EPA Guidance Manual for Facilities that Generate, Treat, Store and Dispose of Hazardous Wastes."[10] This document points out that there are situations where it may be appropriate to apply acceptable knowledge to characterize hazardous waste. One of these, which is applicable to the type of waste that will be accepted for disposal in the WIPP, is that the physical nature of the waste does not lend itself to the acquisition of a representative sample. Additionally, the RCRA regulations codified in 40 CFR Parts 260 through 265, 268, and 270, authorize the use of acceptable knowledge as a method which can be used in appropriate circumstances by waste generators, or treatment, storage, or disposal facilities to make hazardous waste determinations. Acceptable knowledge, as an alternative to sampling and analysis, can be used to meet all or part of waste characterization requirements under RCRA.

Acceptable knowledge refers to applying knowledge of the waste based on the materials or processes used to generate the waste. Acceptable knowledge includes information regarding the physical form of the waste, the base materials composing the waste, the nature of the radioactivity present, and the process generating the waste. Acceptable knowledge is used to assign matrix parameter categories and EPA hazardous waste numbers to waste streams and to determine the waste material parameters and radionuclides present in waste streams. The collection and use of acceptable knowledge information applies to both retrievably stored and newly generated waste streams.

To satisfy the characterization requirements of the WAP, acceptable knowledge is confirmed by radiography, drum headspace gas sampling and analysis, and solidified waste sampling and analysis. Acceptable knowledge is primarily used in TRU waste characterization activities to delineate TRU waste streams, to determine if TRU debris wastes exhibit a toxicity characteristic (40 CFR 261.24), and to determine if TRU wastes are listed (40 CFR 261.31). The physical form and the increased health and safety risks associated with obtaining a representative sample of TRU debris wastes, clearly justify the use of acceptable knowledge in making hazardous waste determinations.

DOE complex waste generators apply knowledge of their waste based on the materials and processes used to generate the waste. A generator site can establish the characterization of a waste stream by demonstrating an understanding of the materials which are introduced into the process, and the process(es) which those materials undergo. Understanding the process(es) which a material may undergo is very important, particularly with respect to toxicity characteristic wastes, because some chemical processes may result in a change in concentration of the RCRA constituents. Assignment of F-listed wastes also depends on knowledge of the process that produces the waste. A change in concentration of the RCRA constituents during a process could result in a new waste stream containing constituents with concentrations that are above the regulatory threshold. In the case of certain compounds which may be either listed or toxicity characteristic, the use of acceptable knowledge is the only viable route to determine whether a substance was utilized for its solvent properties or not. If a constituent was used for its solvent properties, the waste stream would be assigned an F code. If the constituent was not utilized for its solvent properties, it would be evaluated for the assignment of a D code, if appropriate.

The Land Withdrawal Act[1] included a number of requirements and restrictions on the wastes that can be disposed of at the WIPP Among these requirements and restrictions are that the waste be generated by atomic energy defense activities and that it is neither high-level waste nor spent nuclear fuel. DOE can verify compliance with these conditions only through the use of historical information about the processes that generated a particular waste stream. This historical information is a component of the acceptable knowledge record that is assembled and assessed by the waste generators.

Consistency among sites in using acceptable knowledge information to characterize TRU waste involves a three phase process: 1) compiling the minimum acceptable knowledge documentation in an auditable record; 2) confirming acceptable knowledge information using radiography, and headspace gas and solidified waste sampling and analysis; and 3) auditing acceptable knowledge records. The consistent presentation of acceptable knowledge among sites in auditable records will allow WIPP personnel to verify the completeness of acceptable knowledge and determine that the accuracy of acceptable knowledge has been documented for TRU waste characterization during the audit process.

AUDITING ACCEPTABLE KNOWLEDGE RECORDS

The DOE/CAO audits the TRU waste generators to grant TRU waste certification authority to the generators. The DOE/CAO conducts audits at least annually thereafter to verify ongoing compliance with approved plans and procedures including those for waste characterization using acceptable knowledge. The information resulting from DOE/CAO audits is used by the DOE/CAO to help sites across the DOE complex prevent or solve problems associated with the compilation and use of acceptable knowledge for TRU waste characterization. Past and current issues with respect to the compilation, use, and defensibility of acceptable knowledge for TRU waste characterization along with the solutions to those problems and their prevention are addressed in this section.

The Audit Process

CAO conducts an initial audit of each site to evaluate waste stream and program documentation prior to certifying the site for shipment of TRU waste to the WIPP facility. The initial audit establishes a baseline that will be reassessed annually. The audits are used to ensure the consistent compilation, application, and interpretation

of acceptable knowledge information throughout the DOE complex and to evaluate the completeness and defensibility of site-specific acceptable knowledge documentation related to hazardous waste determinations.

Acceptable knowledge audit checklists typically include, but are not limited to, the following elements for review during the audit:

- Documentation of the process used to compile, evaluate, and record acceptable knowledge is available and implemented
- Personnel training and qualifications are documented
- All of the required acceptable knowledge documentation has been compiled in an auditable record
- Procedures exist for:
  - assigning EPA hazardous waste numbers to waste streams
  - assigning a matrix parameter category to a waste stream
  - determining waste material parameters present in a waste stream
  - determining the radionuclides present in a waste stream
  - resolving inconsistencies in acceptable knowledge documentation
  - confirming acceptable knowledge information through: a) radiography or visual examination, b) headspace gas sampling and analysis, and c) solidified waste sampling
- Results of other audits of the TRU waste characterization programs at the site are available in site records

Auditors assess all documents associated with the evaluation of the acceptable knowledge documentation for at least one debris waste stream and one solidified waste stream during the audit. For these waste streams, auditors review all procedures and associated processes developed by the site for: documenting the process of compiling acceptable knowledge documentation; correlating information to specific waste inventories; assigning EPA hazardous waste numbers; assigning matrix parameter categories; determining waste material parameters; determining the radionuclides; and identifying, resolving, and documenting discrepancies in acceptable knowledge records. The adequacy of acceptable knowledge procedures and processes is assessed and any discrepancies in procedures are documented in the audit report.

Auditors review the acceptable knowledge documentation for selected waste streams for logic, completeness, and defensibility. The criteria used by auditors to evaluate the logic and defensibility of the acceptable knowledge documentation include completeness and traceability of the information, clarity of presentation, degree of compliance with the requirements of the QAPP and WAP with regard to acceptable knowledge confirmation data, nonconformance procedures, and oversight procedures. Auditors evaluate compliance with written site procedures for developing the acceptable knowledge record. A completeness review is done to evaluate the availability of the minimum required TRU waste management and TRU waste stream information. Records are reviewed to assess the correlations to specific waste streams and to assess the basis for making waste determinations. Auditors verify that sites include all required information and conservatively assign all potential EPA hazardous waste numbers indicated by the acceptable knowledge records. All deficiencies found in the acceptable knowledge documentation are included in the audit report.

Auditors verify and document that sites use management controls and follow written procedures to make waste determinations for newly generated and retrievably stored wastes. Auditors review procedures used by sites to confirm acceptable knowledge information using radiography or visual examination, headspace gas sampling and analysis, and solidified waste sampling and analysis. Procedures to document changes in acceptable knowledge documentation, EPA hazardous waste number assignments, matrix parameter category assignments, waste material parameter determinations, and radionuclide determinations to specific waste streams are also evaluated.

After the audit is complete, CAO prepares a final audit report that includes all observations and findings identified during the audit. Sites are required to respond to all audit findings and identify corrective actions. If acceptable knowledge procedures do not exist, the minimum required information is not available, or findings of

noncompliance associated with waste determinations are identified, CAO will not grant the site characterization and certification authority for the subject waste. Waste stream characterization and certification authority may be revoked or suspended if findings during subsequent annual audits indicate a lack of compliance with approved acceptable knowledge procedures.

Acceptable Knowledge Issues

To date, the Department of Energy, Carlsbad Area Office has certified three generator/storage sites: Los Alamos National Laboratory (September 1997), Rocky Flats Environmental Technology Site (March 1998), and Idaho National Engineering and Environmental Laboratory (April 1998). These sites have undergone initial and final audits of their certification and acceptable knowledge processes and have successfully met all WAP criteria for characterizing their TRU waste via acceptable knowledge. Issues that the audit team encountered during audits of the adequacy, implementation, and effectiveness of the sites' acceptable knowledge procedures/processes are summarized below.

Adequacy

Procedural inadequacy was a common problem encountered by the audit team. The WIPP requires the "proceduralization" of every aspect of the acceptable knowledge process, from compilation and evaluation of the acceptable knowledge documentation, to reconciliation of discrepancies in the documentation, to waste stream designation and assignment of EPA hazardous waste codes. The following procedural inadequacies were noted by the audit team:

- The responsible party(ies) for some tasks identified in the procedures was not specified
- A list of the documents generated as a result of implementing the procedure was not specified
- Proper approvals for procedures were not obtained prior to implementation
- Approvals for procedures were not adequately documented
- Various requirements were omitted from procedures, such as a specification to look for prohibited waste items
- Necessary or required procedure steps, or forms, or references to other related procedures were not specified

Implementation and Effectiveness

If the acceptable knowledge process procedures are adequate and complete, the satisfactory implementation of these procedures results in accurate and defensible characterization of the waste by the generator, i.e. an effective process. When procedures are not implemented correctly, the result is an incorrect determination, or an inability to characterize the waste using acceptable knowledge, or an ineffective process. The audit team noted several deficiencies with respect to the implementation and effectiveness of acceptable knowledge process procedures:

- Various processes, such as that for amending acceptable knowledge records, were not established
- Some procedures did not reflect current practice
- Some procedures were not being property implemented
- The acceptable knowledge documentation was not traceable to source documents the acceptable knowledge documentation was not compiled into an auditable package or record
- Some sites that subcontracted the acceptable knowledge process work did not include requirements for qualification/training of personnel or a requirement to prepare and train the site personnel in the statement of work for the subcontractor
- The required analytical data and/or acceptable knowledge documentation was not available or insufficient to support the conclusions or EPA hazardous waste code assignments
- Retrieval of records (source documents, etc.) was difficult, time consuming, or impossible
- Documentation of training for various acceptable knowledge processes (review of acceptable knowledge documentation, etc.) was non-existent or insufficient
- EPA hazardous waste codes were removed without sufficient documentation that a discrepancy process was followed
- Acceptable knowledge documentation contains statements that are not corroborated by the source documentation

- The process for the assignment of EPA hazardous waste codes was not consistent with QAPP/WAP requirements
- The acceptable knowledge summary report did not list all potential constituents as shown in supporting documentation
- Documentation to justify that the waste was generated as a result of atomic energy defense activities was insufficient
- Acceptable knowledge documentation for radionuclide distribution was not adequate to support radioassay data to confirm the radionuclide inventory and obtain total activity in TRU waste
- The EPA hazardous waste code for a constituent identified in the acceptable knowledge documentation as being present in the waste was not assigned
- Inconsistencies or discrepancies between acceptable knowledge documentation and/or analytical data were not reported (packaging configuration, volume of waste, etc.)

CONCLUSIONS

Acceptable knowledge provides a reasonable and appropriate means to characterize nuclear waste for disposal. Acceptable knowledge is the only route by which certain characterization decisions (e.g. the origin of the waste being from defense activities, the use of solvents) may be made. The DOE and the waste generator sites have developed and implemented an adequate system for the collection, assessment, and utilization of acceptable knowledge for characterizing waste to be disposed of at the Waste Isolation Pilot Plant.

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PERFORMANCE EVALUATION SOIL SAMPLES FOR VOLATILE ORGANIC COMPOUNDS UTILIZING SOLVENT ENCAPSULATION TECHNOLOGY

James Dahlgran
U.S. Department of Energy, Idaho National Engineering and Environmental Laboratory,
850 Energy Drive, NIS 4149, Idaho Falls, ID 83401
Curt Thies
Thies Technology, 3720 Hampton, Suite 207, St.Louis, MO 63109-1438

Abstract
A mixture of volatile organic compounds (VOCs) was encapsulated and mixed with soil to produce a product suitable for use as a double blind source of VOCs in soil performance evaluation sample. Two independent laboratories analyzed the standard encapsulated VOC/soil mixture for benzene, toluene, ethylbenzene and xylene by using U.S. EPA SW-846 Method 5030 in conjunction with SW-846 Method 8020. One laboratory received the sample as a single blind standard while the other laboratory received the sample as a double blind standard. The percent relative standard deviation (%RSD) for triplicate analyses ranged from 2.4 to 7.7. The lowest %RSD was for meta/para-xylene (2.4%) from the sample analyzed as a double blind sample. Analytical results from these pilot studies indicate that it is possible to prepare standard soil samples contaminated with known amounts of VOCs, which unlike current market technology, will enable soil samples to be submitted to environmental analytical laboratories as a truly blind sample.

Introduction

For most environmental analytical procedures, demonstrating proficiency of an analytical method is accomplished utilizing known spiked samples, blanks, surrogate spikes and appropriate performance evaluation standards. For analysis of volatile organic compounds (VOCs) in soils, the performance evaluation standards are primarily methanolic solutions that contain target analytes and are spiked into a soil sample immediately prior to analysis.

Demand for precise performance evaluation samples for VOCs in soil matrices has stagnated due to lack of sample preparation technology. Current technology for preparing volatile performance evaluation samples utilize solvent spiking procedures[1] or vapor fortification methodologies developed by J. Hewitt[1] of the U.S. Army Cold[2] Regions Research and Engineering Laboratory. Private sector companies typically provide analysts a dilute solution of analytes in a solvent, usually methanol. These methanol solutions are introduced either into the analytical technique (purge and trap or headspace analyses) or placed onto sand[3] (used to simulate soil) immediately prior to instrumental analysis. These practices do not adequately replicate soil sample handling procedures in the analytical laboratory. Liquid standards also inappropriately provide the analysts with an opportunity to analyze the spiking solution.

Although vapor-fortified soils provide a means of examining spiked soils that are analogous to soils isolated from the environment, such standards are difficult to disseminate to analytical laboratories as a double blind quality control standard. An ideal VOCs in soil standard should provide analyte concentrations across the concentration range of 5 µg/kg to 100 µg/g. Vapor fortification methodology can be customized to decrease concentrations below 100 µg/g, but it is less amenable to water soluble analytes such as acetone or 2-butanone and some target analytes are lost due to the varying absorbtivity of vastly differing soil matrixes. Early attempts to spike, homogenize and transfer soil performance standards were unsatisfactory.[4]

To create a true volatiles in soil performance evaluation standard:
1. Volatile target analytes of interest must be unknown to the analyst.
2. Target analytes must be provided to the analyst in the soil matrix.
3. Volatile components must be protected from potential soil biological activity.
4. The standard must be stable over an extended period of time.
5. The target analytes must provide the laboratory with a wide range of VOC concentrations that are accurate and reproducible independent of analytical methodology applied.

In order to meet these specifications, a novel method of spiking native soil samples is required. The objective of this work is to demonstrate that microencapsulated VOCs provide a novel method of spiking soils and offer an improved means of assessing precision and accuracy of VOC analyses of contaminated soils reported by different analytical laboratories.

Experimental

Microcapsules loaded with a VOC mixture (1:1:1 (V/V/V) toluene, p-xylene and ethylbenzene) were formed by complex coacervation[5]. Figure 1 is a diagram of a typical complex coacervation encapsulation protocol. The shell of the microcapsules formed is primarily gelatin cross-linked with glutaraldehyde.

Standard contaminated soil samples were produced by dispersing a known weight of microcapsules loaded with the VOC mixture into a known weight of soil. Dry subsurface soil taken from the Idaho National Engineering and Environmental Laboratory (INEEL) was sieved (60-80 mesh) and mixed with microcapsules to form a uniform soil/microcapsule mixture. Figure 2 shows the steps envisioned for the preparation of a standard performance evaluation soil sample that unitizes microencapsulated VOCs.

VOCs in soil standards were characterized by gas chromatography. A Hewlett Packard 5880 Series II flame ionization gas chromatograph was used. For toluene, ethylbenzene and p-xylene mixture, the column was a 30 meter X 0.53 mm J&W Scientific DB-624 capillary column. For gasoline, the column was a 30 meter X 0.32 mm J&W Scientific DB-1 fused silica capillary column.

In order to analyze the VOC content of capsules and soil containing capsules, a known weight of sample was equilibrated in methanol at room temperature for a finite period. The samples were gently swirled to assure complete wetting of the soil with the solvent. The methanol solution obtained was assayed directly (in the case of gasoline in soil) or diluted with acetone and subsequently assayed (in the case of 1:1:1 toluene/ethylbenzene/p-xylene). Equilibration time was 30 min. for all samples.

Results and Discussion

In order to have a stable standard soil sample contaminated with VOCs, it is necessary to be able to prepare in a reproducible manner VOC-loaded microcapsules that are stable for prolonged periods when mixed with a soil sample. For a microcapsule loaded with VOCs to be stable, the capsule shell or coating must have essentially zero permeability to the VOCs encapsulated. The shell must also be susceptible to water and/or methanol, since the analytical methodology used to characterize VOC contaminated soil involves these solvents. Dry microcapsules shells formed by complex coacervation are able to retain VOCs for prolonged periods as long as they are not subject to high humidity storage conditions. In the presence of water or water/methanol mixtures, the predominately gelatin shells become permeable thereby enabling release of the VOCs.

The first objective of the study was to demonstrate that a mixture of pure solvents could be encapsulated and retained. The solvent mixture encapsulated was a 1:1:1 (V/V/V) mixture of toluene, ethylbenzene and p-xylene. Three batches of capsules were made in order to examine lot-to-lot reproducibility. The capsules produced were clean, uniform free-flowing powders suitable for incorporation into a soil sample. Triplicate analyses of 2 gram samples of each capsule batch established that the capsules were 95.8 weight % solvent (relative percent standard deviation; 1.0%). When 5.08 grams of one capsule sample, fraction passing 60 mesh screen, was combined with 100.2 grams clean INEEL subsurface soil, the contaminated soil produced contained approximately 56.5 milligrams (estimated by calculation) of toluene/ethylbenzene/p-xylene mixture per gram of soil.

In order to examine homogeneity and accuracy this standard contaminated soil sample, three one-gram and three five-gram samples of contaminated soil were assayed. Table 1 summarizes the replicate analytical data obtained. Overall variability at one standard deviation was about 5% for all components at either the 1.0 gram or 5.0 gram aliquot size. This single analysis indicates that the concept of preparing an accurate performance standard by utilizing microcapsules is realistic. It demonstrated adequate homogeneity in the sample at various sample sizes as well as relative agreement with the amount of material expected (estimated 56.5 mg/gram vs. found 48.6 mg/gram).

A second pilot involved the encapsulation of gasoline and preparation of soil sample contaminated with gasoline. Four batches of capsules loaded with gasoline were prepared. The mean gasoline loading of these four samples was 73.2% (standard deviation 6.2). Three ~2 gram samples of gasoline-loaded capsules were subjected in triplicate to analysis and found to 3274 µg/gram toluene (std. dev. = 248, %RSD = 7.6), 4347 µg/g ethylbenzene (std. dev. = 296, %RSD = 6.8) and 14922 µg /g p-xylene (std. dev. 931, %RSD = 6.2).

Ten grams of gasoline-loaded capsules were combined with 193.0 grams of soil to produce a pilot performance evaluation sample. Three samples of this contaminated soil sample placed into individual 40 milliliter,

precleaned sampling vials each containing approximately 20 grams, were shipped to an environmental analytical laboratory for analysis for benzene, toluene, ethylbenzene and xylenes (BTEX). Each sample was analyzed in triplicate utilizing U.S. EPA SW-846 Method 5030 in conjunction with SW846 Method 8020. Table 2 contains results of these analyses.

Another sample was sent as a double blind sample to a second analytical laboratory for analysis. Table 3) summarizes results of these analyses. Other than a disagreement concerning the quantitation of benzene, results obtained independently by the two laboratories agree well.

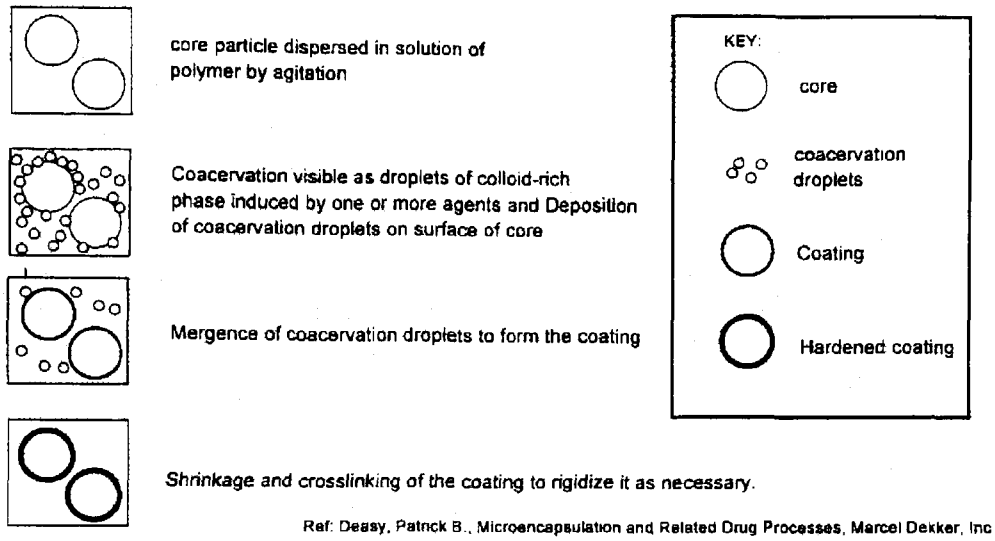

Figure 1. Coacervation of Solvents for Addition to Soil Sample

The analytical data obtained to date demonstrates using microcapsules to prepare soil performance evaluation standards is attainable. The performance evaluation soil standard has the advantage of being as close to a real world soil sample as technologically feasible and has demonstrated the ability to measure the quality associated with the entire analytical methodology. This technology is capable of producing a performance evaluation sample containing volatile target organic analytes within well-defined concentration ranges. The encapsulated process can provide variable concentration ranges for numerous target volatile analytes. The resulting performance evaluation sample will be amenable to many of the current US EPA methodologies for the analysis of environmentally significant volatile organics in soils including analysis carried out by thermal desorption techniques.

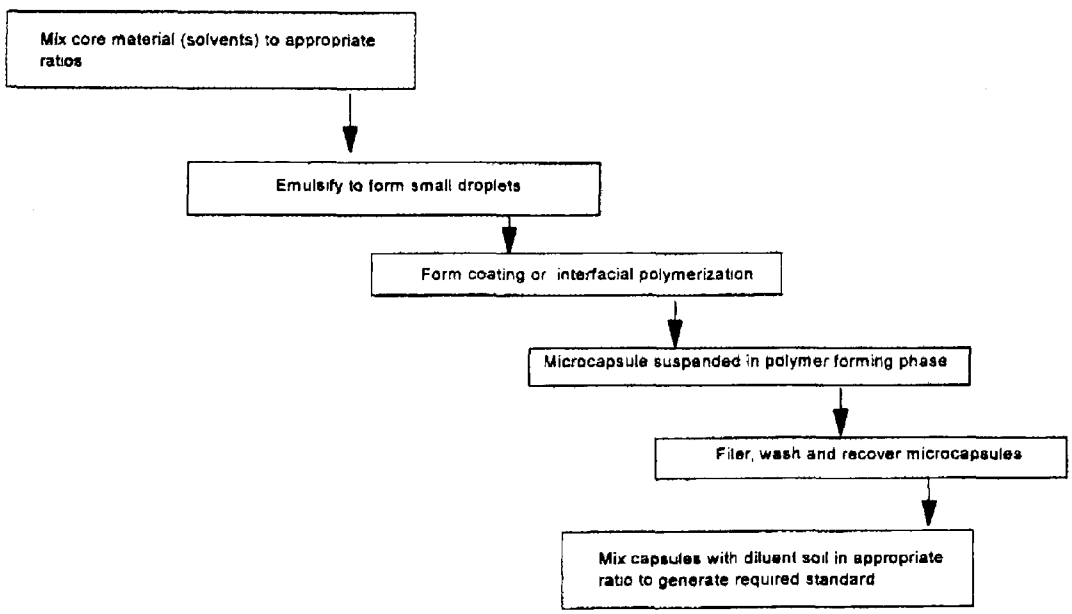

Figure 2. Typical Steps of Standard Preparation Process

Current efforts are focused on reducing the concentration of target analytes to the 5 - 200 ppb range and to examine product storage stability. Once through this pilot examination, the carrier solvent will be spiked with other analytes including; acetone, carbon tetrachloride, chloroform, methylene chloride, trichloroethane, tetrachloroethylene. The author has submitted soil samples that contain microencapsulated VOCs to the Mixed Analyte Performance Evaluation Program, operated by the U.S. Department of Energy, for round robin study utilizing contracted environmental analytical laboratories.

Table 1. Data from Simulated Contaminated Soil Sample that Contains Microcapsules Loaded with a 1:1:1 (V/V/V) Toluene/ Ethylbenzene/p-Xylene Mixture. (units are milligrams per grain of soil)

Sample Weight (g.)		Toluene	Ethylbenzene	p-Xylene
1.0	Average	11.96	22.21	22.41
	Std. Dev.	0.57	1.05	1.08
	%RSD	4.8	4.7	4.8
5.0				
	Average	12.00	22.78	23.02
	Std. Dev.	0.62	1.16	1.17
	%RSD	5.1	5.1	5.1

Table 2. Gasoline in Soil Pilot Performance Evaluation Standard - Single Lab Analysis. (units are milligrams per gram of soil)

	Benzene	Toluene	Ethylbenzene	o-Xylene	m & p-Xylene
Sample 1	444	143	187	341	898
	406	134	206	306	846
	407	130	168	303	841
Sample 2	367	131	192	267	792
	402	130	198	286	793
	416	133	205	280	828
Sample 3	387	131	197	298	814
	384	124	191	261	766
	406	131	200	287	836
Average	402.1	131.9	193.8	292.1	823.8
Std. Dev.	20.5	4.7	10.9	22.5	36.3
%RSD	5.1	3.6	5.6	7.7	4.4

Table 3. Gasoline in Soil Pilot Performance Standard Sent as Double Blind to Second Lab for Analysis. (units are milligrams per gram of soil)

	Benzene	Toluene	Ethylbenzene	o-Xylene	m & p-Xylene
Sample 1	2.5 U	120	150	270	750
	2.5 U	120	150	270	760
	2.5 U	99	120	230	610
	2.5 U	100	110	250	680
Average		109.8	130	255	700
Std. Dev.		10.2	16.7	16.6	60.4
%RSD		9.3	12.9	6.5	8.6
Sample 1	NA	120	200	350	900
Confirmation	NA	120	210	360	940
	NA	120	220	3 80	960
	NA	120	210	350	920
Average		120	210	360	930
Std. Dev.		0	7.1	12.2	22.4
%RSD			3.4	3.4	2.4

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U.S. EPA AND U.S. A.F. INTERAGENCY AGREEMENT FOR FIELD ANALYTICAL SERVICES

Raymond A. Flores
US EPA Region 6, Houston Community College,10625 Fallstone Road, Houston TX 77099-4303
281-983-2139 ext. 139
FLORES.RAYMOND@EPAMAIL.EPA.GOV
George H. Lee
Analytical Services Division, AL/OEA, Armstrong Laboratory, Brooks AFB, TX 78235-5114
210-536-6166
GLEE@GUARDIAN.BROOKS.AF.MIL

The interagency agreement (IAG) between the parties above will provide for more timely analyses of EPA samples while at the same time making more efficient use of the federal government's resources. At the time of the writing of this abstract the IAG has just reached implementation phase and consequently data is limited. We are confident that with the data generated in the next four months, we will be able to show that time and money are saved by the use of this IAG. As the Project officers for the EPA-AF IAG, we will use the data from each field project in making the cost savings comparison. We will discuss project startup and implementation. The onsite analytical capabilities of the Air Force, both field screening techniques and field confirmation methods, will be examined. USAF's Armstrong Laboratory located at Brooks Air Force Base, San Antonio Texas, will provide onsite analyses for USEPA Region 6's Superfund Division. The elements of the Superfund Program that can request work are the Brownfields, Removal, Emergency Response, Remedial, and Site Assessment Teams. The Air Force Responders will be onsite in a time frame dependent upon the nature of the site activity. Most site activities are non-emergency. Activities which are not time critical such as Brownfields and Remedial for example, will allow sufficient time for a significant amount of preplanning for onsite activities. Other activities which are more time critical require immediate action. Air Force responds to those activities in which there is a threat or possible threat of risk to human health in less than 24 hours dependent on site location. In the near future, AF is projected to have a mobile laboratory which can be driven to the site immediately upon notice.

Onsite field screening and confirmation techniques have been projected to be a more cost effective way to perform portions of the chemical analysis evaluation of a site as early as 1988. Air Force's trained personnel and specialized equipment can be used for EPA projects in EPA Region 6 and of course for Air Force's needs worldwide. Air Force benefits in a number of ways such as becoming familiarized with EPA's SOPs for site activities. EPA benefits by having access to a cost-effective service with unique capabilities and world wide experience. This IAG provides for technology transfer and more efficient resource utilization.

SUMMARY

This agreement between Federal Agencies pursuing common goals allows for greater efficiency and cost effectiveness for all and provides an opportunity for technology transfer. We recommend the use of interagency agreements in similar cases. An IAG can be a commensal relationship with mutual advantages.

SEVERAL ORGANIC PARAMETERS ON UNDERLYING HAZARDOUS CONSTITUENTS LIST CAN NOT BE MEASURED AT THE UNIVERSAL TREATMENT STANDARDS

Howard C. Johnson
Sample Management Risk Technologies
Clifford S. Watkins
Sample Management Risk Technologies, Idaho National Engineering and Environmental Laboratory,
Sample Management Office, Lockheed Martin Idaho Technologies Company,
P.O. Box 1625-3960, Idaho Falls, Idaho 83415

ABSTRACT

The Idaho National Engineering and Environmental Laboratory (INEEL) has several permitted treatment, storage and disposal facilities. The INEEL Sample Management Office (SMO), operated by Lockheed Martin Idaho

Technologies Company (LMITCO), conducts all analysis subcontracting activities for Department of Energy Environmental Management programs at the INEEL. In this role, the INEEL SMO has had the opportunity to subcontract the analyses of various wastes (including ash from an interim status incinerator) requesting a target analyte list equivalent to the constituents listed in 40 Code of Federal Regulations (CFR) § 268.48. Per 40 CFR § 268.40, these analyses are required to ensure that treated wastes do not contain underlying hazardous constituents (UHC) at concentrations greater than the universal treatment standards (UTS) prior to land disposal. The language in 40 CFR § 268.40 (d) (3) states that, "The treatment or disposal facility may demonstrate compliance with organic constituents if good-faith analytical efforts achieve detection limits for the regulated organic constituents that do not exceed the treatment standards specified in this section by an order of magnitude."

The INEEL SMO has conducted this "good-faith effort" by negotiating with several commercial laboratories to identify the lowest possible quantitation and detection limits that can be achieved for the organic LTHC analytes. The results of this negotiating effort has been the discovery that no single laboratory (currently under subcontract with the INEEL SMO) can achieve a detection level that is within an order of magnitude of the UTS for all organic parameters on a clean sample matrix (e.g., sand). This indicates that for a typical waste sample, the chances of the order of magnitude requirement not being met for many more than just the "problem analytes" is likely. This does not mean that there is no laboratory that can achieve the order of magnitude requirements for all organic UHCs on a clean sample matrix. The negotiations held to date indicate that it is likely that no laboratory can achieve the order of magnitude requirements for a difficult sample matrix (e.g., an incinerator ash). The authors suggest that the regulation needs to be revised to address the disparity between what is achievable in the laboratory and the regulatory levels required by the UTS.

INTRODUCTION

The INEEL SMO conducts all analysis subcontracting activities for the Department of Energy Environmental Management programs at the INEEL. Contracted analyses are primarily in the following analytical disciplines; radiological, inorganic, organic and physical properties testing. Within each discipline numerous analytical tests are requested on a large variety of sample matrices. Analytical test requirements range from field screening or processing information to data required to satisfy U.S. Environmental Protection Agency (EPA) and Idaho Division of Environmental Quality (ID-DEQ) requirements. The INEEL SMO subcontracts analytical work on a variety of wastes (including ash from an interim status incinerator). Analytical requests have included a target analyte list equivalent to the constituents listed in 40 CFR § 268.48. Per 40 CFR § 268.40, these analyses are required to ensure that treated wastes do not contain UHCs at concentrations greater than the UTS prior to land disposal. The language in 40 CFR § 268.40 (d) states:

> "Notwithstanding the prohibitions specified in paragraph (a) of this section, treatment and disposal facilities may demonstrate (and certify pursuant to 40 CFR § 268.7(b)(5)) compliance with the treatment standards for organic constituents specified by a footnote in the table "Treatment Standards for Hazardous Wastes" in this section, provided the following conditions are satisfied:
> (1) The treatment standards for the organic constituents were established based on incineration in units operated in accordance with the technical requirements of 40 CFR part 264, subpart 0, or based on combustion in fuel substitution units operating in accordance with applicable technical requirements;
> (2) The treatment or disposal facility has used the methods referenced in paragraph (d)(1) of this section to treat the organic constituents; and
> (3) The treatment or disposal facility may demonstrate compliance with organic constituents if good-faith analytical efforts achieve detection limits for the regulated organic constituents that do not exceed the treatment standards specified in this section by an order of magnitude."

The INEEL SMO has sought this "good-faith effort" by negotiating with several commercial laboratories to identify the lowest possible quantitation or detection limits that can be achieved for the organic UHCs. The primary emphasis has been on the nonwastewater standard. At this time, the wastewater standard for the organic UHCs has not been performed by all of the INEEL SMO contracted laboratories. The results of this negotiating effort has been the discovery that no single laboratory (currently under subcontract with the INEEL SMO) can achieve the detection level of the UTS for all organic parameters of the UHC list on a clean sample matrix (e.g., sand). This indicates that for a typical waste sample, the chances of the order of magnitude requirement not being met for many more than just the "problem analytes" is likely. This does not mean that there is no laboratory that can achieve the order of magnitude requirements for all organic UHCs on a clean sample matrix. The INEEL SMO continues to seek laboratory capability to analyze for the UHCs to the UTS in a cost-effective manner.

Additionally, the regulated community should be aware that the "order-of-magnitude" provision might not be allowed on incinerator ash from an interim status incinerator. In the September 19, 1994 final rule, the "order-of-magnitude" provision is only applicable where incinerated wastes were treated in permitted (Part 264 Subpart O) units.

Within the capabilities of the current INEEL SMO subcontracted laboratories, no two laboratories analyze the UHCs to the UTS the same way. In the guidelines of USEPA SW-846 a variety of approved methods can be used to analyze for the various constituents. The SW-846 methods being used to analyze for the complete UHC list by the laboratories currently contracted through the INEEL SMO are:

- Method 1311 Toxicity Characteristic Leaching Procedure
- Method 8015A Nonhalogenated Volatile Organics by Gas Chromatography
- Method 8015M (modified) Nonhalogenated Volatile Organics
- Method 8080A Organochlorine Pesticides And Polychlorinated Biphenyls By Gas Chromatography
- Method 8081 Organochlorine Pesticides, Halowaxes And PCBs As Aroclors By Gas Chromatography: Capillary Column Technique
- Method 8081A Organochlorine Pesticides (PCBs) By Gas Chromatography
- Method 8082 Polychlorinated Biphenyls By Gas Chromatography
- Method 8140 Organophosphorus Pesticides
- Method 8141 Organophosphorus Compounds By Gas Chromatography: Capillary Column Technique
- Method 8150 Chlorinated Herbicides By Gas Chromatography
- Method 8151 Chlorinated Herbicides By GC Using Methylation Or Pentafluorobenzylation Derivatization: Capillary Column Technique
- Method 8260A Volatile Organic Compounds By Gas Chromatography Mass Spectrometry (GC/MS): Capillary Column Technique
- Method 8270B Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique
- Method 8310 Polynuclear Aromatic Hydrocarbons
- Method 8316 Acrylamide, Acrylonitrile And Acrolein By High Performance Liquid Chromatography (HPLC)

The UHC list is extensive and there are many "problem analytes" to analyze. The methodology is left to the capability of the laboratory and the laboratory's discretion. It would not be practical or reasonable for the INEEL SMO to specify to a laboratory a required method for every constituent. Under the fixed contracts, obsolete methods are still listed but current methodology is used whenever possible, incorporating the June 13, 1997 promulgated methods from the Third Edition of the EPA-approved test methods manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods."

To procure UHC organic analyses, it becomes necessary to negotiate with each contracted laboratory concerning achievable detection and quantitation limits for the entire UHC list. The negotiations held to date indicate that it is likely that no laboratory can achieve the order of magnitude requirements for a difficult sample matrix (e.g., an incinerator ash). When negotiating with commercial laboratories that are under fixed price subcontracts government contractors like LMITCO have difficulty authorizing additional financial support, for the "research project" samples. Analytical difficulties arise when dealing with complex matrices such as an incinerator fly ash. For example, alternate solvent system extractions may be more effective for the semivolatile organic compounds. Laboratories currently contracted through the INEEL SMO routinely extract semivolatiles using acetone/hexane or acetone/methylene chloride systems. They have found fewer fly ash matrix interferences when they substituted a methylene chloride only extraction system. The alternate solvent system also requires additional calibration with a resulting burden on the laboratory under a fixed price contract.

The organic UHC list is extensive and standards are hard to locate for the entire list. For example, one of the contracted laboratories had difficulty initially procuring a standard for 4,4'-Methylene-bis-(*o*-chloroaniline) CAS# 101-14-4. No laboratory contracted through the INEEL SMO has determined quantitation limits or calibrated for the 40 additional analytes that will become "underlying hazardous constituents" August 26, 1998. Commercial laboratories contracted through the INEEL SMO have expressed concerns about the effort and expense that will be required to obtain standards, conduct MDL determinations, etc. in order to analyze for the added constituents. The 40 additional constituents are identified in Table 1 UTS.

SUMMARY

The current INEEL SMO contracted laboratories operate within the highly competitive commercial laboratory industry. With laboratory capacity available to DOE (i.e. possessing a NRC license to receive radioactively contaminated samples) limited nationwide, extensive "non-routine" analytical requests on complex matrices are not desired by the laboratories. Obtaining the full suite of UHC analyses can be difficult. The inability to determine if a treated waste has achieved the required treatment standard concentrations can place programs in a position subject to violation of regulatory requirements. The authors' suggest that the regulation needs to be revised to address the disparity between what is achievable in the laboratory and the regulatory levels required by the UTS.

The authors' poster delineates the achievable detection limits for organic UHC parameters at several commercial laboratories. The intent of the poster is to bring this issue to the attention of the regulators and regulated community. Another benefit is to discuss analytical approaches used by other laboratories that may achieve greater sensitivities for the difficult organic analytes on the UHC list.

Table 1 UTS identifies the organic hazardous constituents, along with the nonwastewater and wastewater treatment standard levels. 40 CFR § 268.48 also states: "For determining compliance with treatment standards for underlying hazardous constituents as defined in § 268.2(i), these treatment standards may not be exceeded. Compliance with these treatment standards is measured by an analysis of grab samples, unless otherwise noted in the following Table 1 UTS". Included in the table are the negotiated quantitation limits for the nonwastewater standard from three INEEL SMO contracted laboratories (A, B, and C). These limits can be compared to the listed regulatory nonwastewater standard concentration. Presently the most difficult ash samples are requiring five to ten fold dilutions -in addition to alternate solvent system extractions- which further limit the ability of the laboratory to achieve quantitation limits at (or below) the UTS for all of the UHCs. The negotiated quantitation limits are the laboratories "ideal" quantitation limits on a clean matrix (e.g., sand) and do not represent the current achievable limits on difficult sample matrices (e.g., incinerator fly ash). When the laboratories quantitation limit is at the treatment standard concentration, the INEEL SMO requires the laboratory to have the instrument detection limit for that analyte less than 0.33 times the treatment standard. This limit is also specified in the task order statement of work between the laboratory and the INEEL SMO.

Table 1. UTS -- Universal Treatment Standards
(Note: NA means not applicable.)

Regulated constituent/common name Organic Constituents	CAS (1) Number	Wastewater standard Concentration in mg/l (2)	Nonwastewater standard Concentration in mg/kg (3) unless noted as "mg/l TCLP"	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory A	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory B	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory C
A2213 (6)	30558-43-1	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Acenaphthylene	208-96-8	0.059	3.4	0.33	0.67	3.4
Acenapthene	83-32-9	0.059	3.4	0.33	0.67	3.4
Acetone	67-64-1	0.28	160	0.01	0.01	160
Acetonitrile	75-05-8	5.6	38	0.02	0.05	38
Acetophenone	96-86-2	0.010	9.7	0.33	0.67	9.7
2-Acetylaminofluorene	53-96-3	0.059	140	0.33	0.67	140
Acrolein	107-02-8	0.29	NA	0.01	NA	NA
Acrylamide	79-06-1	19	23	**50**	23	23
Acrylonitrile	107-13-1	0.24	84	0.01	0.05	84
Aldicarb sulfuric (6)	1646-88-4	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Aldrin	309-00-2	0.021	0.066	0.005	0.066	0.066
4-Aminobiphenyl	92-67-1	0.13	NA	0.33	NA	NA
Aniline	62-53-3	0.81	14	0.33	0.67	14
Anthracene	120-12-7	0.059	3.4	0.33	0.67	3.4
Aramite	140-57-8	0.36	NA	0.66	NA	NA
alpha-BHC	319-84-6	0.00014	0.066	0.005	0.002	0.066
beta-BHC	319-85-7	0.00014	0.066	0.005	0.004	0.066
delta-BHC	319-86-8	0.023	0.066	0.005	0.006	0.066
gamma-BHC	58-89-9	0.001	0.066	0.005	0.002	0.066
Barban (6)	101-27-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Bendiocarb (6)	22781-23-3	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Bendiocarb phenol (6)	22961-82-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Benomyl (6)	17804-35-2	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Benzene	71-43-2	0.14	10	0 005	0.005	10

Benz(a)anthracene	56-55-3	0.059	3.4	0.33	0.67	3.4
Benzal chloride	98-87-3	0.055	6.0	1.65	0.05	6.0
Benzo(b)fluoranthene (difficult to distinguish from benzo(k) fluoranthene	205-99-2	0.11	6.8	0.33	0.67	6 8
Benzo(k)fluoranthene (difficult to distinguish from benzo(b) fluoranthene)	207-08-9	0.11	6.8	0.33	0.67	6.8
Benzo(g,h,i)perylene	191-24-2	0.0055	1.8	0.33	0.67	1.8
Benzo(a)pyrene	50-32-8	0.061	3.4	0.33	0.67	3.4
Bromodichloromethane	75-27-4	0.35	15	0.005	0.05	15
Bromomethane/Methyl bromide	74-83-9	0.11	15	0.01	0.05	15
4-Bromophenyl phenyl ether	101-55-3	0.055	15	0.33	0.67	15
n-Butyl alcohol	71-36-3	5.6	2.6	0.5	2.6	2.6
Butylate (6)	2008-41-5	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Butyl benzyl phthalate	85-68-7	0.017	28	0.33	67	28
2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	0.066	2.5	1.65	1.3	2.5
Carbaryl (6)	63-25-2	0.006	0 14	**undetermined**	**undetermined**	**undetermined**
Carbenzadim (6)	10605-21-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Carbofuran (6)	1563-66-2	0.006	0 14	**undetermined**	**undetermined**	**undetermined**
Carbodfuran phenol {6}	1563-38-8	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Carbon disulfide	75-15-0	3.8	4.8 mg/l TCLP	.005 mg/l TCLP	4.8 mg/l TCLP	4.8 mg/ TCLP
Carbon tetrachloride	56-23-5	0.057	6.0	0.005	0.005	6.0
Carbosulfan (6)	55285-14-9	0.028	1.4	**undetermined**	**undetermined**	**undetermined**
Chlordane (alpha and gamma isomers)	57-74-9	0.0033	0.26	0.005	0.009	0.26
p-Chloroaniline	106-47-8	0.46	16	0.33	0.67	16
Chlorobenzene	108-90-7	0.057	6.0	0.005	0.005	6.0
Chlorobenzilate	510-15-6	0.10	NA	0.33	NA	NA
2-Cloro-1,3-butadiene	126-99-8	0.057	28	0.01	0.05	0.28
Chlorodibromomethane	124-48-1	0.057	15	0.005	0.005	15
Chloroethane	75-00-3	0.27	6.0	0.01	0.05	6.0
bis(2-chloroethoxy) methane	111-91-1	0.036	7.2	0.33	0.67	7.2
bis(2-Chloroethyl)ether	111-44-4	0.033	6.0	0.33	0.67	6.0
Chloroform	67-66-3	0.046	6.0	0.005	0.005	6.0
bis(2-Chloroisopropyl) ether	39638-32-9	0.055	7.2	0.33	0.67	7.2
p-Chloro-m-cresol	59-50-7	0.018	14	0.33	0.67	14
2-Chloroethyl vinyl ether	110-75-8	0.062	NA	0.01	NA	NA
Chloromethane/Methyl chloride	74-87-3	0.19	30	0.01	0.05	30
2-Chloronaphthalene	91-58-7	0.055	5.6	33	0.67	5.6
2-Chlorophenol	95-57-8	0.044	5.7	0.33	0.67	5.7
3-Chloropropylene	107-05-1	0.036	30	0.02	0.05	30
Chrysene	218-01-9	0.059	3.4	0.33	0.67	3.4
o-Cresol	95-48-7	0.11	5.6	0.33	0.67	5.6
m-Cresol (difficult to distinguish from p-cresol)	108-39-4	0.77	5.6	Reported as p-cresol	Reported as p-cresol	Reported as p-cresol
p-Cresol (difficult to distinguish from m-cresol)	106-44-5	0.77	5.6	0.33	0.67	5.6
m-Cumenyl methylcarbamate (6)	64-00-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Cyclohexanone	108-94-1	0.36	0.75 mg/l TCLP	0.1 mg/l TCLP	0.75 mg/l TCLP	0.75 mg/l TCLP
o,p'-DDD	53-19-0	0.023	0.087	0.01	0.087	0.087
p,p'-DDD	72-54-8	0.023	0.087	0.01	0.087	0.087
o,p'-DDE	3424-82-6	0.031	0.087	0.01	0.087	0.087
p,p'-DDE	72-55-9	0.031	0.087	0.01	0.087	0.087
o,p'-DDT	789-02-6	0.0039	0.087	0.01	0.087	0.087
p,p'-DDT	50-29-3	0.0039	0.087	0.01	0.087	0.087
Dibenz(a,h)anthracene	53-70-3	0.055	8.2	0.33	0.67	8.2
Dibenz(a,e)pyrene	192-65-4	0.061	NA	0.01	NA	NA

1,2-Dibromo-3-chloropropane	96-12-8	0.11	15	0.02	0.05	15
1.2-Dibromoethane/ Ethylene dibromide	106-93-4	0.028	15	0.02	0.05	15
Dibromomethane	74-95-3	0.11	15	0.01	0.05	15
m-Dichlorobenzene	541-73-1	0.036	6.0	0.33	0.67	6.0
o-Dichlorobenzene	95-50-1	0.088	6.0	0.33	0.67	6.0
p-Dichlorobenzene	106-46-7	0.090	6.0	0.33	0.67	6.0
Dichlorodifluoromethane	75-71-8	0.23	7.2	0.01	0.05	7.2
1, 1-Dichloroethane	75-34-3	0.059	6.0	0.005	0.005	6.0
1,2-Dichloroethane	107-06-2	0.21	6.0	0.005	0.005	6.0
1,1-Dichloroethylene	75-35-4	0.025	6.0	0.005	0.005	6.0
trans-1,2-Dichloroethylene	156-60-5	0.054	30	0.005	0.005	30
2,4-Dichlorophenol	120-83-2	0.044	14	0.33	0.67	14
2,6-Dichlorop henol	87-65-0	0.044	14	0.33	0.67	14
2,4-Dichlo phenoxyacetic acid/2,4-D	94-75-7	0.72	10	10	10	10
1,2-Dichloropropane	78-87-5	0.85	18	0.005	0.005	18
cis-1,3-Dichloropropylene	10061-01-5	0.036	18	0.005	0.005	18
trans-1,3-Dichloropropylene	10061-02-6	0.036	18	0.005	0.005	18
Dieldrin	60-57-1	0.017	0.13	0.01	0.01	0.13
Diethylene glycol, dicarbamate (6)	5952-26-1	.0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Diethyl phthalate	84-66-2	0.20	28	0.33	0.67	28
p-Dimethylamino-azobenzene	60-11-7	0.130	NA	0.33	NA	NA
2,4-Dimethyl phenol	105-67-9	0.036	14	0.33	0.67	14
Dimethyl phthalate	131-11-3	0.047	28	0.33	0.67	28
Dimetilan (6)	644-64-4	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Di-n-butyl phthalate	84-74-2	0.057	28	0.33	0.67	28
1,4-Dinitrobenzene	100-25-4	0.32	2.3	1.65	1.6	2.3
4,6-Dinitro-o-cresol	534-52-1	0.28	160	1.65	3.3	160
2.4-Dinitrophenol	51-28-5	0.12	160	1.65	3.3	160
2,4-Dinitrotoluene	121-14-2	0.32	140	0.33	0.67	140
2,6-Dinitrotoluene	606-20-2	0.55	28	0.33	0.67	28
Di-n-octyl phthalate	117-84-0	0.017	28	0 33	0.67	28
Di-n-propylnitrosamine	621-64-7	0.40	14	0.33	0.67	14
1,4-Dioxane	123-91-1	12.0	170	0.33	0.5	0.1
Diphenylamine (difficult to distinguish from diphenylnitrosamine)	122-39-4	0.92	13	0.33	13	13
Diphenylnitrosamine (difficult to distinguish from diphenylamine)	86-30-6	0.92	13	0.33 cannot be separated from Dipheylamine	13 reported as Dipheylamine	13 reported as Dipheylamine
1,2-Diphenylhydrazine	122-66-7	0.087	NA	0.33	NA for nonwastewater, reported as decomposition product azobenzene for wastewater	NA
Disulfoton	298-04-4	0.017	62	0.02	0.03	6.2
Dithiocarbamates (total) (6)	137-30-4	0.028	28	**undetermined**	**undetermined**	**undetermined**
Endosulfan I	959-98-8	0.023	0.066	0.005	0.066	0.066
Endosulfan II	33213-46-9	0.029	0.13	0.01	0.13	0.13
Endosulfan sulfate	1031-07-8	0.029	0.13	0.01	0.13	0.13
Endrin	72-20-8	0.0028	0.13	0.01	0.13	0.13
Endrin aldehyde	7421-93-4	0.025	0.13	0.01	0.13	0.13
EPTC (6)	759-94-4	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Ethyl acetate	141-78-6	0.34	33	0.01	33	33
Ethyl benzene	100-41-4	0.057	10	0.005	0.005	10
Ethyl cyanide/ Propanenitrile	107-12-0	0.24	360	0.25	360	360
Ethyl ether	60-29-7	0.12	160	0.01	160	160

bis(2-Ethylthexyl) phthalate	117-81-7	0.28	28	0.33	0.67	28
Ethyl methacrylate late	97-63-2	0.14	160	0.33	0.05	160
Ethylene oxide	75-21-8	0.12	NA	10	NA	NA
Famphur	52-85-7	0.017	15	0.1	1.3	15
Fluoranthene	206-44-0	0.068	3.4	0.33	0.67	3.4
Fluorene	86-73-7	0.059	3.4	0.33	0.67	3.4
Formetanate hydrochloride (6)	23422-53-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Formparanate (6)	17702-57-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Heptachlor	76-44-8	0.0012	0.066	0.005	0.002	0.066
Heptachlor epoxide	1024-57-3	0.016	0.066	0.005	0.056	0.066
Hexachlorobenzene	118-74-1	0.055	10	0.33	0.67	10
Hexachlorobutadiene	87-68-3	0.055	5.6	0.33	0.67	5.6
Hexachlorocyclo-pentadiene	77-47-4	0.057	2.4	0.33	0.67	2.4
HxCDDs (All Hexa-chlorodibenzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
HxCDFs (All Hexa-chlorodibenzo-furans)	NA	0.000063	0.001	0.0005	0.001	0.001
Hexachloroethane	67-72-1	0.055	30	0.33	0.67	30
Hexachloropropylene	1888-71-7	0.035	30	0.33	0.67	30
Indeno (1,2,3-c,d) pyrene	193-39-5	0.0055	3.4	0.33	0.67	3.4
Iodomethane	74-88-4	0.19	65	0.01	0.05	65
Isobutyl alcohol	79-83-1	5.6	170	0.1	5	170
Isodrin	465-73-6	0.021	0.066	0.1	**0.66**	0.066
Isolan (6)	119-38-0	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Isosafrole	120-58-1	0.081	2.6	0.33	0.67	2.6
Kepone	143-50-0	0.001	0.13	0.05	**1.3**	0.13
Methacrylnitrile	126-98-7	0.24	84	0.02	0.05	84
Methanol	67-56 -1	5.6	0.75 mg/l TCLP	**5 mg/l TCLP**	Analyzed as total 10 mg/kg, equivalent to 0.5 mg/l TCLP	0.75 mg/l TCLP
Methapyrilene	91-80-5	0.081	1.5	0.33	0.67	1.5
Methiocarb (6)	2032-65-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Methomyl (6)	16752-77-5	0.028	0.14	**undetermined**	**undetermined**	**undetermined**
Methoxychlor	72-43-5	0.25	0.18	0.05	0.12	0.18
3-Methylcholanthrene	56-49-5	0.0055	15	0.33	0.67	15
4,4-Methylene bis(2-chloroaniline)	101-14-4	0.50	30	1.65	30	30
Methylene chloride	75-09-2	0.089	30	0.005	0.005	30
Methyl ethyl ketone	78-93-3	0.28	36	0.01	0.01	36
Methyl isobutyl ketone	108-10-1	0.14	33	0.01	0.01	33
Methyl methacrylate	80-62-6	0.14	160	0.33	0.05	160
Methyl methansulfonate	66-27-3	0.018	NA	0.33	NA	NA
Methyl parathion	298-00-4	0.014	4.6	0.02	0.06	4.6
Metolcarb (6)	1129-41-5	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Mexacarbate (6)	315-18-4	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Molinate (6)	2212-67-1	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Naphthalene	91-20-3	0.059	5.6	0.33	0.67	5.6
2-Naphthylamine	91-59-8	0.52	NA	0.33	NA	NA
o-Nitroaniline	88-74-4	0.27	14	1.65	3.3	14
p-Nitroaniline	100-01-6	0.028	28	1.65	3.3	28
Nitrobenzene	98-95-3	0.068	14	0.33	0.67	14
5-Nitro-o-toluidine	99-55-8	0.32	28	0.33	0.67	28
o-Nitrophenol	88-75-5	0.028	13	33	0.67	13
p-Nitrophenol	100-02-7	0.12	29	1.65	3.3	29
N-Nitrosodiethylamine	55-18-5	0.40	28	0.33	0.67	28
N-Nitrosodimethylamine	62-75-9	0.40	2.3	0.33	67	2.3
N-Nitroso-di-n-butylamine	924-16-3	0.40	17	0.33	0.67	17
N-Nitrosomorpholine	59-89-2	0.40	2.3	0.33	0.67	2.3
N-Nitrosopiperidine	100-75-4	0.013	35	1.65	1.3	**undetermined**
N-Nitrosomethyl-ethylamine	10595-95-6	0.40	2.3	0.33	0.67	2.3
N-Nitrosopyrrolidine	930-55-2	0.013	35	0.33	0.67	**undetermined**

Oxamyl (6)	23135-22-0	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Parathion	56-38-2	0.014	4.6	0.02	0.03	4.6
Total PCBs (sum of all PCB isomers, or all Aroclors)	1336-36-3	0.10	10	0.8	10	10
Pebulate (6)	1114-71-2	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Pentachlorobenzene	608-93-5	0.055	10	0.33	0.67	10
PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
PeCDFS (All Penta-chlorodibenzo-furans)	NA	0.000035	0.001	0.0005	0.001	0.001
Pentachloroethane	76-01-7	0.055	6.0	0.33	0.01	6.0
Pentachloronitrobenzene	82-68-8	0.055	4.8	1.65	0.67	4.8
Pentachlorophenol	87-86-5	0.089	7.4	1.65	3.3	7.4
Phenacetin	62-44-2	0.081	16	0.33	0.67	16
Phenanthrene	85-01-9	0.059	5.6	0.33	0.67	5.6
Phenol	108-95-2	0.039	6.2	0.33	0.67	6.2
o-Phenylenediamine (6)	95-54-5	0.056	5.6	**undetermined**	**undetermined**	**undetermined**
Phorate	298-02-2	0.021	4.6	0.02	0.02	4.6
Phthalic acid	100-21-0	0.055	28	3.3	28 reported as Phthalic anhydride	**undetermined**
Phthalic anhydride	85-44-9	0.055	28	0.66	28	**undetermined**
Physostigmine (6)	57-47-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Physostigmine salicylate (6)	57-64-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Promecarb (6)	2631-37-0	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Pronamide	23950-58-5	0.093	1.5	0.33	0.67	1.5
Propham (6)	122-42-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Propoxur (6)	114-26-1	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Prosulfocarb (6)	52888-80-9	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Pyrene	129-00-0	0.067	8.2	0.33	0.67	8.2
Pyridine	110-86-1	0.014	16	0.33	0.67	16
Safrole	94-59-7	0.081	22	0.33	0.67	22
Silvex/2,4.5-TP	93-72-1	0.72	7.9	7.9	7.9	7.9
1,2,4,5-Tetrachloro-benzene	95-94-3	0.055	14	0.33	0.67	14
TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
TCDFS (All Tetra-chlorodibenzofurans)	NA	0.000063	0.001	0.0005	0.001	0.001
1,1,1,2-Tetrachloroethane	630-20-6	0.057	6.0	0.01	0.05	6.0
1,1,2,2-Tetrachloroethane	79-34-5 1	0.057	6.0	0.005	0.005	6.0
Tetrachloroethylene	127-18-4	0.056	6.0	0.005	0.005	6.0
2,3,4,6-Tetrachlorophenol	58-90-2	0.030	7.4	0.33	0.67	7.4
Thiodicarb (6)	59669-26-0	0.019	1.4	**undetermined**	**undetermined**	**undetermined**
Thiophanate-methyl (6)	23564-05-8	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Tirpate (6)	26419-73-8	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Toluene	108-88-3	0.080	10	0.005	0.005	10
Toxaphene	8001-35-2	0.0095	2.6	0.5	0.16	2.6
Triallate (6)	2303-17-5	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Tribromomethane/ Bromoform	75-25-2	0.63	15	0.005	0.005	15
1,2,4-Trichlorobenzene	120-82-1	0.055	19	0.33	0.67	19
1,1,1-Trichloroethane	71-55-6	0.054	6.0	0.005	0.005	6.0
1,1,2-Trichloroethane	79-00-5	0.054	6.0	0.005	0.005	6.0
Trichloroethylene	79-01-6	0.054	6.0	0.005	0.005	6.0
Trichloromonofluoro-methane	75-69-4	0.020	30	0.005	0.005	30
2,4,5-Trichlorophenol)	95-95-4	0.18	7.4	1.65	3.3	7.4
2,4,6-Trichlorophenol	88-06-2	0.035	7.4	0.33	0.67	7.4
2,4,5-Trichlorophen-oxyacetic acid/2,4,5-T	93-76-5	0.72	7.9	7.9	7.9	7.9

1,2,3-Trichloropropane	96-18-1	0.85	30	0.01	0.05	30
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.057	30	0.01	0.05	30
Triethylamine (6)	10-144-8	0.081	1.5	**undetermined**	**undetermined**	**undetermined**
tris-(2,3-Dibromopropyl) phosphate	126-72-7	0.11	0.10	**3.3**	**0.33**	***undetermined***
Vernolate (6)	1929-77-7	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Vinyl chloride	75-01-4	0.27	6.0	0.01	0.05	6.0
Xylenes-mixed isomers (sum of o-, on, and p-xylene	133020-7	0.32	30	0.005	0.005	30

Footnotes to Universal Treatment Standards Table:

(1) CAS means Chemical Abstract Services. When the waste code and/or regulated constituents we described as a combination of a chemical with it's salts and/or esters; the CAS number is given for the parent compound only.

(2) Concentration standards for wastewaters are expressed in mg/l and are based on analysis of composite samples.

(3) Except for Metals (EP or TCLP) and Cyanides (Total and Amemable) the nonwastewater treatment standards expressed as a concentration were established, in part, based upon incineration in units operated in accordance with the technical requirements of 40 CFR part 264, subpart O, or 40 CFR part 265, subpart O, or based upon combustion in fuel substitution units operating in accordance with applicable technical requirements. A facility may comply with these treatment standards according to provisions in See 268.40(d). All concentration standards for nonwastewaters are based on analysis of grab samples.

(4) Both Cyanides (Total) and Cyanides (Amenable) for nonwastewaters are to be antlyzed using Method 9010 or 9012, found in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods". EPA Publication SW-846, as incorporated by reference in 40 CFR 260.11, with a sample size of 10 grams and a distillation time of one hour and 15 minutes.

(5) These constituents am not "underlying hazardous constituents" in characteristic news, according to the definition at See. 268.2(i).

(6) Between August 26, 1997, and August 26, 1998, these constituents are not "underlying hazardous constituents" as defined at Sec. 268.2(i).

REFERENCES

Protection of the Environment, 40 Code of Federal Regulations.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846 Third Edition, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., December, 1996.

RCRA Regulations and Keyword Index, Elsevier Science Inc., New York, New York, 1997 Edition.

IGNITABILITY PERFORMANCE EVALUATION STUDY ARE YOUR WASTE STREAMS BEING CORRECTLY CHARACTERIZED?

Lester J. Dupes, Rock J. Vitale
Environmental Standards, Inc., 1140 Valley Forge Road, Valley Forge, Pennsylvania 19482-0911
Debra J. Caillouet
Stationary Environmental & Energy, Chrysler Corporation,
800 Chrysler Drive E, Auburn Hills, Michigan 48326-2757

ABSTRACT

Thirteen commercial laboratories were evaluated for consideration of providing waste stream characterization support. An initial single-blind performance evaluation (PE) study was performed to determine the accuracy of the laboratory-reported results when compared to known values.

The initial PE study was conducted for constituents typically analyzed for hazardous waste characterization. These constituents included Toxicity Characteristic Leaching Procedure (TCLP) volatiles, TCLP semivolatiles, TCLP metals, and ignitability. A review of the ignitability tests performed by SW-846 Method 1010 and 1020 exhibited a wide range of both positive and negative bias from the known flashpoint temperature of the pure compound used as the PE sample. Results were compared to reproducibility criteria generated from American Society of Testing Materials (ASTM) Method D93-96.

Because of the erratic ignitability results observed for many of the participating laboratories, the laboratories were requested to perform a self-audit inspection of their current SOP and actual laboratory procedures. These self-audit results were used to ensure inter-laboratory consistency and compliance to SW-846 Method 1010 and Method 1020.

A second round of PE samples were subsequently submitted to each of the thirteen participating laboratories for analysis. These results showed some improvement for several of the laboratories, whereas other laboratories again reported results with a significant bias. The results of this study exhibited a wide range of ignitabilities which would have represented incorrect waste characterization if the PE samples were actual waste stream samples. This paper will focus on discussion of the PE sample results, the laboratory self-audit results, and method compliance issues.

INTRODUCTION

A comprehensive laboratory evaluation process was performed to identify commercial laboratories to provide waste characterization testing services. This evaluation included an initial technical survey of approximately 40 laboratories. The survey results were used to further reduce the potential candidates to 13 laboratories. Laboratory audits specifically focused on waste characterization analyses and performance evaluation (PE) samples for specific parameters of interest for the characterization of complex wastes was used to further evaluate the 13 short-listed laboratories. The parameters included ignitability, TCLP volatiles, TCLP semivolatiles, and TCLP metals. An initial set of single-blind PE samples were prepared as whole volume samples by a reputable commercial PE provider.

A single-blind PE study sample is defined as a "test" sample in which the laboratory is aware that the sample submitted is a PE sample but does not have knowledge relative to the analytes or true concentrations contained in the PE. A single-blind sample permits the data user to better understand a laboratory's analytical accuracy and by inference, draw conclusions on the accuracy of actual waste sample results.

The matrix of the ignitability PE sample was a pure compound. The TCLP volatile sample was an aqueous matrix, and the TCLP metals sample was a soil matrix. The PE samples for all 13 laboratories were prepared from the same lot number to further reduce variance and permit a direct and meaningful comparison between laboratories. Whole-volume samples, which require no further dilution or preparation by the laboratory prior to analysis, were chosen to further reduce variables caused by different technicians or chemists. The PE samples were prepared and shipped on ice under Chain-of-Custody procedures to each laboratory directly from the provider.

In addition, an actual complex industrial waste stream sample was also used in this PE study. This waste stream was selected to provide the laboratories with a representative "real-world" sample that the laboratories may receive as an actual sample for waste testing. In particular, a paint purge solvent was selected for testing. This paint purge solvent is relatively homogeneous and has previously been characterized as hazardous due to a flashpoint temperature below the regulatory limit and volatile concentrations above the regulatory limit.

To collect this sample, the PE provider furnished bottles to the industrial facility for packaging this solvent. This sample was collected and shipped back to the PE provider for homogenization and repackaging for delivery to the 13 laboratories. This PE sample was shipped by ground carrier and was not refrigerated. Since it was not certified, this sample was to be evaluated only for interlaboratory comparison purposes and was analyzed for ignitability, TCLP volatiles and TCLP metals.

Performance by the individual laboratories was evaluated not only for the results proximity to the certified values but also for communications, data packaging and reporting, method compliance, and timeliness of deliverables. These latter issues were evaluated using techniques and procedures addressed in a previous manuscript (Dupes and Rose, 1995). The issues are not discussed any further herein.

INITIAL PERFORMANCE EVALUATION SAMPLE RESULTS

In general, the laboratories reported acceptable results for the TCLP volatile organic compounds and metals, relative to the program requirements. However, ignitability results ranged from 114°F to 153°F, with only four laboratories meeting acceptance criteria for this parameter. The ignitability PE sample was certified by the provider of the pure compound to have a flashpoint of 140°F ± 5°F. This certified value represents the flashpoint of the compound as determined by various manufacturers of this compound. The temperature of the PE sample was specifically chosen to determine variance around 140°F This temperature is also defined as the regulatory limit for characterization of the waste as hazardous. Wastes that flash at a temperature of <140°F are considered hazardous and wastes that flash at >140°F are considered non-hazardous by the definition for ignitability (40 CFR Part 261).

Ten of the laboratories reported the temperatures higher than the regulatory limit of 140°F. resulting in a classification as non-hazardous. Results for the three laboratories classifying the PE sample as hazardous reported results of 129°F, 114°F, and 120°F. Those temperatures are all well below the lower acceptance limits of 135°F for the PE sample. Six other laboratories were slightly above the 145°F acceptance criteria. A summary of the results is presented in Table 1.

The "real world" purge solvent sample submitted to the laboratories was consistently identified by all laboratories as hazardous based on flashpoint. The reported flashpoints ranged from 66-76°F (several laboratories reported the sample flashed at less than their reporting limit of room temperature).

The variance in the certified (pure compound) PE results may have been due to the use of thermometers which have not been adequately calibrated against a National Institute of Standards and Technology (NIST) standard thermometer (this is routinely noted in a number of audits recently performed by the authors), the lack of correction for barometric pressure, or analytical variance of the methodologies used by the laboratories. Each of the laboratories management or quality assurance staff were required to conduct an intensive self-audit review of the PE sample analysis, general analysis conditions, and quality control procedures to determine potential causes for the wide range of flashpoint temperatures obtained for the PE sample.

SELF-AUDIT QUESTIONS AND FINDINGS

Upon completion of the initial PE study, a self-audit questionnaire was generated for completion by each of the participating laboratories. The audit questionnaire consisted of 26 questions obtained from a technical review of SW-846 Methods 1010 and 1020A; ASTM Methods D93-80, D93-90, D93-96, D3278-96, and E502-84. These questions included verification of the method used and referenced for analysis of the initial PE study sample, sample storage conditions, instrument analysis conditions, analysis procedures, thermometer calibrations, quality control measures, acceptance criteria, and corrective actions.

The questionnaire was provided to each of the laboratories for completion by laboratory management or quality assurance personnel. In addition to providing written responses to the questions, a copy of the laboratory standard operating procedure was requested for review.

A review of the thirteen laboratory responses and SOPs were conducted to determine possible reasons for the significant variation observed. A summary of issues identified in the self-audit checklists by the authors is presented below.

- According to the original request for analysis, all laboratories were requested to perform Method 1020A. Several laboratories did request a change to Method 1010, which was granted and documented. However, many laboratories did not request this change. Whenever a method change is necessary, data users (viz., the client) should be contacted prior to implementing the method change.

- Several laboratories used compounds (i.e. acetic acid, mixed xylene, and kerosene) that were not stated in the method for quality control purposes. The laboratories were directed to use *p*-xylene conforming to the ASTM specifications, as required by Method 1010. The acceptance criteria should be 81±2°F as required by ASTM D93-90 or 81±1°F as required by ASTM D93-96.

- Several laboratories did not store the ignitability PE sample at 4±2°C. Although it could be argued that a pure single-component compound used for the PE would be unaffected by volatile constituent loss, actual waste samples are typically complex mixtures, and lighter fractions can be lost due to volatilization. All laboratories were requested to store future samples scheduled for ignitability at 4±2°C to reduce the possibility of loss of lighter fraction volatile constituents.

- Five laboratories had not calibrated or could not demonstrate that the thermometer used for ignitability determination had been calibrated with a NIST-standard thermometer within the last year. One laboratory noted a 2-5°F difference upon calibration of three different thermometers. In addition, a laboratory also noted that after the recalibration a mercury gap in one thermometer was noted and that the gap increased as the temperature increased. All laboratories were directed to recalibrate the thermometers on an annual basis. A multi-point calibration should be performed to determine accuracy at several temperatures, and correction factors must be taken into account when measuring flashpoint temperatures.

- Six laboratories did not correct for barometric pressure, as required by the ASTM D93 methods. Several of the laboratories noted that the correction would be very small (< 0.2°F); however, one laboratory noted the flashpoint temperature would increase by 0.9°F All laboratories were directed to correct for the ambient barometric pressure of the laboratory, as required by ASTM methodologies referenced in Method 1010 and Method 1020A.

- Many of the laboratories did not report a duplicate result for the ignitability analysis by Method 1010. Although not specifically stated in Method 1010 or ASTM D93, duplicate analyses of all samples should be performed to comply with ASTM E502, which indicates that the average results for flashpoint should be reported. This will also provide a consistent approach with respect to Method 1020A, which requires duplicate analyses. Sufficient volume (>150 ml) should be collected or provided in order to conduct duplicate analyses by Method 1010.

- All laboratories indicated the Pensky Martens apparatus used for analysis by Method 1010 is located in a hood to reduce surrounding drafts and for health and safety considerations. However, several laboratories indicated that the hood was turned on during the actual testing, which can cause loss of volatiles through drafts. Several laboratories indicated that problems have occurred when hoods containing the apparatus are turned on during analysis. Laboratories were directed to limit the amount of draft around the apparatus.

- Three laboratories did not meet *p*-xylene acceptance criteria of 81±2°F (ASTM D9390) or 81±1°F (ASTM D93-96) prior to analysis of the PE sample. One laboratory reported an acceptance range for *p*-xylene of 80-91°F. Two laboratories did not report *p*-xylene results on the logbook pages. These practices are not acceptable. All *p*-xylene calibrations must meet acceptance criteria and be recorded prior to sample analysis. Several laboratories have implemented the use of an additional laboratory control sample (LCS) near the regulatory limit of 140°F This is not a method requirement but is recognized as a good laboratory practice.

- One laboratory was increasing the rate of temperature of the sample by 2°F/minute ; prior to application of the test flame. The laboratories were directed to follow the rate of temperature increase, as specified in the ASTM D93 Method as 9-11°F/minute.

- One laboratory reported that the sample was stirred during the actual application of the test flame to the sample. Samples must not be stirred during the application of, the test flame to the vapor space, as required by the ASTM method.

- Several laboratories indicated the introduction of the test flame into the vapor space is maintained from 0.5-1.5 seconds. Analysts should attempt to consistently introduce the test flame into the vapor space for 1 second, as required by the ASTM protocol referenced by Method 1010.

- One laboratory reported the ignitability results to the nearest tenth degree. One laboratory reported the raw results on a stenopad, which did not include, the analysis test name, method number, analyst name, laboratory name, or QC results. The laboratories were directed to report result to the nearest 1°F Adequate documentation of quality control (QC) results, barometric pressure, analysis date, etc. must be maintained by all laboratories through the use of formal logbooks.

- Several laboratories had not reviewed their SOP within the last year to verify method compliance and actual laboratory procedures. All laboratories were directed to review and update laboratory SOPs on an annual basis to reflect the actual procedures performed and to monitor for continuing method compliance.

SECOND ROUND IGNITABILITY PE STUDY

Upon completion of the self-audit review, laboratories were notified of the findings and requested corrective actions prior to performing the second ignitability PE sample study. Three ignitability PE samples were selected for the second round study. The flashpoint of the PE samples was specifically designed by the authors to provide a range of flashpoints. The flashpoint-certified values of Flashpoint Sample #1, Flashpoint Sample #2, and Flashpoint Sample #3 were 140°F, 120°F, and 170°F, respectively. These three flashpoints provide a sample that would be considered hazardous (120°F), a sample at the hazardous regulatory limit (140°F) and a sample that would be considered non-hazardous (170°F). The actual compounds used for the PE samples were chosen and prepared by the same commercial PE provider used for the initial study. The expected flashpoint temperature

represents the flashpoint for the compound as determined by various manufacturers of this compound. All PE samples were pretested prior to use by the PE supplier by Pensky Martens closed-cup procedures (US EPA SW-846 Method 1010) and were corrected for barometric pressure of 620 mm. All PE samples were contained in glass bottles with Teflon-lined caps and were shipped on ice under Chain-of-Custody to the 13 participating analytical laboratories. Sufficient volume (150 ml) was sent to each laboratory to permit duplicate analyses of the PE sample.

ANALYTICAL RESULTS AND CRITERIA FOR EVALUATION

Reproducibility criteria were calculated based on ASTM D93-96, which provides precision and bias data for the ASTM method. Reproducibility in this ASTM method is defined as "the difference between two single and independent results obtained by different operators working in different laboratories on identical material that would, in the long run, in the normal and correct operation of the test method, exceed the following values only one case in 20" (ASTM D93-96).

where:

$R = BX$

$B = 0.078$
X = the reported result in °C
R = reproducibility

Since the ASTM method is unclear as to which temperature should be used in calculating the reproducibility criteria, criteria for the three flashpoint PE samples were generated by using the expected flashpoint (converted to degrees Celsius) in the equation listed above. The criteria calculated should represent a range encompassing the expected value of the PE sample. The following criteria were calculated for the PE samples:

Sample Identifier	Expected Flashpoint	Reproducibilily Criteria
Flashpoint Sample #1	140°F	± 8°F
Flashpoint Sample #2	120°F	± 7°F
Flashpoint Sample #3	170°F	± 11°F

According to the previous ASTM Method revision D93-90, reproducibility criterion of ± 6°F should be used for evaluation of the analytical data. According to the ASTM D93-90 method, this criteria applies to all liquid samples with flashpoint temperatures less than 220°F Evaluation of the data using the more stringent criteria in D93-90 excluded only two more results when compared to the criteria calculated by Method D93-96. A summary of the results are presented in Tables 2, 3 and 4.

All participating laboratories except one analyzed the three PE samples by SW-846 Method 1010. One laboratory analyzed the samples by SW-846 Method 1020. Three provided results after the due date, missing the specifically stated date as a requirement in the documentation accompanying the PE samples.

DISCUSSION OF SECOND ROUND IGNITABILITY PE STUDY RESULTS

Upon review of the PE sample results, the inter-laboratory accuracy of the results obtained from the laboratories was observed to be variable. Four laboratories reported results which, when compared to the known flashpoint, were greater than the Method D93-96 criteria for all analyses (except for the analysis of Flashpoint #1 sample by one laboratory, which was within criteria). Reported results, when compared to the known flashpoint, ranged from 10° to 70°F absolute difference from the known value of the PE samples. Results reported by one laboratory were biased very low (-27° to -70°F below the known flashpoints of the materials). Results reported by the laboratories are unacceptable and may indicate a recurring problem relating to the analyses being performed by these laboratories.

Two laboratories reported two of the three results outside the Method D93-96 criteria. When compared to the known flashpoint, reported results ranged from 8° to 12°F absolute difference from the known value of the PE samples.

Five laboratories reported one of the three results outside the calculated Method D93-96 criteria. When compared to the known flashpoint, reported results ranged from 7° to 13°F absolute difference from the known

value of the PE samples. One laboratory reported duplicate results, but did not report and average result for each PE sample. Finally, two laboratories reported results for all three of the PE samples within the Method D93-96 criteria.

In general, a majority of the laboratories reported a positive bias when compared to the known flashpoints of the samples. Furthermore, several laboratories did not follow the instructions provided after the self-audit. Two laboratories did not report the results to the nearest 1°F Instead, the laboratories reported results to one decimal place. In addition, two laboratories did not analyze all samples in duplicate as requested. Finally, one laboratory sent the PE samples from the facility being considered for program inclusion, where ignitability is apparently no longer performed, to an affiliated network laboratory. This transfer occurred without notification to the authors. This network facility was not previously audited for this program.

SUMMARY

Based upon a review of the initial ignitability study, self-audit review, and subsequent PE study, the use of ignitability data for actual waste testing should be highly scrutinized. The regulatory-approved methods require a significant amount of operator experience in conducting tests that are consistent and method compliant. Evaluating ignitability through audits and frequent double-blind PE studies should be implemented to verify acceptable performance. Without continuous review of this method, inaccurate ignitability results could be causing your waste to be disposed of improperly.

ACKNOWLEDGMENTS

Mr. Chuck Wibby and Environmental Resource Associates for providing technical assistance in identification and evaluation of compounds for the ignitability performance evaluation study, providing assistance in collection, homogenization, and repackaging of the Chrysler waste stream sample and supply of all PE samples in this study.

Mr. Brian Miller, of Chrysler Corporation for collection, packaging, and shipment of the waste stream sample used in this PE study.

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Table 1. Initial Ignitability Performance Evaluation Study

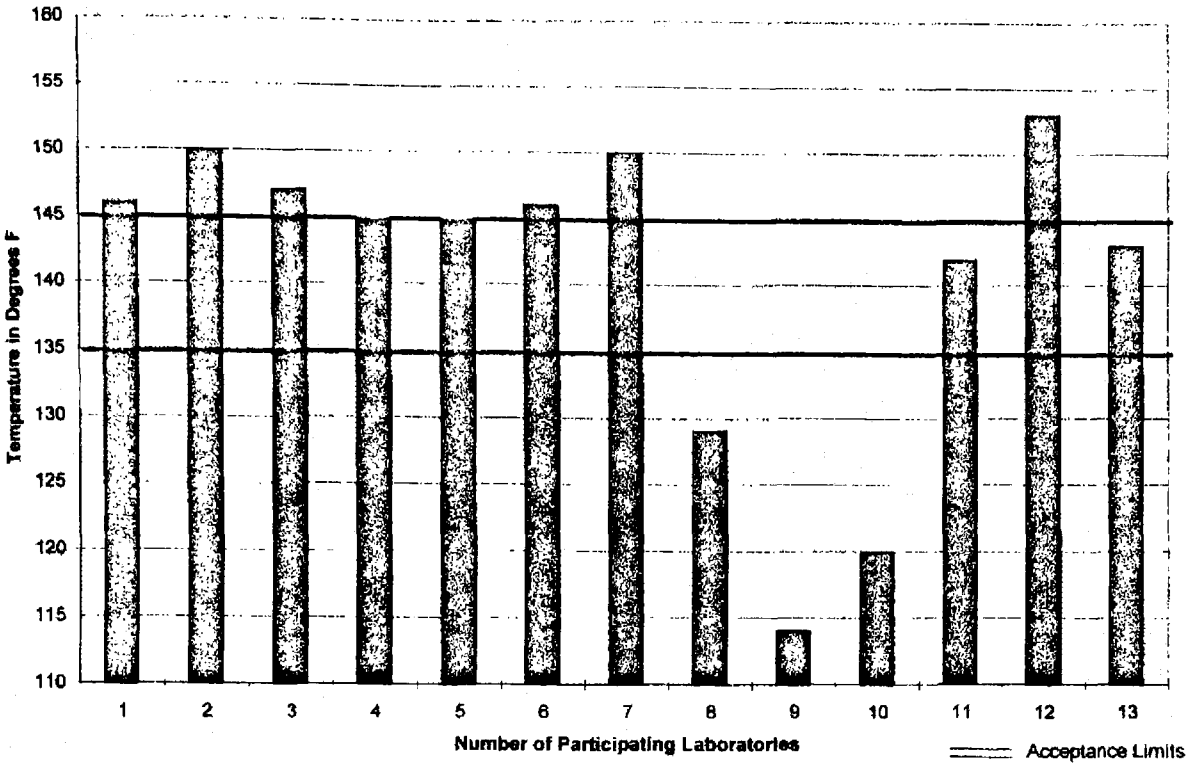


Table 2. Ignitability Performance Evaluation Study PE Flashpoint Sample #1

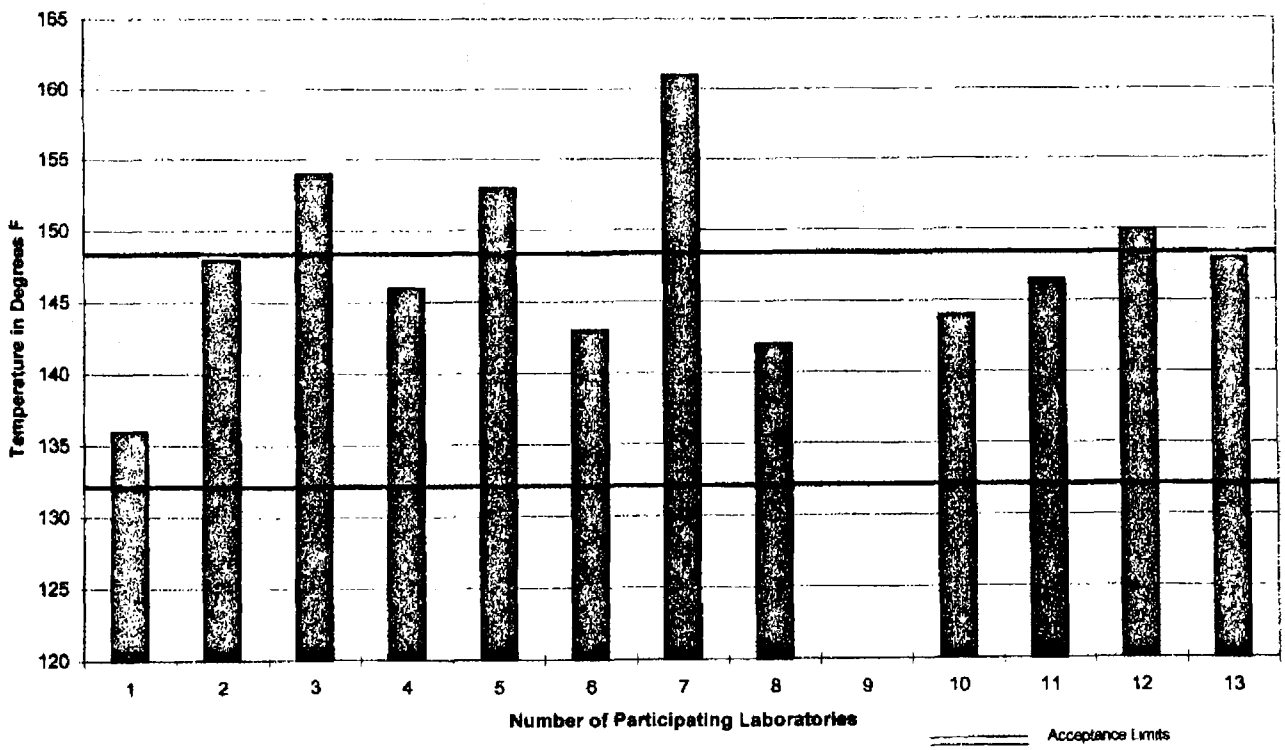


Table 3. Ignitability Performance Evaluation Study PE Flashpoint Sample #2

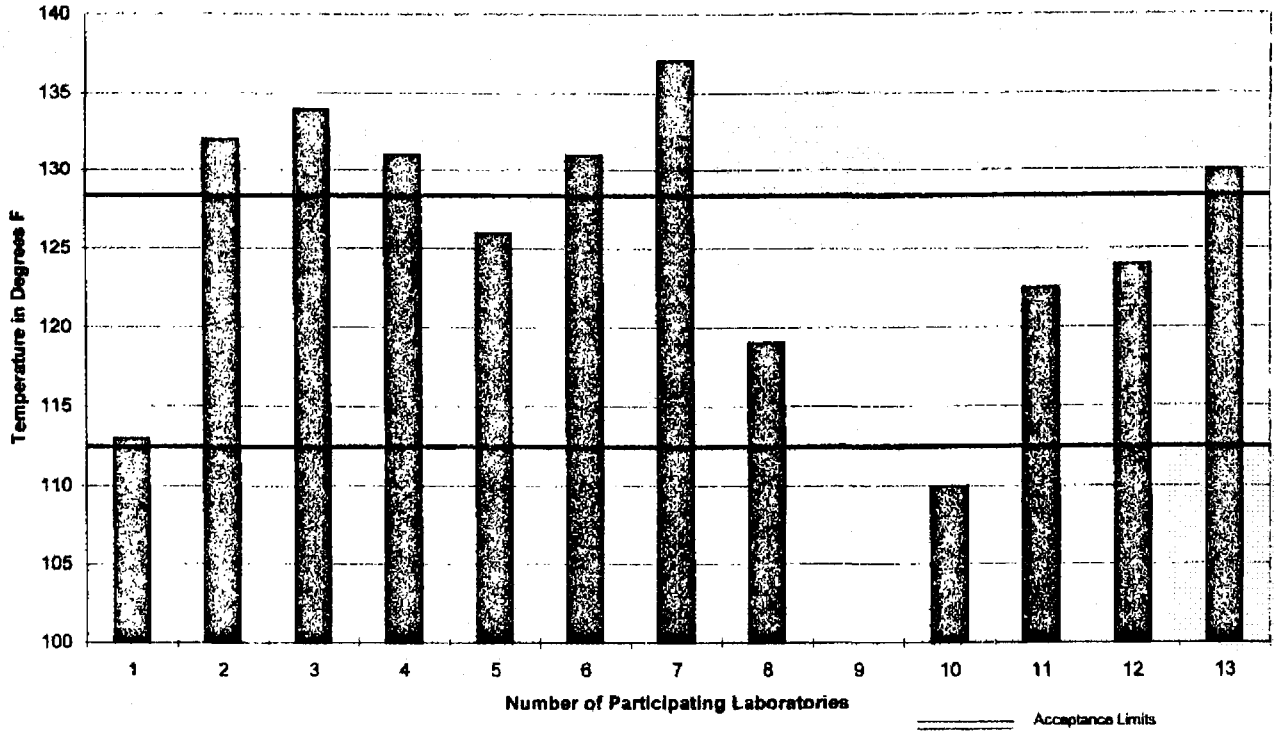
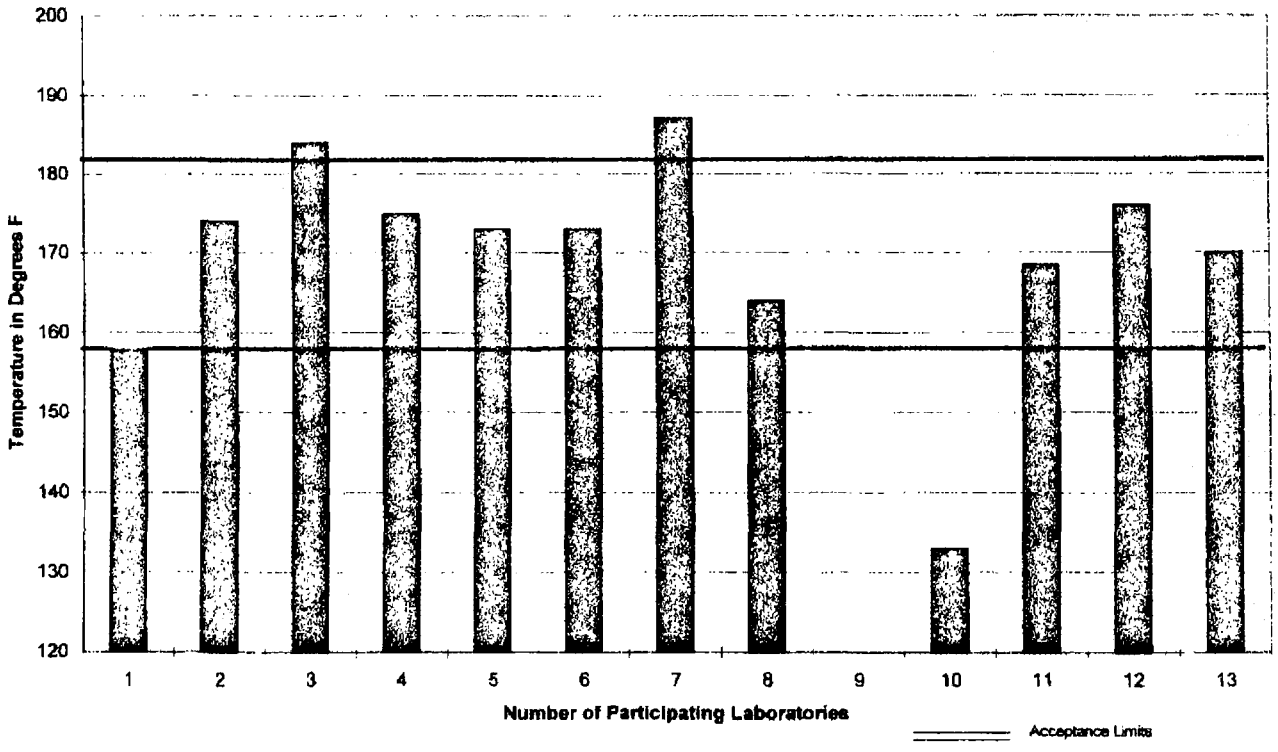


Table 4. Ignitability Performance Evaluation Study PE Flashpoint Sample #3



TECHNIQUES FOR IMPROVING THE ACCURACY OF CALIBRATION IN THE ENVIRONMENTAL LABORATORY

Dennis A Edgerley
Quanterra Environmental Services, 880 Riverside Parkway, West Sacramento, California 95605

Abstract
Consistent and reliable procedures for generating calibrations are essential to accurate laboratory results. Unfortunately the interpretation of acceptable practice is often based on misunderstanding or derived from practices commonly utilized in non-environmental methods, and therefore does not provide a reliable means for maintaining data quality. This paper presents a demonstration that some common practices used in the calculation and evaluation of calibration factors, including the use of unweighted regression and the associated correlation coefficient, are inappropriate for environmental analysis due to high relative errors which result at the low end of the curve. Alternate criteria for evaluation of calibration curves are proposed based on the Relative Standard Error (%RSE). Statistical derivations and examples are presented to demonstrate how this approach provides an improved measure for the evaluation of calibration data based on weighted regression. Other related considerations for assessing acceptability of calibration data are also presented.

Introduction

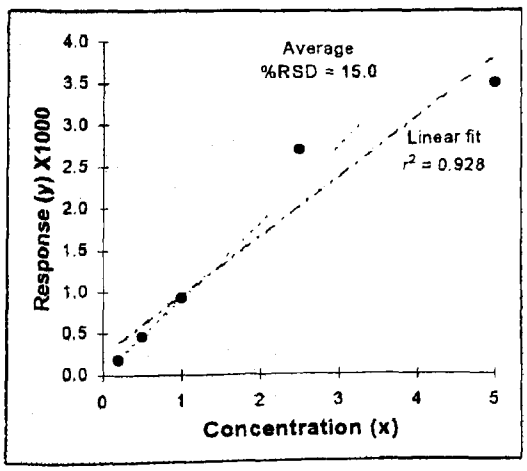
Any analytical measurement must employ reference elements to ensure traceability to relevant basic quantities. The quality of a calibration depends on the uncertainty of the reference, the appropriateness of the reference and how well the calculation procedures match the requirements of the analysis. A majority of the methods employed in the environmental laboratory are based on a relative calibration where standards of known content and concentration are analyzed by a suitable detector. The responses of samples analyzed under the same conditions are then used to calculate concentrations by numerical interpolation to a response curve from the calibration standards.

The only criterion for initial calibration in SW-846 method 8000A[1] reads, *"If %RSD is less than 20 an average calibration factor can be used otherwise data should be fitted to a curve."* There are many examples of well defined and reproducible calibrations which either due to nonlinearity, or a non-zero intersection of the axis will not meet this 20% criterion for acceptability. Recognizing this, update III to SW-846, Method 8000B[2] provides additional direction on use mid evaluation of least squares regression, adding criteria for higher order curves. However, several critical issues are not sufficiently considered and overall the current guidance remains incomplete with regard to error weighitng and evaluation of acceptability.

Linear Calibration

The most commonly adopted option for handling calibration data, which is linear but does not meet the criteria for averaging, involves the calculation of coefficients for a linear equation of the form:

$$y = Ax + B \qquad \text{Equation 1}$$



Concentration is defined here as the independent variable (x) and response as the dependent variable (*y*) in compliance with method 8000B. A least squares regression is employed and the value of the correlation coefficient (r) or the coefficient of determination (r^2) is evaluated as a measure of acceptability. A value of 1.00 represents a perfect correlation. Generally in practice, a value of r^2 greater than 0.990 is considered satisfactory.

The practical difficulty encountered in this approach is displayed in Figure 1. For the example data set, the line based on an average calculation (shown as a dotted line) easily meets the 20% acceptance criteria for %RSD, yet r^2, does not meet the criteria for acceptability with a value of 0.928.

Figure 1

To understand this inconsistancy we must examine more closely the statistical difference between an average calculation and the regression line. The average calibration factor is determined according to equation 2.

$$\overline{C} = \frac{1}{n}\sum_{i=1}^{n} C_i \qquad \text{Equation 2}$$

Where:

$\overline{C}$ = Average Calibration factor
C_i = Calibration factor for calibration level i (y_i/x_i)
n = number *of* calibration levels

This and all following equations may also be adapted to internal standard methods by substituting the relative response calculated as in Equation 3 for the measured response (y_i).

$$y_i^{\text{Relative}} = y_i \times \frac{x_i^{IS}}{y_i^{IS}} \qquad \text{Equation 3}$$

y_i = response of target analyte
x_i^{IS} = concentration of internal standard
y_i^{IS} = response of internal standard

Graphically the average and associated error limits based on ±1 standard deviation are shown in Figure 2. This type of normalized plot makes visual examination of the data more straight-forward[3] as values at the low end of the calibration are shown at the same relative scaling as those toward the high end.

The average represents the value which will minimize the variance in the calibration factors (s^2_C) for all calibration points[4] For reference the calculation of variance is shown in Equation 4.

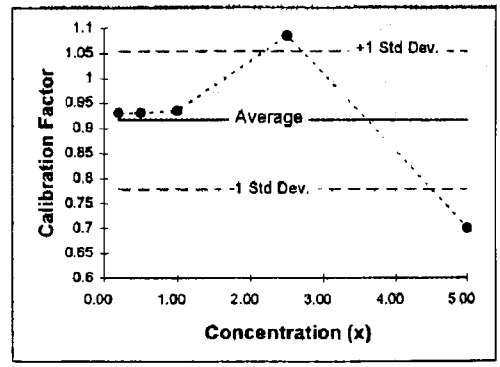


Figure 2

$$s_C^2 = \frac{\sum_{i=1}^{n}\left(C_i - \overline{C}\right)^2}{n-1} \qquad \text{Equation 4}$$

If $\hat{y}_i$ is defined as the expected response for calibration level i from the relationship $\hat{y}_i = x_i\overline{C}$, by substitution the variance can also be expressed as:

$$s_C^2 = \frac{\sum\left[\frac{y_i - \hat{y}}{x_i}\right]^2}{n-1} \qquad \text{Equation 5}$$

Using the method of least squares we can determine a mathematical relationship between the dependent and independent variables which minimizes the residual variance. By definition the residual variance represents the variability due to experimental error[5] and does not include that contribution to variance which is attributable to differences in the independent variable. The residual variance of *y* on *x* is defined as:

$$s_{yx}^2 = \frac{\sum_{i=1}^{n}\left(y_i - \hat{y}\right)^2}{n-1} \qquad \text{Equation 6}$$

A comparison of equations 5 and 6 demonstrates that the average value is the same as a coefficient derived from least squares regression if a weighting of $1/x^2$ is applied. The average calibration factor gives a result which is identical to that produced by the method of least squares using (1/concentration^2) weighting and intercept

forced through zero.

Alternatively a generalized equation for calculating the coefficient which fits the simple relationship $y = Ax$ and minimizes the residual variance without weighting is determined by substituting Ax for y in Equation 6 and setting the derivative with respect to A equal to zero. This gives for the calibration factor:

$$A = \frac{\sum_{i=1}^{n} x_i y_i}{\sum_{i=1}^{n} x_i^2} \qquad \text{Equation 7}$$

For the example data set, calibration coefficients and residual variances are compared in table 1. The coefficients determined from these two approaches are quite different and it is obvious that an average calibration coefficient does not minimize the residual variance of y on x.

Table 1

Calculation type	CF	s^2
Average	0.916	1.335
Linear fit	0.784	0.768

Transforming the vertical axis of Figure 2 to a non-normalized form gives the plot shown in Figure 3. A comparable plot for the unweighted regression line using the same set of example data is presented in Figure 4. Both figures represent graphically, with the dashed lines, effective error weighting based on ±1 standard deviation.

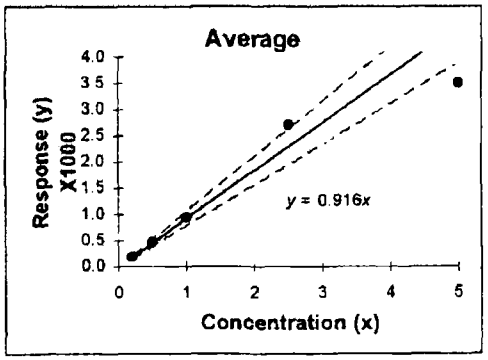


Figure 3

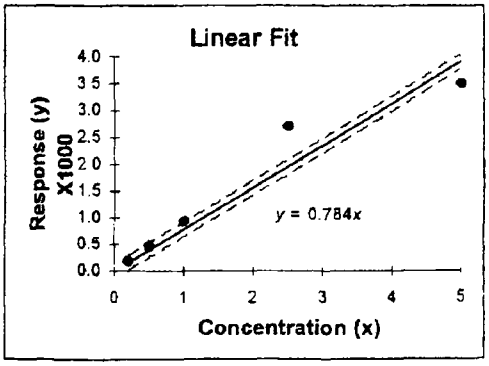


Figure 3 demonstrates that $1/x^2$ weighting gives a relationship that emphasizes precision at the low end of the calibration range. In environmental analyses frequently the objective is to ensure that target analytes do not exceed defined regulatory or action limits, hence reducing quantitation error at low concentrations is especially important.

Figure 4

Deriving the best form for a calibration curve must include consideration of the weighting factors which are appropriate to the requirements of the analysis. As was shown empirically for the single factor calibrations and can be proven for the general case[6], the value of the coefficients is sensitive to the weighting. Method 8000B requires that at least three replicates at a minimum of 5 concentration levels are used to derive weighting factors which are defined as the inverse of the standard deviation squared for each concentration. In practice this is an especially burdensome requirement, both in the amount of data required and the computational difficulty which results when using individually derived weighting values for each calibration level. Faced with the options in method 8000B, most laboratories will probably choose curve fitting without any consideration of weighting regardless of the potential negative impact on data quality.

For many methods in the environmental laboratory errors in measurement are proportional to the magnitude of the parameter measured. Likewise it is common to consider percentage errors relative to the concentration as we have demonstrated in the case of the average calibration calculations. Rather than perform multiple replicates each time a calibration is run, the laboratory should make an initial determination of the relationship between concentration and the standard deviation throughout the calibration range, Where a direct proportionality is found, all subsequent calibrations should be based on the 1/concentration^2 weighting which is consistent with average calibration curves. Conversely, if standard deviations are of equal absolute magnitude throughout the concentration range, calibrations should be unweighted and average calibration factors should not be used.

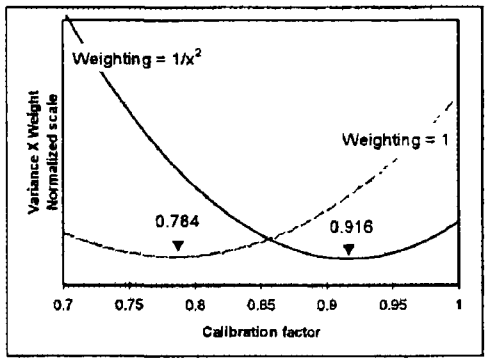
When the weighting is expressed as a function of the concentration most data systems are capable of perforating the calculation.

Percent Relative Standard Error

The magnitude of the residual variance with error weighting applied will provide a measure of the experimental error for the derived curve. Figure 5 shows the relationship between variance and calibration coefficient for a fitting equation of the form: $y = Ax$.

The value of relative standard deviation defined according to Equation 8 has widespread acceptance as a measure of the error associated with an average calibration.

$$\%RSD = 100x\frac{1}{\overline{C}}x\sqrt{\frac{\sum_{i=1}^{n}\left(\overline{C}-C_i\right)^2}{n-1}} \qquad \text{Equation 8}$$



Because standard deviation is equal to the square root of variance, it can be shown that %RSD is also equal to the square root of the weighted residual variance of y on x, calculated as a percentage, using a derivation similar to that for Equation 5.

Likewise the coefficient of determination (r^2) is normally, recognized as an indication of error associated with regression curves.

Figure 5

$$r^2 = \frac{\Sigma\left(y-\overline{y}\right)^2-\Sigma\left(y-\hat{y}\right)^2}{\Sigma\left(y-\overline{y}\right)^2} \qquad \text{Equation 9}$$

Since for any set of data the $\Sigma\left(y-\hat{y}\right)^2$ term is not dependent on the form of the calibration curve function or the coefficients, the value of $(1-r^2)$ will be directly proportional to the unweighted residual variance as defined in Equation 6.

It becomes apparent that for an average calibration, the coefficient of determination calculated will not provide an optimum measure of error as r^2 applies only to an unweighted least squares determination. The %RSD on the other hand is only meaningful as a measure of error when applied to an average calibration. A generalized indicator of error, *Percent Relative Standard Error (%RSE),* which can be applied to any form of weighted regression function is derived similarly to %RSD making adjustment for the degrees of freedom in the relationship by replacing the n *1* factor with $n - p$ where p is an integer equal to the number of coefficients as defined in Equation 10.

%RSE is equivalent to %RSD when calculated for the average. In Figure 6 the least squares line derived using (1/concentration^2) weighting is compared to the average line and the unweighted least squares line for the same data set used in the previous figures. In this example the elimination of the zero point is responsible for an increase in the %RSE for the weighted line ($p = 2$).

$$\%RSE = 100x\sqrt{\frac{\sum_{i=1}^{n}\left[\frac{y_i-y_i}{y_i}\right]^2}{n-p}} \qquad \text{Equation 10}$$

Where:

y_i = Actual response of calibration level
$\hat{y}_i$ = Calculated response from curve
p = number of terms in the fitting equation
(average = 1, linear = 2, quadratic 3)
n = number of calibration points

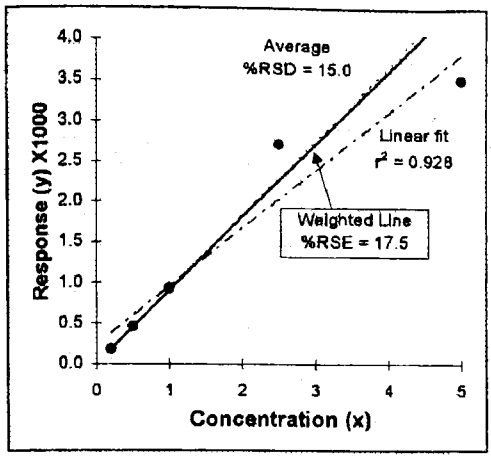


Figure 6

The improved low-end accuracy for this weighted line compared to the unweighted regression line is shown in Table 2. Concentrations measured close to the lowest calibration point would be reported with values approaching 100% lower by using an unweighted linear calibration as compared to the weighted curve.

Table 2

	% Error (calculated - True)	
Concentration	Weighted	Unweighted
0.2	1.7	109
0.5	1.2	29.9
1.0	2.7	2.8
2.5	16.7	25.1
5.0	28.7	8.9

Only recently, in the update to SW-846 method 8000B and also in a draft of guidance for development or modification of water methods[7] has the EPA recognized the importance of considering weighting in calibration calculations. These documents do not, however provide options for evaluating weighted regression fits. The coefficient of determination (COD) used in method 8000B for evaluating polynomial curves is "weighted" only to adjust for the degrees of freedom in the fitting equation and does not provide a measure of error which is suitable for regression curves derived with error weighting.

Non-Linear Calibration

While it is reasonable to use the simplest mathematical relationship, which gives acceptable accuracy, it should not always be assumed that an average or linear curve is preferred. Some detector systems commonly used in the environmental laboratory are inherently non-linear. As an example the electron capture detector (ECD) commonly utilized for its sensitivity to chlorinated pesticides and herbicides can for most analytes provide calibrations which are linear over a 20X concentration range. It is often difficult to optimize detector conditions for multiple analytes with widely varying electron affinities and even under ideal conditions many ECD detectors show linearity within 20% RSD only over a narrow concentration range. The calibration data plotted in Figure 7 was curved for enhanced accuracy over a 32X range by applying a quadratic fit. While the %RSD for the average was not acceptable at 44.9% the quadrati curve gives a %RSE of only 3.7%.

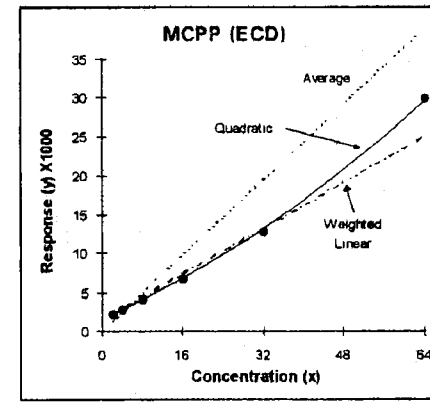


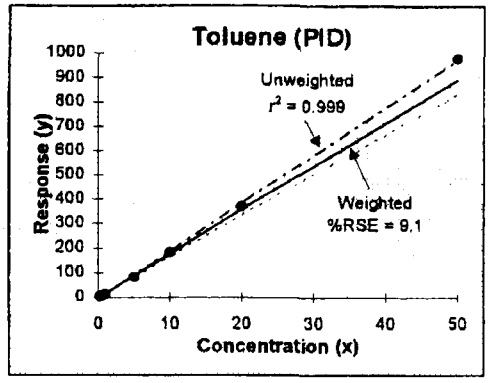
Figure 7

In lieu of higher order curve fitting the approach often defaults to reducing the calibration range, which normally requires re-analysis of some or all calibration points as well as increasing the number of sample dilutions, both of which will add to the cost of the analysis without necessarily providing significant improvement in quality. A simple recalculation of the curve parameters based on a quadratic fit allows the full concentration range of the calibration data to be utilized with improved accuracy. The use of second or higher order curves should not be applied simply to achieve minor improvements in the %RSE that will allow an otherwise unacceptable curve to be used. Justification for higher order calculations should be based primarily on an understanding of the performance characteristics of the detector or the method. The use of higher order curve fitting should also not be substituted for proper instrument maintenance, nor should an effort be made to extend calibrations beyond the detector saturation level.

Evaluation of Calibrations

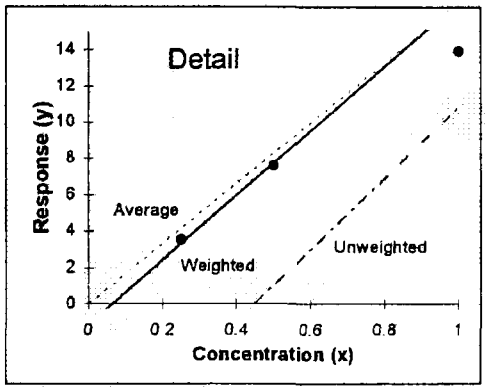
Whenever possible, data evaluation should be performed against rigid criteria that will prevent any tendency for analyst bias to affect reported results and allow automated data validation processes to be implemented. In a production-oriented laboratory setting, visual examination of every calibration curve is not routinely performed.

Rather curves are evaluated against calculated criteria only. Modern data systems allow regression parameters to be calculated with very little analyst effort. Although the %RSE calculation is not commonly provided it can usually be implemented either in a user function or by exporting the results to a spreadsheet.



The behavior of the calibration curve near the reporting limit should also be a primary consideration for environmental methods. According to the proposed update to SW-846 method 8000B, data should be considered unreliable for instrument response less than 3 times the y-intercept from the curve if the value is positive, or less than the concentration calculated from zero response if the y-intercept is negative. The use of weighted curve fitting will greatly reduce the possibility that the intercept exceeds these limits. The unweighted line in Figure 8a appears to provide a very good fit to the data with r^2 = 0.999. The expanded view near the low end of the calibration shown in Figure 8b clearly demonstrates the improved fit for the weighted line.

Figure 8a



Recommendations for the minimum number of data points needed to prepare a calibration vary from one to fifteen depending on the method and the order of the fitting equation. Normally five points are considered adequate for linear curves. Some problems may be corrected by elimination of data points from the calibration calculation. This should only done if they are either the highest or lowest concentration and the number of points remaining meets the minimum requirements of the method. The analyst should also be aware that removing the low point might adversely affect the reporting limit, as quantitation must not be performed outside the concentration range of the calibration.

Figure 8b

When second order curves are evaluated, the acceptability should include an evaluation of the curve inflection points. In Figure 9, the quadratic curve (solid line) provides a significant improvement in %RSE over the weighted least squares line (dashed). However, the *y*-value of the curve inflection for this line is below the response of the highest data point, thus quantitation near the upper end of the calibration range could give erroneously high results.

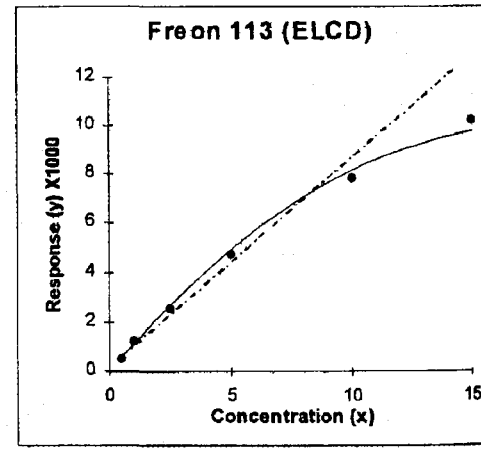


Figure 9

As a rule, all points in the calibration curve should demonstrate a consistent relationship between concentration and response (response increases with increasing concentration). According to SW-846 method 8000B *"... the curve must be continuous, continuously differentiable and monotonic over the calibration range."*

Summary

The correlation coefficient as a criterion for evaluating regression curves does not apply to weighted regressions that are necessary for accurate low concentration reporting of environmental data. The correlation coefficient is also not consistent with the %RSD criterion used to evaluate average curves, often leading to calibration data that is not acceptable for a linear regression based on the correlation coefficient but does meet %RSD criterion of an average calibration.

The Percent Relative Standard Error (%RSE) provides an improved criteria for evaluation of calibration curves in environmental laboratory methods. The advantages of this approach are as follows:

- All curve types can be calculated with the same (1/concentration^2) weighting applied, This places emphasis on relative error with improved accuracy at concentrations near the reporting limit.

- The %RSE criterion is consistent for evaluation of all curve fitting types. Interpretation of acceptability for calibration curves is simplified with the same criterion applied to all curve types and no conflicting criteria.

- The most appropriate curve fitting model can be applied to each set of calibration data with evaluation criteria between different curve types directly comparable.

The evaluation of all calibration data should include, as a minimum, the following checks:

- %RSE < maximum limit
- concentration level of low standard ≤ reporting limit
- low point intersection values < reporting limit
- Number of calibration levels meets method requirements
- All points must be monotonically increasing
- Also for second or higher order curves inflection points should not be within the calibration range

With the widespread availability of powerful computer hardware and software in the laboratory, it is unnecessary to sacrifice data quality for the sake of simplification. Analysts should be familiar with the productivity and quality benefits of least squares curve-fitting algorithms. Clients and regulators must understand the importance of weighted curve fitting and the need for complete and consistant evaluation criteria, which will provide high quality results for the lowest cost.

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QUALITY CONTROL PROTOCOL FOR ANALYSIS OF DRUGS AND EXPLOSIVES USING ION MOBILITY SPECTROMETRY

Juliana Homstead and Edward J. Poziomek
Old Dominion University, Department of Chemistry and Biochemistry, Norfolk, VA 23529
(757)440-4005
email: epoziome@ODU.EDU

Ion mobility spectrometry (IMS) is widely used as a screening tool in the detection of contraband drugs and explosives. It is also gaining popularity as a semiquantitative instrument used in the research of these and other compounds, including hazardous environmental contaminants. We have successfully used IMS in studies involving cocaine and TNT, and have developed a quality control protocol to assess and ensure the quality of our data. This protocol employs cocaine hydrochloride as the reference standard in the positive mode and trinitrotoluene (TNT) as the reference standard in the negative mode. A five point calibration curve was

generated for each of the reference compounds in order to determine a concentration level suitable for quality control (QC) check solutions. We have established peak amplitudes and reduced mobility constant (K_0) for the QC check solutions that must be met each day before proceeding with analyses. Any deviation from these criteria requires assessment of the problem and appropriate corrective action. We have found this procedure helpful in maintaining data quality and in providing an early indication of potential problems.

REFERENCE MATERIAL FOR THE ANALYSIS OF METALS IN SLUDGE

Stuart J. Nagourney, Nicholas J. Tummillo, Jr., John Birri, Kenneth Peist, Bruce MacDonald and Jean S. Kane

INTRODUCTION

New Jersey Department of Environmental Protection (NJDEP) regulations limit the levels of discharged toxic substances in sludge effluents by sewage treatment plants. Once maximum contaminant levels are established, they become part of the facility's operating permit. When chemical analyses indicate that these permit levels are exceeded, the NJDEP has statutory authority to assess significant monetary penalties.

Sludge samples vary widely in their physical and chemical composition, ranging from liquids with low dissolved solids content and small quantities of organics and metals, to multi-phase samples and cakes with solids contents often greater than 50 % and concentrations of metals and other constituents at percent levels. Since permit limits for metals are based on the amount leached during mineral acid digestion, these acid extractable concentrations, rather than total concentrations, are the values of interest. With several options for methods of sample preparation and measurement being proposed by State and Federal agencies, comparability of data among methods is a critical issue. Reference materials of similar matrix and composition to the various sludge matrices, and having known metal levels with defined uncertainties, are essential to insure that an accurate assessment of the data being generated is made,

To expand the utility of existing environmental SRMs, NIST has initiated efforts provide data on the acid-extractable levels of metals in selected new solid sample environmental SRMs. A recent paper by these authors described a collaborative project among the NJDEP, USEPA, Region II Technical Support Branch and NIST to develop sludge reference materials from domestic and industrial sources having reference values for their acid-extractable metals content. The study was successful for the domestic material, resulting in the derivation of reference values for EPA acid-extractable methods as part of SRM 2781, Domestic Sludge. The addendum to SRM 2781 contains leachable mass fractions for 14 metals and compares the leach recoveries to total metal concentrations obtained separately. This paper discusses the analysis of the industrial sludge material, NIST SRM 2782.

EXPERIMENTAL

Reference Samples

The candidate industrial sludge reference material SRM 2782, was prepared from more than 100 kg of electroplating waste supplied by AT&T Bell Laboratories, Murray Hill, NJ. This material was shipped to NIST, wherein it was freeze-dried, processed, radiation sterilized and homogenized by contractors according to procedures used to prepare United States Geological Survey and NIST geological reference materials. Samples were aliquotted and shipped to the participating laboratories, the NJDEP Bureau of Radiation and Inorganic Analytical Services (BRIAS) and USEPA, Region II, Technical Support Branch, for chemical analysis.

Sample Preparation

The NJDEP used open vessel hot plate digestion (NJDEP Method 100) for all of their acid digestions. The USEPA used open vessel hot plate digestion (USEPA Method 3050) for the industrial sludge and Method 3050 and closed vessel microwave digestion techniques (USEPA Method 3051) to prepare the domestic sludge for measurement. EPA prepared two sets of samples using microwave digestion, one without and one with HCl.

Instrumentation

The NJDEP used a Perkin-Elmer (PE) Model 5000 atomic absorption spectrometer (AAS) for its flame atomic absorption (FAAS) metal measurements. A similar unit, equipped with a PE Model 500 furnace and a PE AS-50

autosampler, was used for the graphite furnace atomic absorption (GFAAS) measurements. The NJDEP also employed a Thermo-Jarrell Ash Model 25 sequential inductively coupled plasma emission spectrometer (ICPOES) for some of its metal determinations. The USEPA used a CEM Model MDS-2000 microwave digestion system for some sample preparations and a Thermo Jarrell-Ash Model 61 Simultaneous ICPOES and a PE 5100 GFAAS, equipped with a model AS-600 furnace and AS-60 autosampler for its metal determinations. The USEPA performed the metals measurements by either simultaneous ICPOES and GFAAS, using one technique per metal. The NJDEP employed more than one technique to measure most of the metals.

Sample Processing
Each laboratory analyzed its own digests by one or more instrumental methods. Once completed, the two laboratories exchanged extracts and conducted another series of measurements using the same techniques.

RESULTS AND DISCUSSION

Developing "reference" values for the composition of real environmental samples requires inclusion of random errors of measurement and any systematic bias which might be inherent in the method(s) employed to estimate the true value. Issues such as the method of measurement, the complexity and composition of the sample matrix and the concentration and heterogeneity of the analytes all contribute to the overall uncertainty. While relative uncertainties of -20% to + 20% are expected when EPA methods such as FAAS, GFAAS and ICPOES are applied to nonaqueous media, reference values based upon these methods are still useful as confirmation of results of environmental monitoring such as the analysis of sludge effluents from treatment plants.

Current Results for Industrial Sludge
The initial set of analyses performed on NIST SRM 2782 yielded poor agreement between the two laboratories. For the most recent series of tests, the precision of the 6 aliquots of NIST SRM 2782 ranged from 0.2 % to 2.0 % for all elements measured by both participating laboratories. There is no discernable change in the level of precision of the replicate measurements obtained in the earlier and later studies Table 1 compares the results obtained by both laboratories in the initial ('94) and most recent ('96) studies. There is no discernable pattern in the NJDEP data from 1994 to 1996; the more recent series of USEPA results are generally higher than those obtained previously. Differences between the grand means of all results obtained for each element by the two laboratories for the more recent set of measurements were within 6% for 6 elements and 10% for 12 of the 17 metals studied; 2 others were within 12 %. Cd, Cr and K were the only elements outside this range,

Analysis of Variance (ANOVA) can be utilized to evaluate whether the individual element means obtained by the two laboratories for each element, generated by different methods of sample preparation and analysis, are statistically significant. As shown in Table 2, for the 14 metals where agreement between the grand means was within 12 %. ANOVA analyses, as shown by the F value (ratio of variance between data sets to the variance within a data set) and P value (measure of the probability the actual sample set fell within hypothetical frequencies for infinitely large data populations) showed that the means obtained by the two laboratories agreed within specified tolerances for 11 of the 14 metals; the exceptions being Ba, Cr and Mn. This serves as further corroboration to the extent of the agreement between the results.

The USEPA obtained good results for 14 metals where extractions were obtained by both Method 3050 (hot plate digestion) and Method 3051 (microwave digestion), with analyses performed by ICP-OES. Agreement is within ± 6 % for all metals studied but Na and K; with a range in bias from - 4.8 % for Al to +5.2 % for Zn. These results are shown in Table 3. The values for the alkali metals Na and K are approximately 30-40 % higher for the microwave technique. When the t-test for means assuming unequal variance is applied, for 6 metals (Ba, Ca, Cu, Mn, Ph and Zn), the differences between the calculated means obtained by each method were statistically significant. However, these detected differences are relatively small, especially when compared to the control limits assigned to acid-extractable analytes measured in non-aqueous media. All standard deviations are ± 2 sigma.

Comparison of Leachable Concentrations for Domestic Sludge and Industrial Sludge
The addendum to the Certificate of Analysis for NIST SRM 2781, domestic sludge compares the % leach recoveries of selected metals with the values obtained for their total mass fractions. For elements where leachable metal results were obtained from both the USEPA and NJDEP laboratories, a ratio of leachable metal concentration to total metal concentration (obtained by NIST) was calculated. For the domestic sludge these ratios were between 0.82 and 0.96 for 9 out of 11 elements; only Al (0.50) and Cr (0.71) were below this range. Preliminary values supplied by NIST for the industrial sludge material shows a different pattern; for the 14

elements for which such data is available, only 6 have ratios of leachable to total that are greater than 0.80. Na, K, Mg, Al have ratios below 0.20, the ratio for V is 0.21, Ba and Ni are 0.60 and 0.62 respectively, while Ca is 0.72. Only certain transition elements (Cu, Ph, Zn, Mn, Fe and Co) have leachable/total ratios for the industrial sludge that are greater than 0.80. The results are summarized in Table 4. Note that for the industrial sludge all of the ratios for the alkali and alkaline earth metals as well as Al are 0.72 or below. While the reasons for the specific analyte-matrix interactions are uncertain, it is apparent that the more complex nature of the industrial sludge plays a key role in how much metal is leached by the regulatorily-approved digestion methods, and that the amount that leaches varies significantly by element and group. This issue must be considered when evaluations of leachable metal concentrations are made for environmental assessment and policy considerations.

Table 1. Industrial Sludge - Grand Means

Element	Mean DEP'94	Mean EPA'96	Mean DEP'94	Mean DEP'96	DEP/EPA '96
Al	1502 ± 43	1587 ± 107	1380 ± 50	1528 ± 46	1.038
Ba	150 ± 1	161 ± 11	132 ± 4	144 ± 4	1.118
Ca	4687 ± 470	4950 ± 144	4320 ± 141	4685 ± 151	1.056
Cd	4.0 ± 0.1	11.4 ± 3.0	15.4 ± 0.8	2.3 ± 0.1	-
Co	70.0 ± 6	51.6 ± 7	54.4 ± 2	56.0 ± 3	0.921
Cr	79.8 ± 1	76.7 ± 4	55 3 ± 2	58.3 ±1	-
Cu	2485 ± 146	2459 ± 37	2270 ± 53	2420 ± 42	
Fe	255020± 17000	256600± 2300	232000±5600	253000±14000	1014
K	116±1	121 ±2	58.9 ±6	78.6 ±21	-
Mg	508±37	498 ±69	441 ±17	470± 15	1.059
Mn	274 ±13	274 ±7	224 ±7	247±7	1.109
Na	2430± 18	2431 ±20	2000 ±123	2573 ±307	0.945
Ni	125±2	95.5 ±6	908±2	96.1 ±4	0.994
Pb	581 ±18	558± 9	519 ±30	553 ±22	1.010
V	23.2± 1	17.5 ±2	20.6 ±1	15.9± 1	1.100
Zn	1266 ±31	1181 ±59	1170±21	1158 ±71	1.019

Table 2. Industrial Sludge - ANOVA Analyses

	F	P
Al	0.82	0.38
Ba	33.9	0.00
Ca	1.73	0.22
Co	0.25	0.62
Cr	3.67	0.00
Cu	0.51	0.49
Fe	4.09	0.06
Mg	2.25	0.14
Mn	69.6	0.00
Na	0.06	0.81
Ni	4.20	0.09
Pb	3.52	0.09
V	2.32	0.14
Zn	0.07	0.79

CONCLUSIONS AND RECOMMENDATIONS

Reference values have been derived for the leachable concentration of 14 metals in an industrial sludge standard reference material (NIST SRM 2782). Both open vessel hot-plate acid digestion (NJDEP Method 100 or USEPA Method 3050) or microwave digestion (USEPA Method 3051) are appropriate methods for sample preparation of these materials and the leachable concentrations may be measured by either FAAS, sequential or simultaneous ICPOES. This information supports the application of performance-based methodology since there are several combinations of sample preparation and measurement systems that can achieve similar results. Following complete statistical review by NIST, sludge Standard Reference Materials from both domestic and industrial sources-will be commercially available. Reference values for their acid extractable metals content and associated uncertainties will be provided to support the quality assurance of sludge metal measurements. Analyses of these SRMs should be required as part of a POTW's compliance data submitted to regulatory agencies Such as the USEPA and NJDEP. It is also recommended that these materials become part of any future laboratory certification program for sludge effluents.

Table 3. Industrial Sludge - Method Comparison

Element	Method 3050		Method 100		3050/100
	Mean	SD	Mean	SD	
Al	1520	18	1540	8	0.987
Ba	148	2	144	1	1.027
Ca	4870	58	4720	34	1.032
Co	58.5	0.9	57.0	0.9	1.026
Cr	57.9	0.6	58.2	2.4	0.994
Cu	2500	37	2420	45	1.033
Fe	260000	4500	236000	1100	1.102
K	72.4	11.8	80.1	1250	0.904
Mg	470	5	490	7	0.959
Mn	256	3	246	3	1.041
Na	2300	39	2470	60	0.931
Ni	99.6	3.7	95.1	1.1	1.047
Pb	545	6	524	13	1.040
Zn	1210	15	1210	11	1.000

Table 4. Domestic Sludge -Recoveries and Comparisons w/Certificate

Element	Domestic Sludge Ratio: Leachable / Total	Industrial Sludge Ratio: Leachable / Total
Ag	0.88	-
Al	0.50	0.11
Ba	-	0.60
Cd	0.86	-
Ca	0.93	0.72
Co	-	0.82
Cr	0.71	-
CU	0.96	0.94
Fe	0.87	0 95
K	-	0.02
Pb	0.91	0.97
Mg	0.82	0.18
Mn	0.82	0.86
Na	-	0.19
Ni	0.90	0.62
V		0.21
Zn	0.88	0.93

- Only NJDEP or USEPA leachable results were available, mean values between the two laboratories was not computed.

PERSPECTIVES ON DIOXIN ANALYSIS

Stevie Wilding
USEPA, Region III, Office of Analytical Services and Quality Assurance,
839 Bestgate Road, Annapolis, MD 21401
Phone: 410-573-2733, FAX: 410-573-2771

Dioxin analysis is very complex. Many people do not understand how dioxin analysis is performed within a laboratory or how to validate the data when they receive it. Through my technical assistance to internal and external customers concerning dioxin analysis, it has become clear they do not understand and are afraid to

understand the methodology of dioxin analysis. Prior to validating PCDD/PCDF data, it is imperative to have complete knowledge of the method used. The purpose of this paper is to try and simplify dioxin analysis. To break the analysis into understandable pieces and to compare it to other organic analyses. The basis for the Dioxin/Furan analysis is Selected Ion Monitoring (SIM) Gas Chromatography/Mass Spectrometry (GC/MS). The objective of this paper is to explain SIM GC/MS and isotope dilution for the average nonchemist. The advantages and disadvantages of using isotope dilution and SIM over the "routine" organic methods will be discussed.

INTERPRETATION OF GROUND WATER CHEMICAL QUALITY DATA

G.M. Zemansky
Compass Environmental, Inc., 3000 W. 19th Court, Lawrence, Kansas 66047-2300

ABSTRACT
Ground water is sampled to assess its quality for a variety of purposes. Whatever the purpose, it can only be achieved if results are representative of actual site conditions and are interpreted in the context of those conditions.

Substantial costs are incurred to obtain and analyze samples. Field costs for drilling, installing, and sampling monitoring wells and laboratory costs for analyzing samples are not trivial. The utility of such expenditures can be jeopardized by the manner in which reported results are interpreted as well as by problems in how samples were obtained and analyzed. Considerable attention has been given to standardizing procedures for sampling and analyzing ground water. Although following such standard procedures is important and provides a necessary foundation for understanding results, it neither guarantees that reported results will be representative nor necessarily have any real relationship to actual site conditions. Comprehensive data analysis and evaluation by a knowledgeable professional should be the final quality assurance step, it may indeed help to find errors in field or laboratory work that went otherwise unnoticed, and provides the best chance for real understanding of the meaning of reported results.

The focus of this paper is on the interpretative part of the process. Although formal interpretation necessarily comes late in a project, when data have been generated and the report is being written, it will be most useful if relevant elements can be integrated into the project from the beginning. When this is done, it increases the likelihood of achieving project objectives as well as understanding the data. To facilitate interpretation, the following steps should be included:

1. Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate quality control/quality assurance (QC/QA) checks of field and laboratory work (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional. The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

Application of this sequence *of* steps and their importance in interpretation of ground water quality data are discussed in this paper. The discussion includes several illustrative case examples.

INTRODUCTION
There area number of reasons we might want to know about groundwater chemical quality. For example, we

might be interested in using an aquifer as a source of water today or we may want to ensure that current practices haven't caused contamination so that ambient ground water quality remains legally acceptable whether or not it is used in the future. At first glance, you'd think that obtaining and interpreting ground water quality data would be a fairly straight forward exercise. Simply follow the usual scientific approach: (1) take a sample; (2) analyze it; and (3) compare analytical results to a set of criteria. However, obtaining reliable data and properly interpreting them turns out to be more complicated than that; even in the relatively simple case of surface water. When it comes to ground water, everything seems more complex.

To begin with, obviously, with ground water you can't just go down to the stream and get a sample. Because ground water is underground, you need to do more preparation in advance of sampling. This involves obtaining background subsurface information and an access point. Such information will be helpful, both in planning how to obtain a sample as well as in interpreting analytical results when they become available. Whether you use a standard monitoring well, direct push technology, or something else, getting access to sample isn't always easy and can influence the quality of the sample obtained. There are also a number of potentially confounding factors with regard to the next step of the process, laboratory analysis. Sample quality can change between the time a sample is obtained and the time it is analyzed and, even if it doesn't, the overall reliability of laboratory results is not the sure thing many people assume it is. Finally, selection of appropriate criteria to compare data to may not always be straight-forward. Relevant criteria may either not exist or be incomplete.

Comprehensive data interpretation by a knowledgeable professional should be the final quality assurance step of any project involving ground water quality data. It may indeed help to find errors in field or laboratory work that went otherwise unnoticed and provides the best chance for real understanding of the meaning of reported results. Proper project planning should prepare for this final step by obtaining relevant information early on and including relevant data collection into field segments of the project. The following steps must be integrated into and carried out throughout the project to facilitate final interpretation:

1. Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate QC/QA checks (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional.

The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

BACKGROUND INFORMATION

Background information serves several functions: (1) it facilitates obtaining access to sample groundwater; (2) it provides guidance regarding selection of appropriate sampling methods and analytical variables; (3) it places ground water quality data into context; and (4) it provides a quality assurance check. The following background information is necessary to fulfill these functions: (1) regional and site-specific geology; (2) regional and site-specific hydrology; (3) information on the environmental chemistry of variables of concern to the project; and (4) broad information on potential anthropogenic influences including site conditions and possible contaminant sources. The latter includes not only those conditions which may have impacted ground water, but those which could have influenced sample quality as a result of installation and testing of monitoring wells or otherwise during the sampling process. For example, shallow contamination can be carried down into a deeper aquifer during field work and airborne chemicals may cause trace contamination of ground water samples if they enter an open borehole, monitoring well, or sample being placed into a container.

FIELD PROCEDURES

Access Points

The nature of subsurface conditions will influence the type of access point that is possible. Sample quality will also be impacted by the type of access point selected. Commonly used ground water access points include: (1) monitoring wells; (2) wells or piezometers installed for other purposes; and (3) direct push technology.

The nature of the access point has, in particular, a relationship to the level of total suspended solids (TSS) likely to be present in samples. TSS levels would be expected to be relatively high in samples obtained using direct push technology and low in samples obtained from a water supply well. Assuming proper design and installation (including development), TSS levels in samples obtained from monitoring wells will normally be low except where fine-grained materials are screened. However, development is something that is often neglected or treated in a pro-forma manner when monitoring wells are installed. Additional development, as opposed to routine purging, may also be required when there are long periods between sampling events. This is illustrated in Table 1, showing results for inorganic variables in unfiltered samples from a well that was properly developed prior to initial sampling but was not redeveloped when sampled again after two years.

Sampling Methods

Available sampling methods are often constrained by the type of access point utilized. Since they will have a direct bearing on sample quality, the sampling methods used must be taken into account in planning sampling events and in interpretation of the data obtained. This category includes consideration of both field equipment and procedures. For example, regulatory agencies are more frequently requiring analysis of unfiltered samples. This may introduce substantial variation into the process, particularly for inorganic variables.

Sample Handling and Preservation

The order of sampling, type of container, and sample preservation method utilized can affect the quality of samples analyzed in the laboratory. As discussed further below, U.S. Environmental Protection Agency (USEPA) specified sample preservation methods and maximum allowed holding times do not always ensure sample quality will not change between the field and laboratory analysis.

Field Analysis/Observations

Reliable sample preservation methods do not exist for some water quality variables. In other cases, field measurements carried out for other purposes (i.e., well purging) are routinely available and preferable (e.g., to laboratory analysis for the same variable) or field observations can be made that provide useful information otherwise lost if not recorded at the time. USEPA requires field analysis (by specifying immediate analysis) for only five variables: (1) chlorine residual; (2) pH; (3) dissolved oxygen (by probe); (4) sulfite; and (5) temperature.

The validity of some USEPA maximum holding times and preservation combinations is questionable. For example, although USEPA recognizes that pH and dissolved oxygen levels may change substantially if not analyzed in the field and therefore requires immediate analysis without holding for them, substantial changes in alkalinity may occur for the same reasons but 14 days holding time is allowed for this variable. Because it is allowed and more convenient, samples are frequently analyzed in the laboratory for alkalinity instead of the field. Similarly, USEPA allows maximum holding times of 48 hours and seven days for color and total suspended solids (TSS), respectively. USEPA also allows seven and 14 days holding time for unacidified and acidified volatile aromatic compounds, respectively. Both color and TSS may change substantially in samples over these allowed time frames and research has shown both substantial loss of volatile aromatic compounds in less than seven days in unacidified samples and that substantially greater holding times than 14 days are appropriate for many compounds when samples are acidified.[1]

When sampling ground water, field analysis should routinely occur for the purge variables conductivity, pH, and temperature, using appropriate equipment operated, calibrated, and maintained in accordance with manufacturer recommendations. The following field observations related to sample quality may also be made: (1) color; (2) odor; and (3) turbidity. Although this information is essentially "free" for the taking, it is often not recorded. In particular, the latter observation can provide at least a qualitative indication *of* the presence of TSS and their possible effect on inorganic variables. The difference that filtering makes in reported concentrations of many inorganic variables when unfiltered samples contain high solids concentrations is substantial and readily demonstrated with split samples.

LABORATORY ANALYSIS

Too often, the analytical laboratory for a project is selected on the basis of cost only. Such cost savings may prove to have been very expensively purchased if quality isn't also delivered. Laboratory qualifications should be carefully researched in advance of selection. This can be done by such things as reviewing historic results on performance evaluation samples, auditing the facility, submitting performance evaluation samples, and checking references. Checks should continue throughout the project with the appropriate use of blank, duplicate, and performance evaluation samples.

Unfortunately, no laboratory is perfect. Even the better laboratories often get some wrong answers when analyzing USEPA performance evaluation samples. These are in a relatively clean matrix, without the kinds of interferences that can complicate real world samples, and are being analyzed under test conditions. A laboratory would be foolish not to make its best effort on these samples. You can expect somewhat lower quality with regard to samples being routinely analyzed for the average client. Routine QC/QA and data validation practices are not the complete answer to data quality. In particular, the latter usually don't include various data cross-checks or take into account what is known about site conditions. In the worst case, laboratory reported analytical results can be more artifacts of the sampling and analysis process than representative of ambient ground water quality.

There are a number of factors which can influence laboratory results. But even when analytical laboratories are performing well, it should be recognized that: (1) at best, they can only analyze samples in the condition received; and (2) standard limits of precision and accuracy allow considerable variation. As noted above, a number of factors may result in samples reaching the laboratory which are less than representative of site conditions. Even when laboratory QC/QA requirements are met, the level of allowed variation limits the conclusions which can be based on laboratory data. USEPA Superfund acceptance criteria for percent recovery of matrix spikes (MS) and laboratory control standards (LCS) are shown in Table 2.[2,3]

Data reported by laboratories should be carefully reviewed or "validated" before being utilized. USEPA national functional guidelines for data review under Superfund are an example of typical validation guidelines. These specify a number of checks intended to assure that correct procedures were followed (e.g., holding times, calibration, blanks, matrix spikes and spike duplicates, and laboratory control standards). Although this type of review is useful, it is important to realize its limitations. The standard conclusion one consulting company uses after a successful validation process contains the statement that "the data collected during this investigation are valid as qualified for use in representing Site conditions and for use in risk assessments."[4] Since the validation process referred to doesn't take relevant site information or available data cross-checks into account, such a statement goes too far. Neither is it necessarily correct.

CASE EXAMPLES OF INTERPRETING GROUND WATER DATA

Organic Contamination at a Superfund Site

Trichloroethylene (TCE) groundwater contamination was recognized at a Superfund site. The presence of other halocarbons associated with TCE degradation, notably cis-1,2-dichloroethylene (c-1,2-DCE) and vinyl chloride, was also recognized. However, the potentially responsible party (PRP) claimed the TCE originated elsewhere and was part of a wider regional problem involving a number of sources and contaminants. Site work performed by the PRP in 1996 identified a variety of other compounds in samples from relatively deep wells drilled using air rotary equipment. The compounds reported in various samples fell within the following categories:

1. Volatile organic compounds (VOCs) -
   a. Halocarbons including TCE and TCE degradation products.
   b. Petroleum hydrocarbons, including aromatic compounds (e.g., xylenes).
   c. Trihalomethanes, particularly chloroform and bromodichloromethane.

2. Semivolatile organic compounds (SVOCs) -
   a. Petroleum hydrocarbons (benzoic acid and naphthalene).
   b. Phenol and other phenolic compounds.
   c. Phthalates, particularly bis(2-ethylhexyl)phthalate.

Review of these data indicated that other interpretations were much more likely. Among the reasons the data were suspect were the following:

1. With the exception of halocarbons, most of the compounds involved had <u>not</u> been reported in samples from shallow wells previously drilled using hollow-stem augers. Contamination in such cases generally moves from surface or near-surface sources downward. Furthermore, the concentrations involved were generally low and appeared to be randomly distribution rather than in a pattern suggesting any relationship to possible sources.

2. Air rotary drilling is a possible source of petroleum hydrocarbon and phenolic compound contamination.

3. Some of the boreholes had been left open to the atmosphere for substantial periods of time (i.e., on the order

of months) after drilling before monitoring wells were installed in them. The ones open the longest were also adjacent to an Interstate Highway. Petroleum hydrocarbons have been identified in vehicle emissions and ambient urban air.[5] Research has also indicated the potential for petroleum hydrocarbons and phenolic compounds in urban air to be transported into ground water.[6,7]

4. PRP consultants had not decontaminated at least some downhole equipment (particularly water level indicators) when used between boreholes or between monitoring wells. This may cause cross-contamination.

5. THM contamination is common in chlorinated tap water from surface sources, but unusual in ambient ground water. Thousands of gallons of chlorinated tap water from a surface source known to contain substantial concentrations of trihalomethane compounds had been introduced into most of the boreholes as a part of the testing program during field work.

6. Phthalates are recognized by USEPA as a common SVOC laboratory contaminant.[8]

7. Background regional information strongly indicated the PRP was the source of halocarbon contamination and that there was no other more widespread regional problem involving halocarbons or other compounds.

Resampling in 1997 provided further confirmation of this interpretation. Data for the 19 wells sampled in both years are shown in Table 3 (parts a and b). With the exception of a reduced number of low concentration hits for phthalate compounds (which are recognized as common laboratory contaminants) and, in one case, a trihalomethane compound, only halocarbons were reported in 1997 This indicates that the various other compounds reported in 1996 samples were a transitory impact of drilling, testing, sampling, and analysis rather than regional ground water contamination. This transitory impact dissipated over time as a result of natural mechanisms such as flushing by ambient ground water flow and biodegradation. The change in apparent distribution of halocarbon contamination between 1996 and 1997 apparent from these results may also indicate that shallower contamination was carried downward by intrusive work performed in 1996 and that this also produced a transitory impact on ground water samples.

Ground/Surface Water Relationship at a RCRA Site

Ground water monitoring at landfills and other Resource Conservation and Recovery Act (RCRA) facilities is oriented towards ensuring that a release of contaminants, if it occurs, will be detected. In general, detection monitoring requires that data from wells downgradient of the facility and subject to impact in event of a release be statistically compared to data from upgradient background wells. If the comparison results in a statistically significant difference with a downgradient increase, a release is assumed. However, other regional conditions must be considered if such comparisons are to be useful.

In this case, there is a network of monitoring wells installed up and downgradient of a land treatment unit (LTU) located at a refinery adjacent to a major river. Statistical analysis showed that concentrations of some variables were elevated in downgradient wells and that the elevations were statistically significant. Did this mean that a release had occurred?

A linkage between the river and the adjacent alluvial ground water aquifer would be expected based on general principles. This was confirmed by analysis of two lines of evidence: (1) correlation of ground water elevations with river flow (a surrogate for stage); and (2) statistical analysis of water quality data. Time series plots of ground water elevations versus river flow showed an evident visual correlation, which was confirmed by linear regression analysis. The correlation was best for those wells closest to the river (correlation coefficient of 0.80) and decreased with distance from the river. A comparison of water quality data is supportive. Data indicating central tendency for upgradient monitoring wells and the river are presented for six variables in Table 4. For the three major ions in Table 4, including chloride, river concentrations far exceed those in upgradient ground water. In these cases, statistical analysis shows that concentrations in samples from downgradient monitoring wells are significantly higher than upgradient ground water. The reverse is true for the three elements listed. Their concentrations are higher in upgradient ground water than the river and statistical analysis shows that their levels in downgradient monitoring wells are significantly lower than upgradient.

Inorganic Water Quality at a Superfund Site

Consultants for a PRP at a Superfund site involving a limestone aquifer in the midwest US developed several theories regarding the nature of the aquifer involved based on their interpretation of data for inorganic

constituents. Data for alkalinity, aluminum, calcium, iron, silica, sodium, and sulfate were prominent in their interpretation. However, these consultants did not consider relevant site-specific information and admitted they were unaware of the degree of variation that can occur in laboratory analysis of ground water samples that meet acceptance criteria (see Table 2).

A potentially important piece of site-specific information not considered by the PRP's consultants was that most of the borings involved had been drilled considerably deeper than the wells later installed in them. For the wells being installed in such deeper borings, boreholes were first partially filled by pouring in sodium bentonite chips. This occurred for about two-thirds of the relatively deep wells drilled. On the average, approximately one-third of the borehole was filled (i.e., 71 of 221 feet). This process undoubtedly resulted in the introduction of chemicals from the hydrating chips into the water (both as dissolved and suspended solids) as they fell through the water column. Of the analytes relevant to this site, sodium bentonite chips are typically composed of silica and oxides of aluminum, iron, calcium, sodium, magnesium, and potassium (in order of concentration). They also contain a small level of water soluble nitrate. Given the chemistry of silica and calcium and the likelihood that calcium in a limestone aquifer would be expected to already be near saturation, concentrations of these variables would probably not be greatly affected by this. However, concentrations of aluminum, iron, sodium, magnesium, and potassium could be and this appears to have been the case. The potential for this was increased by the fact that, although consultants for the PRP purged three well volumes immediately prior to sampling, they did not develop the monitoring wells after installation.

To evaluate the effect of filling boreholes with bentonite on inorganic ground water quality, monitoring wells sampled both during 1996 (shortly after installation) and 1997 (nearly a year since last sampled) were divided into two groups: (1) bentonite filled (BF); and (2) unfilled (UF). Median data for major cations, major anions, and several other variables grouped into these two categories for both 1996 and 1997 sampling events are presented in Table 5. The 1996 data clearly indicate impact from bentonite filling for most of the variables listed except calcium and silica, BF:UF ratios for sodium, aluminum, and iron indicate nearly an order of magnitude or greater level of enrichment for those variables as a result of bentonite filling. This is also evident in the STIFF diagrams of median grouped data in Figure 1. The STIFF diagram for unfilled wells (Figure 1a) is typical of what would be expected for a limestone aquifer.[9] There are several relatively minor differences between the STIFF diagram for bentonite filled wells (Figure 1b) and unfilled wells (Figure la), but by far the most notable difference is the sodium "bulge" to the lower left of the diagram. The impact of the bentonite appears to have been transitory. With the possible exception of nitrate, the enrichment appears to have been flushed away due to ambient ground water flow by the time wells were resampled nearly a year later. STIFF diagrams for both sets of wells (UF and BF) when resampled in 1997 were similar to each other and the one for unfilled wells in 1996 (Figure 1a).

The PRP's consultants pointed to two aspects of the data to support their interpretation that the aquifer involved was an "open" system (i.e., rapidly recharged from the surface throughout the aquifer): (1) abnormally high concentrations of aluminum and iron in samples from some relatively deep wells (exceeding solubility limits); and (2) lack of any apparent ground water evolution (change in quality along a flow line) between wells at higher elevations and those at lower elevations (a distance of roughly one mile). As discussed above and shown in Table 5, aluminum and iron enrichment appears to have been related to filling boreboles with sodium bentonite chips. Not knowing about this circumstance and since the overlying clay soils involved would be normally expected to be rich in silica as well as aluminum and iron, the consultants interpreting inorganic water quality data for the PRP felt compelled to provide another explanation why silica concentrations were not also enriched when aluminum and iron were. Their explanation was an assertion, without any data, that the soils were lateritic. Lateritic soils develop in hot, wet tropical climates subject to heavy rainfall when the intense chemical weathering that occurs under those conditions removes both soluble materials and much of the silica. Lateritic soils are not characteristic of the temperate climate midwest US.[10] A much more likely explanation for the relative magnitudes of aluminum, iron, and silica has to do with the manner in which samples were taken, preserved, and prepared for analysis. Samples to be analyzed for aluminum and iron are acidified in the field and digested in the laboratory. Since the samples involved were unfiltered, this meant that some particulate aluminum and iron would be included in the measurement. In contrast, samples to be analyzed for silica are not acidified in the field, but are filtered prior to analysis.

With respect to ground water "evolution," this phenomena has generally been documented on a regional rather than a site scale. This may be in part because very substantial "evolution" must occur to be detectable against a background of variation sampling and analysis introduced variation as well as environmental variation. For an extreme example, using the acceptance criteria of 75 to 125 percent recovery for matrix spike samples (see

Table 2), a sample having a true value of 100 mg/L of calcium could be reported to have either 75 or 125 mg/L. Although the higher of these two numbers is 67 percent greater than the low number, either one would be within acceptance criteria. With enough sampling events and statistical analysis of data, it might be possible to detect an "evolutionary" change within acceptance criteria boundaries (e.g., a change from 50 to 65 mg/L along the flow path); however, the possibility of seeing this change with a single set of samples appears slim when so much variation is acceptable.

SUMMARY AND CONCLUSIONS

Comprehensive data interpretation by a knowledgeable professional should be the final quality assurance step of any project involving ground water quality data. It may indeed help to find errors in field or laboratory work that went otherwise unnoticed and provides the best chance for real understanding of the meaning of reported results. Proper project planning should prepare for this final step by obtaining relevant information early on and including relevant data collection into field segments of the project. The following steps must be integrated into and carried out throughout the project to facilitate final interpretation:

1 Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate QC/QA checks (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional.

The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

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Table 1. Effect of Monitoring Well Development[1]

Variable	Spring 1994[2]	Summer 1996[3]
Calcium	92.	104.
Chloride	43.	58.3
Iron	0.08	5.53
Magnesium	2.4	2.84
Manganese	0.069	0.13
Potassium	ND	533
Sodium	5.8	6.38
Appearance	Clear	Turbid

1. Concentrations in mg/L. ND means non-detect at 1 mg/L.
2. New well developed and purged prior to sampling.
3. Well unused for two years. Three well volumes purged prior to sampling.

Table 2. USEPA Superfund Acceptance Criteria

Variable (USEPA Method)[1]	MS[2]	LCS[2]
Elements (6010)	75-125	80-120
VOCs (8240):		
Benzene	76-127	-
Trichloroethylene	71-120	-
SVOCs (8270):		
Pyrene	26-127	-
Phenol	12-110	-

1. Identification of variable and USEPA analytical method with example volatile and semivolatile organic compounds (VOCs and SVOCs, respectively).
2. Matrix spike (MS) and laboratory control sample (LCS) acceptance criteria in percent recovery. Inorganic criteria from USEPA national functional quidelines. Organic criteria from CLP SOW Forms III VOC-1 and SV-1.

Table 3a. Reported Organic Compounds

	Highest Concentrations[1]	
Category	1996	1997
VOCS:		
Halocarbon	236.	172.
Petroleum Hydrocarbon	29.6	ND
Trihalomethane	26.3	5.08
SVOCS:		
Petroleum Hydrocarbon	44.	ND
Phenolic	175.	ND
Phthalate	72.3	43.2

1. Highest reported concentration of any compound in category out of 19 wells sampled in both years.

Table 3b. Reported Organic Compounds

	Number of Wells Reported In[1]	
Category	1996	1997
VOCS:		
Halocarbon	6.	3.
Petroleum Hydrocarbon	2.	0.
Trihalomethane	12.	1.
SVOCS:		
Petroleum Hydrocarbon	3.	0.
Phenolic	7.	0.
Phthalate	12.	6.

1. Number of wells out of 19 sampled in both years in which any compound in the indicated category was reported at any concentration.

Table 4. Ground/Surface Water Relationship

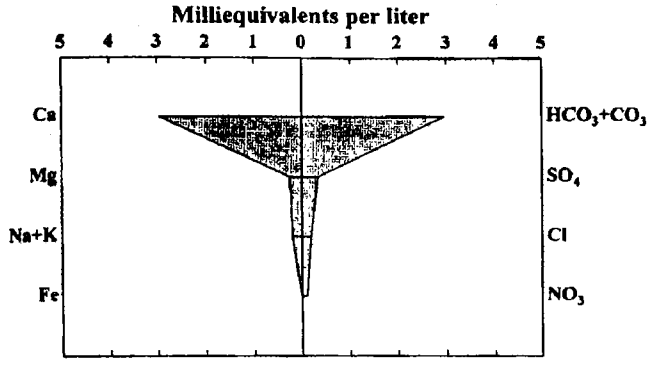
Variable	Wells[1]	River[2]
Major Ions:		
Chloride	6.96	300.
Sodium	6.76	340.
Sulfate	323	150.
Elements:		
Arsenic	6.85	2.
Barium	725.	130.
Iron	13.2	0.01

1. Site data. Mean for upgradient monitoring wells (1994-1997).
2. USGSdata. Median for river at nearby gaging station (1981-1995),

Table 5. Grouped Inorganic Data[1]

	Major Cations			
Data Set	Ca	Mg	K	Na
1996 Data:				
BF	62.2	4.75	1.04	35.55
UF	59.4	2.97	.5	0.5
BF:UF Ratio	1.04	1.60	2.06	8.46
1997 Data:				
BF	58.66	4.47	.55	3.06
UF	58.48	4.02	.5	2.76
BF:UF Ratio	1.00	1.11	1.1	1.11
	Major Anions			
Data Set	HCO_3	Cl	NO_3	SO_4
1996 Data:				
BF	204.	7.31	12.8	33.5
UF	181.	5.82	6.69	16.6
BF:UF Ratio	1.13	1.26	1.91	2.02
1997 Data:				
BF	177.	3.93	7.62	10.2
UF	174.	4.65	4.52	9.5
BF:UF Ratio	1.02	0.845	1.69	1.07
	Other Variables			
Data Set	Al	Fe	Silica	TDS
1996 Data:				
BF	1.21	0.94	8.72	305.
UF	0.10	0.05	9.68	196.
BF:UF Ratio	12.1	18.8	0.901	1.56
1997 Data:				
BF	0.31	0.10	9.2	231.
UF	0.29	0.06	3.8	226.
BF:UF Ratio	1.06	1.67	2.42	1.02

1. All concentrations are median values for grouped data in units of mg/L.



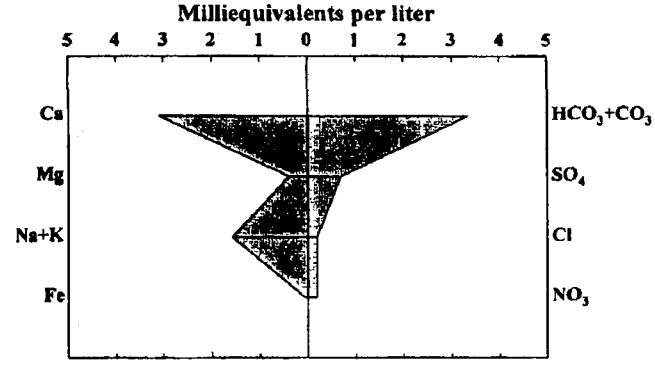


Figure 1. Grouped Median Data STIFF Diagrams - 1996

a. Wells in unfilled boreholes (UF).

b. Wells in bentonite filled boreholes (BF).

GENERAL

SAMPLE INTRODUCTION TECHNIQUES FOR FAST GC ANALYSIS OF ORGANOCHLORINE PESTICIDES

C. Eric Boswell, Michael S. Clark, and Rattana M. Woodard
National Air and Radiation Environmental Laboratory, 540 South Morris Avenue,
Montgomery, Alabama 36115-2601

ABSTRACT

Advances in GC instrumentation in recent years have allowed the analysis of organochlorine pesticides to become more efficient. Pressure programable injectors, for example, have allowed analysts to reduce run times as well as control injector phenomena such as vapor cloud expansion and thermal degradation. GC analysts in environmental laboratories have many options available to them in configuring instrumentation, especially in the techniques they choose for sample introduction. When attempting to maximize the benefits of modern GC instrumentation, analysts must be prepared to adapt their working knowledge of classical GC techniques to newer ones. At the National Air and Radiation Environmental Laboratory (NAREL) we learned that several of our ideas about classical splitless injections had to be modified when we optimized SW846 Method 8081 for speed, Endrin/DDT degradation, and chromatographic resolution.

In an attempt to reduce the run time for SW846 Method 8081, we configured a GC with dual pressure programmable injectors, two dissimilar 0.53 mm capillary columns, and dual ECDs. While the biggest time savings resulted from a relatively high initial oven temperature, having the ability to pressure program the injectors also helped to reduce run times. Programming the injectors at a high initial pressure also reduced Endrin/DDT degradation by insuring a short injector residence time. A high initial oven temperature and high initial injector pressure presented a challenge since high pressure applications typically depend on low initial oven temperatures to achieve solvent focusing. In this analysis solvent focusing is not practical because the boiling point difference between the solvent, hexane, and the earliest elating compound is too large. We found that although we wanted to use techniques that seemed to preclude each other we could empirically match our starting oven temperature with a relatively high initial injector pressure and have a degree of cold trapping to achieve both short GC run times, low Endrin/DDT degradation, and good chromatographic resolution. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections.

INTRODUCTION

When attempting to maximize the benefits of modern GC instrumentation, analysts must balance their desire to improve the efficiency of an analysis with certain pragmatic concerns: (1) ease of maintenance, (2) use of standard consumables, and (3) ruggedness of new procedures. At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections. We also wanted the resulting chromatographic system to be one that was easy to use by any reasonably trained analyst. Most of the modifications employed in our design were in the sample introduction part of the chromatographic analysis.

We configured a GC with dual pressure programmable injectors, two dissimilar 0.53 mm capillary columns, and dual ECDs. Although most of the work was in choosing the appropriate sample introduction techniques, there were other parameters to optimize. For example, we chose a relatively high initial oven temperature to reduce the cycle time of the analysis We also adjusted the detector makeup gas flow to achieve acceptable sensitivity. We wanted to take advantage of injector pressure programming which has become standard equipment on most GCs. We chose splitless injections over direct injections because we believe the splitless technique to be more rugged. In our dual injector system, we kept the injector pressures similar during injection and programmed them differently after the split valve opened to achieve chromatographic resolution. We chose a single taper inlet sleeves because they are easily obtainable and easy to maintain. We chose a compromise initial oven temperature that was hot enough to keep the GC cycle time short and low enough to prevent the earliest eluting compounds from tailing too much. This is different from classical splitless injection technique where the initial oven temperature is kept low until most of the sample can slowly migrate from the inlet sleeve to the head of the column. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation,

good resolution on difficult analyte pairs, and all the benefits of splitless injections.

EXPERIMENTAL

A mix containing twenty pesticides, two surrogate standards, and three internal standards (Ultra Scientific) was prepared from the dilution of certified standard mixes with pesticide grade hexane (Burdick & Jackson). Our experimental results are best discussed in terms of injection technique, pressure programming, and column selection.

We decided to use splitless injections rather than direct injections to both simplify routine maintenance and increase system ruggedness. Using a 4 mm ID single taper inlet liner eased routine column maintenance because the insertion distance of the column into the liner was the only critical step. A 1.0 µL volume of hexane extract will expand to approximately 300 µL of vapor at 6.5 psig. This is easily contained within the 900 µL of available volume in a 4mm ID liner. We found that a pressure increase after injection provided two benefits: (1) the vapor cloud moved onto the analytical column in a smaller plug and (2) the compounds were pushed through the column quicker. We chose 12.4 psig as the injector pressure which resulted in a column linear velocity of 102 cm/sec. We used 120°C as our initial oven temperature. These represent a compromise between classical solvent focusing and high pressure injection. Moving the sample vapor cloud onto the column quickly has several benefits. Along with keeping early eluting peaks from tailing, high pressure injections dramatically reduce Endrin/DDT degradation. Combined Endrin/DDT degradation rarely exceeds 5.0% with this configuration. Optimization of the opening and closing times for the split vent are still crucial for quantitative accuracy.

We chose analytical columns based on chromatographic separation and ruggedness. A 5% diphenyl 95% dimethyl polysiloxane column such as Restek's Rtx-5, provided both the good chromatographic separation and a high temperature limit. As a confirmation column we chose a hybrid column developed by Tammy Carey[1] that met our chromatographic needs. The GC oven temperature program is given in Table 1 along with the other chromatographic conditions. The temperature program was optimized to separate critical pairs such as Endosulfan I/alpha Chlordane and Dieldrin/DDE on the Rtx-5 column and Heptachlor epoxide/gamma-Chlordane and Endosulfan II/DDT on the Hybrid column. Chromatograms of the twenty-two organochlorine pesticides are shown in Figure 1 and calibration curve summaries are given in Tables 2 and 3.

Table 1. Chromatographic Conditions

GC Parameter	Value
Carrier Gas	Helium
Injector	Splitless, 1µL, Purge Delay 0.75 min. Inlet Temperature 250°C
Pressure Program	Initial Linear Velocity: 102 cm/sec. @ 120°C Rtx-5 12.4 psi Hold 0.50 min. to 5.8 psi @ 99.0 psi/min. Hold 4.00 min. to 14.5 psi @ 0.75 psi/min. to 19.0 psi @ 1.5 psi/min. Hybrid 12.4 psi Hold 0.50 min. to 7.5 psi @ 99.0 psi/min. Hold 6.00 min. to 14.0 psi @ 0.75 psi/min. to 20.0 psi @ 1.5 psi/min.
Temperature Program	120°C Hold 0.5 min. to 150°C @ 30°C/min. to 200°C @ 4°C/min. to 285°C @ 20°C/min. Hold 1.0 min.
Detector	N_2 Makeup @ 50 mL/min. Anode Purge @ 5mL/min. ECD @ 310°C

SUMMARY

At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte

pairs, and all the benefits of splitless injections. We also wanted the resulting chromatographic system to be one that was easy to use by any trained analyst. Although most of the work was in choosing the appropriate sample introduction techniques, there were other parameters to optimize. We deviated from classical splitless injection technique slightly to accommodate the use of pressure programmable injectors. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections.

REFERENCES

1. Carey, Tamela; *Chlorinated Pesticide Analysis Using Hybrid Columns* (unpublished), CH2M Hill, Montgomery, AL

Table 2. Calibration Curve Summary of 5% Diphenyl Column

INITIAL CALIBRATION REPORT

INSTRUMENT: GC#5/FRONT (5%DP)
CALIBRATION DATE: 03/09/97
METHOD: SW846/ 8081
SEQUENCE: E030997A
DATA FILES: 010F010 - 014F0101

COMPONENT	5ppb	10ppb	25ppb	50ppb	100ppb	SD	MEAN RRF	%RSD	P/F
Pentachlorobenzene/IS#1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Tetrachloro-m-xylene	0.65	0.66	0.72	0.74	0.73	0.04	0.70	5.13	
alpha-BHC	0.51	0.54	0.63	0.75	0.80	0.11	0.65	17.61	
beta-BHC	0.37	0.37	0.39	0.40	0.39	0.01	0.38	3.40	
Lindane	0.50	0.53	0.60	0.69	0.74	0.09	0.61	14.88	
delta-BHC	0.46	0.47	0.54	0.65	0.69	0.09	0.56	16.77	
Heptachlor	0.70	0.67	0.68	0.67	0.66	0.01	0.68	1.99	
Aldrin	1.16	1.28	1.37	1.40	1.40	0.09	1.32	7.05	
Heptachlor Epoxide	1.47	1.46	1.46	1.43	1.35	0.04	1.43	2.94	
gamma-Chlordane	1.65	1.65	1.70	1.70	1.61	0.03	1.66	2.09	
Endosulfan I	1.35	1.37	1.42	1.41	1.34	0.03	1.38	2.29	
alpha-Chlordane	1.69	1.71	1.78	1.77	1.67	0.04	1.73	2.60	
Dieldrin	1.35	1.29	1.31	1.32	1.25	0.03	1.31	2.65	
DDE	1.44	1.35	1.47	1.59	1.55	0.08	1.48	5.62	
o-p'-DDD/IS#2	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Endrin	1.46	1.40	1.37	1.37	1.28	0.06	1.37	4.26	
Endosulfan II	1.40	1.48	1.53	1.50	1.38	0.06	1.46	4.01	
DDD	1.12	1.05	1.02	1.07	1.01	0.04	1.05	3.60	
Endrin Aldehyde	1.16	1.17	1.18	1.10	1.01	0.07	1.12	5.79	
Endosulfan Sulfate	1.33	1.22	1.17	1.17	1.13	0.07	1.20	5.93	
DDT	1.22	1.12	1.15	1.19	1.17	0.04	1.17	3.05	
Endrin Ketone	1.55	1.51	1.51	1.50	1.43	0.04	1.50	2.56	
Methoxyclor	0.45	0.46	0.45	0.45	0.43	0.01	0.45	2.36	
Pentabromobiphenyl/IS#3	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Decachlorobiphenyl	1.55	1.53	1.44	1.35	1.34	0.09	1.44	6.16	

COMMENTS: _____

Table 3. Calibration Curve Summary of Hybrid Column

INITIAL CALIBRATION REPORT

INSTRUMENT: GC#5/REAR (HYBD)
CALIBRATION DATE: 03/09/97
METHOD: SW846/ 8081
SEQUENCE: E030997A
DATA FILES: 060R010 - 064R0101

COMPONENT	5ppb	10ppb	25ppb	50ppb	100ppb	SD	MEAN RRF	%RSD	P/F
Pentachlorobenzene/IS#1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Tetrachloro-m-xylene	0.76	0.79	0.89	0.80	0.81	0.04	0.81	5.47	
alpha-BHC	0.65	0.65	0.77	0.82	0.94	0.11	0.77	14.20	
Lindane	0.63	0.64	0.75	0.79	0.89	0.10	0.74	13.15	
beta-BHC	0.46	0.39	0.42	0.42	0.47	0.03	0.43	6.62	
Heptachlor	0.95	0.94	0.93	0.90	0.87	0.03	0.92	3.35	
delta-BHC	0.54	0.55	0.63	0.70	0.81	0.10	0.65	15.67	
Aldrin	0.64	0.63	0.68	0.70	0.78	0.05	0.69	7.89	
Heptachlor Epoxide	1.10	1.10	1.12	1.07	1.12	0.02	1.10	1.88	
gamma-Chlordane	1.29	1.44	1.47	1.43	1.50	0.07	1.42	5.17	
alpha-Chlordane	1.30	1.48	1.46	1.39	1.40	0.06	1.40	4.49	
DDE	1.29	1.28	1.29	1.28	1.38	0.04	1.30	2.86	
Endosulfan I	1.35	1.25	1.25	1.20	1.25	0.05	1.26	3.99	
o-p'-DDD/IS#2	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Dieldrin	1.22	1.15	1.19	1.22	1.23	0.03	1.20	2.46	
Endrin	1.15	1.12	1.16	1.12	1.15	0.02	1.14	1.48	
DDD	0.91	0.85	0.87	0.92	0.92	0.03	0.90	3.06	
Endosulfan II	1.06	1.03	1.08	1.07	1.05	0.02	1.06	1.59	
DDT	1.11	1.03	1.04	1.04	1.06	0.03	1.06	2.55	
Pentabromobiphenyl/IS#3	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Endrin Aldehyde	1.09	1.04	1.01	0.93	0.89	0.07	0.99	7.18	
Methyoxyclor	0.61	0.58	0.55	0.51	0.48	0.05	0.55	8.51	
Endosulfan Sulfate	1.40	1.36	1.41	1.23	1.22	0.08	1.32	6.25	
Endrin Ketone	1.80	1.73	1.70	1.63	1.55	0.06	1.63	3.77	
DCB	1.73	1.80	1.82	1.69	1.54	0.10	1.71	5.84	

COMMENTS: _____

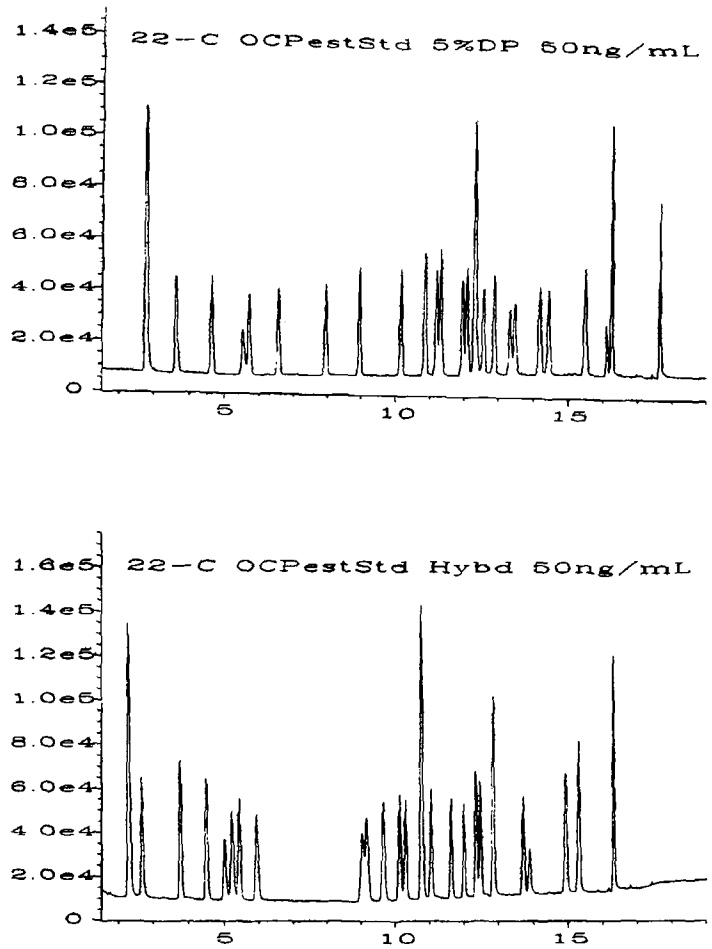


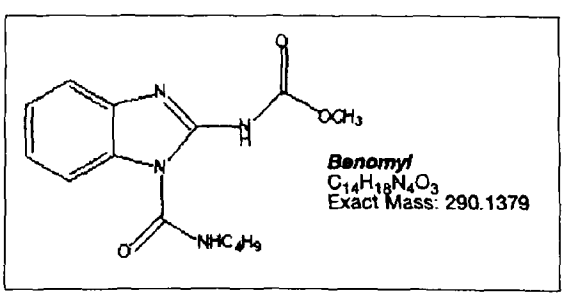
Figure 1. Chromatograms of twenty-two Organochlorine Pesticides on a dueal injector GC system.

IONSPRAY LC/MS METHOD FOR THE QUANTITATION OF MAJOR DEGRADATION PRODUCTS OF BENOMYL

Chris Elicone
PE Sciex, 50 Danbury Road, Wilton, Connecticut 06897
Tong Xuan and S. Madhava Reddy
Florida Department of Environmental Protection Chemistry Section,
2600 Blair Stone Rd., Tallahassee, Florida 32399

OVERVIEW

An existing High Performance Liquid Chromatography (HPLC) UV quantitative method has been directly transferred to an ionspray single quadrupole LC/MS assay resulting in an immediate gain in sensitivity and selectivity. This ionspray method was then modified for narrow bore HPLC, obviating the need to split while reducing the analysis time and improving the limit of quantitation. The narrow bore HPLC method was linear over three orders of magnitude with increased robustness and case of use.



INTRODUCTION

The determination and quantification of polar pesticides and their degradation products in environmental

analytical chemistry is gaining importance because of their persistence and toxicity. Furthermore, many countries have now passed legislation to ensure that pesticides are used safely and responsibly in order to protect the public from unsafe levels of pesticide residues. Due to the high polarity, low volatility and thermolability of carbamates, GC and GC/MS methods are not amenable to this class of compounds. HPLC with UV detection has been the standard analytical method for analysis and quantitation of polar compounds. Benomyl, a carbamate and a widely used systemic fungicide for disease control in crops, poses additional analytical challenges to the environmental chemist due to its extreme instability in the environment. Benomyl decomposes to three stable major degradation products: 2-aminobenzimidazole (2-AB), methyl 1-H-benzimidazol-2-ylcarbamate (MBC), and 3-butyl-2,4-dioxo-s-triazino [1,2-a] benzimidazole (STB).

EPA Method 631 for the determination of benomyl and MBC in industrial and municipal wastewater restricts the detection and quantitation to MBC only since benomyl is hydrolyzed to MBC in this method. This isocratic UV method has a Method Detection Limit (MDL) of 8.7 ppb for MBC.

The UV method adapted in this report monitors the three major degradation products of benomyl by gradient elution. The UV analysis has a method detection limit of 2 ppb for 2-AB, MBC, and STB.

METHOD

Materials

2-AB was obtained from Aldrich Chemical Company (Milwaukee, WI). MBC was obtained from Chem Services (West Chester, PA) and STB was obtained from E.I. du Pont Nemours & Co. (Wilmington, DE). Solvents used for HPLC and extraction were HPLC grade acetonitrile, methanol and water from JT Baker (Philipsburg, NJ). The formic acid used in the HPLC solvents, as well as the injection solvent, was from Sigma (St. Louis, MO). The standard bore (4.6 x 250 mm) HPLC column was a C18 with a 5-µm particle size by Whatman (Clifton, NJ). The narrow bore column (2 x 50 mm) was a Monitor C18 with a 3-µm particle size by Column Engineering (Ontario, CA). A Waters Oasis (Milford, MA) 3-mL, 60-mg SPE cartridge was used for the solid phase extraction.

Preparation. Benlate Extraction Procedure

A Benlate mix spike solution was comprised of a mixture of 2-AB and STB in methanol at a concentration of 2 ppm. 200 mL of water sample was poured into a 400-mL beaker. HPLC grade water was used for blanks and laboratory fortified blanks. The pH of all samples was checked and recorded using a pH meter. For any spiked samples (laboratory fortified blanks and matrix spikes), 200 µL of Benlate mix spike solution was added and mixed well. Two Normal NaOH was added to adjust the pH of all the samples to 10. The solid phase extraction (SPE) cartridge was conditioned by aspirating 5 mL of methanol through the cartridge followed by 10 mL of HPLC grade water without allowing the cartridge to dry. The sample was filtered through the conditioned SPE cartridge under vacuum. The sample beaker was then rinsed with 5 mL of HPLC grade water adjusted to pH 10. The rinse was passed through the SPE cartridge and vacuum dried for 3 min. Elution with 5 mL of methanol and collection of the eluate into a 15 mL centrifuge test tube was completed. The eluate was dried down with nitrogen in a water bath at 40°C to a volume of 1 mL. One mL of 0.2% formic acid was added and mixed well.

HPLC Conditions

A Shimadzu VP series HPLC (Columbia, MD) was used with the gradients, flow rates and columns listed in Table 1.0 and Table 1.1. The flow from the standard bore column was split down from 1 mL/min to approximately 200 µL/min into the Turbolonspray source at ambient temperature. For the narrow bore column no split was necessary and the entire effluent was sent into a Turbolonspray source set to 200°C.

Table 1.0. HPLC Gradient

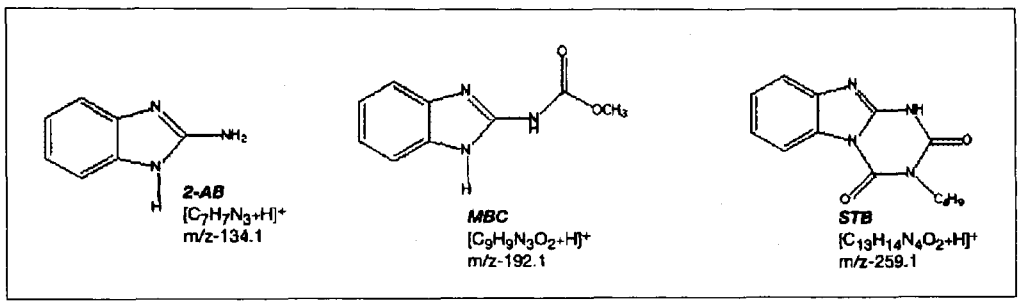
Standard Bore Column		**Solvent A**	**Solvent B**
4.6 x 250 mm	Time (min)	0.1% Formic Acid	Methanol + 0.1% Formic Acid
Flow rate: 1 mL/min	0	70	30
Whatman C18 5 µm	10	30	70
	20	15	85
	20.1	70	30
	30	70	30

Table 1.1. HPLC Gradient

Narrow Bore Column	Time(min)	0.1% Formic Acid	Acetonitrile + 0.1% Formic Acid
2 x 50 mm	0	100	0
Flow rate: 0.2 mL/min	0.85	50	50
Column Engineering	2.25	45	55
Monitor C18 3 µm	4	45	55
	6	30	70
	7	30	70
	7.1	100	0
	10	100	0

Mass Spectrometer

A PE Sciex API 150 (Concord, Ontario, Canada) single quadrupole mass spectrometer was operated in positive ion mode with a Turbolonspray source. The source temperature was ambient for the standard bore HPLC column and was set to 200°C for the narrow bore column. The compounds were monitored using selected ion monitoring (SIM) with the following m/z values:



The ion optics path was optimized for each compound separately in the separations solvent. The values for the orifice, ring and Q0 are listed in Table 2.0. The mass spectrometer was operated at unit resolution with an ionspray voltage of 4600 V.

Table 2.0. Ion Path Voltages

Compound	OR	RNG	Q0
2-AB	45	160	-4
MBC	20	120	-3
ST13	30	155	-4

RESULTS

Initially the primary emphasis was on transferring an already validated UV HPLC method to a single quadrupole MS method altering as few parameters as possible. Only two changes to the original procedure were necessary for the method transfer. Formic acid was added to the mobile phase of the HPLC solvents, and the injection solvent was changed to contain a final concentration of 0.1% formic acid in 50% methanol. All other parameters remained the same. As a consequence of the change in pH, the elution order of the compounds changed but chromatographic resolution was maintained and all compounds were baseline resolved. The eluant from the 4.6-mm column was initially split to 50 µL/min into the Turbolonspray source at room temperature. Occasionally at a high percentage of organic, the 50-µL/min split into the mass spectrometer would lose flow resulting in a loss of signal. This was corrected by decreasing the split ratio sending approximately 200 µL/min into the ion source at the expense of sensitivity. Nevertheless, the limit of quantitation for the standards (0.01 ppm) was an order of magnitude better than that of the UV analysis of standards (0.1 ppm). (See Figure 1.0 and Figure 1.1.)

The Method Detection Limit (MDL) was calculated with the following equation:

$$MDL_{calculated} = t \times s \times V_{ext}/V_{sample}$$

V_{ext} = 2 mL t = Student Coefficient

V_{sample} = 200mL s = Standard Deviation

Table 3.0 contains the solid phase extraction validation data and Table 4.0 contains the MDL calculations for both UV and LC/MS analyses. While the calculated MDL for the UV and LC/MS methods are similar, the actual

MDL achieved by the two methods is an order of magnitude different.

Table 3.0. SPE Validation for Water

Recoveries																	
UV 4.6 x 250 mm		MDL-1		MDL-2		MDL-3		MDL-4		MDL-5		MDL-6		MDL-7			
Compound	Spike Level	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	%Mean	SD	%RSD
2-AB	5 µg/L	2 5	50	2.5	50	2.7	54	2.7	54	3 2	64	3.3	66	3.1	62	57.1	6.7	12
MBC	5 µg/L	5	100	5 3	106	5 4	108	4.6	92	56	112	5.3	106	5.2	104	104	6.4	6
STB	5 µg/L	5 4	108	5.5	110	5.8	112	4.7	94	5.7	114	5.5	110	5 3	106	108	6.6	6
LC/MS 4.6. 250 mm																		
2-AB	2 µg/L	1 74	87	1.86	93	1 76	88	1.9	95	1.86	93	1.94	97	1.64	82	90.7	3.9	4
MBC	2 µg/L	1.98	99	2.12	106	2.04	102	2.2	110	2.18	109	2.26	113	2 18	109	107	5.2	5
STB	2 µg/L	1 57	79	1 64	82	1.54	77	1.58	79	1.54	77	1.62	81	1 66	83	79.7	2	3

Table 4.0. MDL

Method Detection Limit					
UV 4.6 x 250mm					
Compound	Student Coefficient	n	Std. Deviation	MDL (calculated)	MDL (actual)
2-AB	3.143	7	6.7	0.21 ppb	2 ppb
MBC	3.143	7	6.4	0.20 ppb	2 ppb
STB	3.143	7	6.6	0.21 ppb	2 ppb
LC/MS 4.6. 250 mm					
2-AB	3.143	7	3.9	0. 12 ppb	0.2 ppb
MBC	3.143	7	5.2	0.16 ppb	0.2 ppb
STB	3.143	7	2	0.063 ppb	0.2 ppb

In order to improve the setup and ease of use the LC/MS method was altered further. A 2 X 50-mm HPLC column replaced the larger diameter column and the entire eluant flow was sent directly into the Turbolonspray source. The source was operated at 200°C. This source temperature gave the best overall response for the three compounds of interest while not significantly adding to the background signal of the final method. The initial gradient was based on the same column volumes and used the same buffer system of the larger column. The result was a fine separation of 2-AB and MBC but STB did not elute as a sharp peak. With the addition of heat the methanol solvent system generated an additional problem. The background signal increased dramatically making detection of the low standards difficult. All efforts to reduce the background with methanol as the organic solvent failed. Methanol was replaced with acetonitrile, resulting in much lower background counts and a much improved STB peak shape. The gradient was changed to accommodate the stronger solvent. In fact, the peak shapes improved for all three analytes. 2-AB and MBC each elute in roughly 20 µL and are baseline-resolved. STB elutes in approximately 100 µL. Because of this difference in elution volumes a period MS method generated better S/N for each compound. This reduced elution volume from the narrow bore column improved the limit of quantitation (LOQ) even further. While the reduction in column dimension should only result in a four-fold gain in sensitivity, the above changes resulted in a 50-fold gain since only 10 µL were injected onto the 2-mm column versus 100 µL injected onto the 4.6-mm column. The small volume of the 2-mm column as compared to the standard bore column also reduced the analysis time from 30 minutes to 10 minutes.

Figures 1.0, 1.1 and 1.2 are views of the low standards for each method. Each has a S/N greater than 10:1. The LOQ for the standards is 0.1 ppm, 0.01 ppm, and 0.002 ppm for the UV, 4.6, and 2-mm methods, respectively. The resultant calibration curves are shown in Figure 2.0. A linear 1/X weighting was used for the LC/MS analyses while no weighting was used in the UV analysis. Table 5.0 lists the percent deviation of the mean from the theoretical (%DMT) and the %RSD obtained over five days for the various levels using the 2-mm LC/MS method. Table 5.0 demonstrates the high degree of accuracy and consistency required for successful quantitative results.

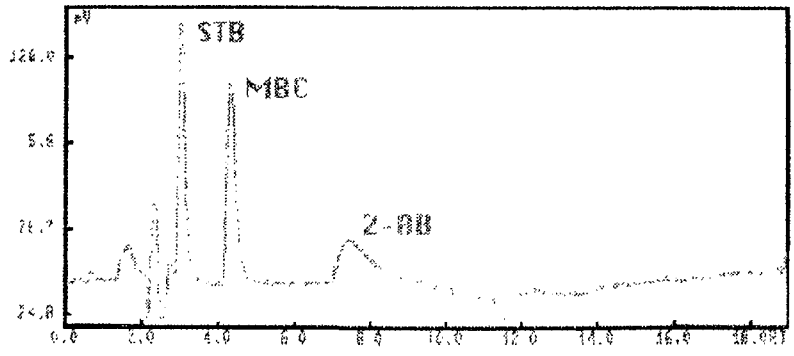


Figure 1.0. UV Low Standard (0.1 ppm; 100-µL injection volume).

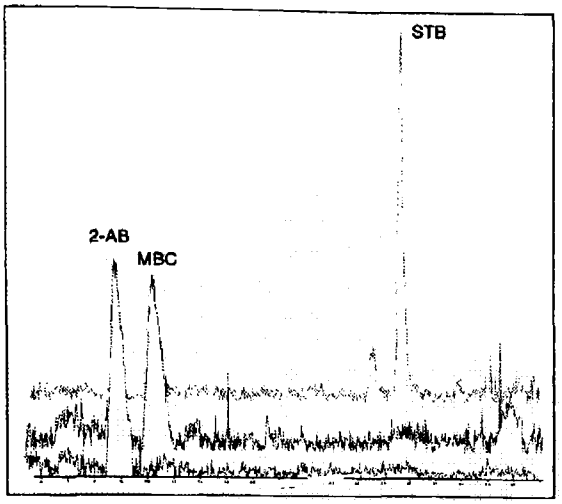


Figure 1.1. 4.6 x 250 mrn Low Standard (0.01 ppm; 100-µL injection volume).

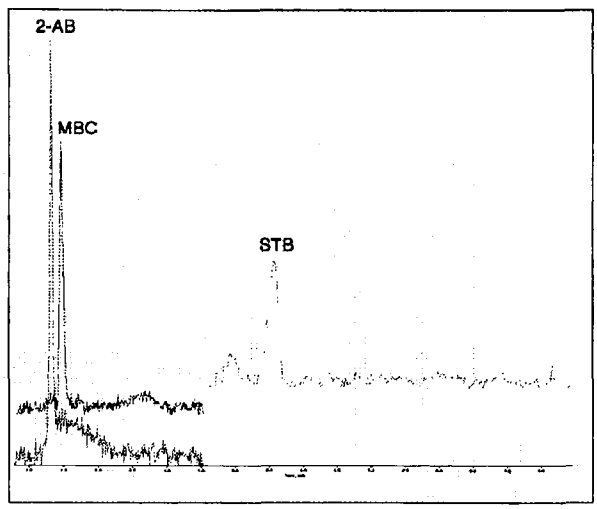


Figure 1.2. 2 x 50 mm Low Standard (0.002 ppm; 10-µL injection volume).

Table 5.0. %DMT Statistics

Five-Day Percent Deviation from Theoretical LC/MS 2 x 50 mm method						
	2-AB		MBC		STB	
Level	%DMT	% RSD	%DMT	% RSD	%DMT	% RSD
	2-AB	2-AB	MBC	MBC	STB	STB
1000 ppb	96.19	1.12	97.8	0.44	99.45	0.05
200 ppb	111.15	0.94	107.69	1.87	105.99	1.38
100 ppb	110.49	2.35	106.79	1.98	105.38	2.06
20 ppb	106.65	1.95	102.2	2.81	98.76	5.81
10 ppb	104.38	4.04	99.57	2.38	91.64	5.67
2 ppb	94.05	2.51	98.91	4.67	108.2	11.72
1 ppb	78.97	13.26	95.67	9.29	114.25	16.74

While the 0.001-ppm standard is detected with the 2-mm method, the %RSD for the accuracy of the three compounds was deemed to be too high for the LOQ. The MDL-7 for the 2 x 50-mm LC/MS method needs to be completed, but based on the previous results for the standards the MDL should be approximately 0.02 ppb.

CONCLUSIONS

A method was developed to quantitate the major degradation products of benomyl in a simple, single quadrupole LC/MS assay. An existing UV HPLC method was slightly modified for analysis by a PE Sciex. API 150 mass spectrometer. An immediate order of magnitude gain in sensitivity over the UV MDL resulted. This LC/MS method obviates the additional step of hydrolysis described in EPA Method 631, allowing for direct quantitation of the major degradation products of benomyl. Currently the benomyl LC/MS method can be used with extraction protocols for water. Additional optimization of the HPLC and MS method produced further gains in sensitivity and also simplified the system setup. The narrow bore method requires the validation process to be completed, but this should not prove difficult based on the clean matrix provided by the SPE protocol and the consistency of the standards analyzed. The increased specificity afforded by MS also allowed for a reduction in HPLC and data analysis time. Future work will result in the development of extraction protocols for waste and sediment. Also, implementation of an internal standard should improve the results obtained by this method.

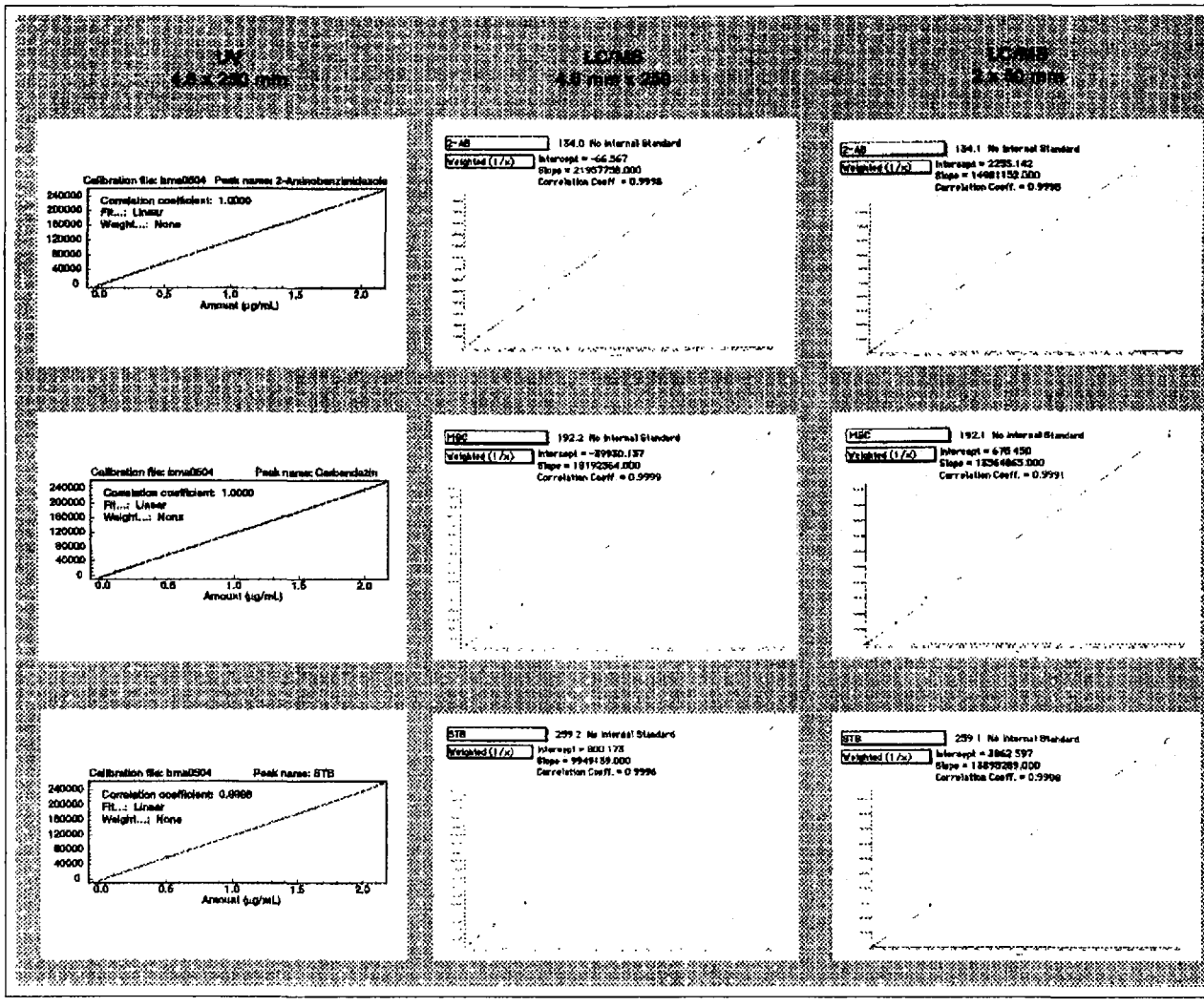


Figure 2.0. Calibration Curves for 2-AB, MBC, and STB.

METHODS OPTIMIZATION OF MICROWAVE ASSISTED SOLVENT EXTRACTION TECHNIQUES FOR VARIOUS REGULATORY COMPOUNDS

Greg LeBlanc, Mike Miller
CEM Corp., PO Box 200, Matthews, NC 28106-0200
(704) 821 7015

We have seen a period of rapid growth in the separation sciences, with gas and liquid chromatography as well as the hyphenated techniques becoming commonplace. There is a need to streamline the extraction techniques preceding these chromatographic analyses. Time and solvent usage have become critical factors. In response to this need several new sample preparation technologies have emerged. As a result analysts are faced with the challenge of adapting current methods or developing entirely new ones depending on the extraction technology they use.

Microwave Assisted Solvent Extraction is a new technique that works with existing solvent regimes with minimal modifications and significant solvent reduction. It also has the benefit of reducing the extraction time. This study will review the methods optimization process when using a closed vessel microwave assisted solvent extraction

technique. It will focus on extraction temperature, sample water content and ratios for solvent mixtures. Recovery data will be presented for pesticides and fungicides from reference soils and vegetable samples.

NEW DEVELOPMENTS IN CLOSED VESSEL MICROWAVE DIGESTION TECHNOLOGY FOR PREPARATION OF DIFFICULT ORGANIC SAMPLES FOR AA/ICP ANALYSIS

Greg LeBlanc, Bobbie Haire and Bob Fidler
CEM Corporation, PO Box 200, Matthews, NC 28106-0200
(704) 821-7015

Microwave digestion techniques are well accepted as a means of preparing samples prior to AA and ICP analysis. Pressurization of the sample vessel accelerates the dissolution process by permitting acids to attain higher temperatures than under ambient conditions. However, it has been historically difficult to control the microwave digestion process under ultra-high temperature and pressure conditions. As well, throughput of difficult high-pressure samples using conventional microwave instrument technology has been limited, thus inhibiting its use for preparation of some difficult organic and inorganic samples. This paper will demonstrate new microwave instrument technology for optimization of ultra-high pressure and temperature conditions for microwave preparation of difficult organic and inorganic samples for AA and ICP analysis. Data will be provided to demonstrate the digestion performance under significantly elevated pressure and temperature conditions as well as the impact of such conditions on the microwave preparation instrumentation.

EVALUATION OF ICP-OES AND ICP-MS FOR ANALYSIS OF THE FULL TCLP INORGANIC TARGET ANALYTE LIST

Marc Paustian and Zoe Grosser
The Perkin-Elmer Corporation, 50 Danbury Road, MS-219, Wilton, CT 06897-0219

Abstract
Toxicity Characteristic testing is performed to assess the potential of a material to leach hazardous constituents after disposal in a landfill. The Toxicity Characteristic Leaching Procedure (TCLP) extract solution is analyzed for 31 organic components and 8 metals and if the regulated limits are exceeded (Table 1) the material is considered hazardous and must be treated appropriately.

Currently, ICP-OES and ICP-MS have the technical capability of determining the full suite of TCLP elements in one run. EPA ICP-OES method 6010B includes Hg in the target analyte list. EPA ICP-MS draft method 6020A now includes Se and Hg in the target analyte list. This provides an opportunity to demonstrate the utility of TCLP analysis using one sample preparation and one technique for analysis.

Compliance with the generally accepted requirements of the RCRA program will be demonstrated for the full suite of TCLP analytes including mercury. ICP-OES and ICP-MS will be compared for the analysis.

The results will be validated with the analysis of the required Quality Control for performance-based methods and will include detection limits, spike recoveries, and duplicate sample analytical data.

Experimental
Raw TCLP extracts were provided by Trinity River Authority in Dallas Texas. They were prepared by digestion with EPA method 3015 using the Multiwave Microwave Digestion System (Perkin-Elmer Corp.). To evaluate the recovery vs. hotplate digestion, for mercury, the samples were also spiked with mercury and digested on a hotplate using method 3020. Gold was added to some samples to evaluate the effect on retention of mercury

during the digestion process and resulted in a concentration of 2 mg/L in the final solution.
The samples were analyzed using ICP-OES and ICP-MS, for comparison. The instrumental conditions are shown in Tables 2 and 3.

Table 1. TCLP Metal Limits

Element	MCL(mg/L)
As	5.0
Ba	100.0
Cd	1.0
Cr (Total)	5.0
Pb	5.0
Hg	0.2
Se	1.0

Table 2. ICP-OES Instrumental Conditions
Optima 3000 DV

Parameter	Settings
RF Power	1500 watts
Nebulizer Flow	0.4 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto integration	5 sec min-20 sec max
Read Delay	45 sec
Rinse	45 sec
Replicates	2
Background Correction	one or two points

Table 3. ICP-MS Instrumental Conditions
ELAN 6000

Parameter	Settings
RF Power	1500 watts
Nebulizer Flow	0.94 L/min
Auxiliary Flow	1.0 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 mL/min
Sample/Skimmer Cones	Nickel
Scanning Mode	Peak Hopping
Lens	Lens Scan Enabled
Read Delay	10 sec
Rinse	35 sec
Replicates	3
Detector Mode	Dual Mode

Results and Discussion
The instruments were qualified by measuring method detection limits using the procedures specified in the Federal Register, part 136[1] The method detection limits are shown in Table 4 and compared with the MCL (shown here in µg/L for easier comparison) for the element. It is generally accepted that the MDL should be ten times less than the MCL to ensure sufficient confidence at the decision-making point. The detection limits for both the ICP-OES and ICP-MS are well below the limits set by the criteria specified.

Table 4. Method Detection Limits

Element	MCL (µg/L)	MDL (µg/L) ICP-OES	MDL (µg/L) ICP-MS
Ag	5000	6	0.007
As	5000	2	0.09
Ba	100,000	0.3	0.01
Cd	1000	0.1	0.03
Cr	5000	0.6	0.05
Hg	200	8	0.34
Pb	5000	2	0.006
Se	1000	3	0.18

The results were measured on the samples digested with the microwave procedure for the full suite of elements. The results are shown in Table 5 and compared with results reported by the supplier. The digested samples compared well with the results provided. The ICP-OES and ICP-MS results compared well with each other, The results were all well below the maximum contaminant levels for all elements.

Table 5. Comparison of Sample Results

Element	ICP-OES Sample 1 (µg/L)	ICP-MS Sample 1 (µg/L)	TR-1 (µg/L)	ICP-OES Sample 2 (µg/L)	ICP-MS Sample 2 (µg/L)	TR-2 (µg/L)
Ag	8	0.1	< 2	6	0.05	<2
As	8	5	<5	6	3.4	<2
Ba	253	214	232	260	218	278
Cd	2	0.4	< 8	1	0.08	< 8
Cr	15	12	11	6	7	5
Hg	< 8	< 0.3	< 0.5	<8	< 0.3	< 0.5
Pb	7	4	4	5	2	< 4
Se	5	4	< 5	2	2	< 5

Predigestion spike recoveries were evaluated for samples digested with the microwave procedure. The samples were spiked with 2.5 mg/L of As, Cr, Pb, Ag, 0. 5 mg/L of Cd, Se, 0.1 mg/L Hg, and 50 mg/L of Ba. The samples labeled "Spike 2" also had gold added (2 mg/L). The spike recoveries are shown in Table 6 for ICP-OES analysis and Table 7 for ICP-MS analysis.

Table 6. ICP-OES Spike Recoveries

Element	Sample 1 Spike 1 %Rec	Sample 1 Spike 2 %Rec	Sample 2 Spike 1 %Rec	Sample 2 Spike 2 %Rec	Blank Spike 1 %Rec	Blank Spike 2 %Rec
Ag	33	2	30	2	63	2
As	104	107	107	108	99	100
Ba	102	102	102	101	101	101
Cd	106	108	107	108	105	106
Cr	100	101	100	101	99	99
Hg	60	62	62	63	54	60
Pb	99	102	100	100	102	103
Se	104	107	105	106	96	96

The spike recoveries were excellent. The silver recoveries diminished with time, as is typical with a nitric-only digestion. Since the ICP-MS analysis was performed first and the ICP-OES analysis was performed after several days had passed the effect is more evident in the ICP-OES results. The addition of small amounts of chloride with the gold solution in the second spike accelerated the precipitation of silver. The mercury spike recoveries were less than expected and may be due to insufficient cooling of the vessels before the solution was transferred. The solutions were not stored in Teflon® bottles, providing another possible source of loss. Since the addition of gold improved the recoveries of mercury only slightly in the microwave digestion, better overall performance may be obtained if the gold is left out. The effect of gold addition on the retention of mercury in a traditional hotplate digestion was investigated. The recoveries compared to spikes digested with microwave are

shown in Table 8.

Table 7. ICP-MS Spike Recoveries

Element	Sample 1 Spike 1	Sample 1 Spike 2	Sample 2 Spike 1	Sample 2 Spike 2	Blank Spike 1	Blank Spike 2
Ag	92	6	97	4	106	7
As	104	100	102	104	93	102
Ba	115	120	116	118	117	116
Cd	101	103	103	103	104	103
Cr	96	96	96	99	100	101
Hg	62	53	92	53	55	54
Pb	109	107	109	106	109	106
Se	103	108	98	107	103	113

Table 8. Effect of Gold on Mercury Spike Recovery

	Sample 1 Spike (% Rec)	Sample 1 Spike Dup. (% Rec)	Sample 1 Spike+Gold (% Rec)	Sample 1 Spike Dup. +Gold (% Rec)
Hot Plate Digestion				
ICP-OES	52.1	32.8	56.9	61.5
ICP-MS	44.4	37.0	51.2	47.5
Microwave Digestion				
ICP-OES	60	62	62	63
ICP-MS	62	62	53	53

The addition of gold only slightly improves the recoveries of mercury using the microwave digestion. The hotplate digestion results show more dramatic recovery improvements. In addition, the duplicates are much more consistent in the hotplate digestion when gold is added before the digestion process.

Summary

Much progress has made in increasing the scope of inorganic methods to include all the analytes of interest. Analyses can be performed more economically when only one sample preparation and one analysis technique are needed to fully evaluate a sample.

This work has demonstrated that mercury can be successfully determined in a digested TCLP extract matrix, as a part of the full suite of elements traditionally measured. Both ICP-OES and ICP-MS show excellent method detection limits for the elements measured and good predigestion spike recoveries with the exception of mercury. Further work is needed to define the mechanism for mercury loss in the digestion and transfer procedure used before the instrumental analysis.

Method 6010B for ICP-OES and proposed 6020A for ICP-MS contain the full list of analytes for TCLP analysis. This work validates the utility of these methods for this type of matrix. Microwave sample preparation procedures are especially useful when mercury is included in the analyte list, coupled with careful sample transfer and storage.

Acknowledgement

The authors would like to thank Bill Cyrus of the Trinity River Authority, Dallas, Texas for providing the TCLP extracts.

References

1. US Code of Federal Regulations 40, Ch. 1, Pt 136, Appendix B.

CLEAN METALS SAMPLING

Roger E. Stewart II
Virginia Department of Environmental Quality, Office of Water Quality Assessment and Planning,
629 East Main Street, Richmond, Virginia 23219

ABSTRACT

Scientific evidence[1] of aquatic organism toxicity to low concentrations of dissolved metals has led to the need for accurate and precise measurements of these compounds in a variety of aqueous matrices. A practical method[2] will be presented for the collection and analysis of freshwater and wastewater samples for trace metals. A hands on demonstration of clean techniques will be presented to show the simplicity and ease of collecting scientifically defensible samples for compliance monitoring purposes. Field sampling equipment specifications, collection procedures, the importance of blanks, and preservation of samples, will be discussed as topics important to designing a procedure for collecting water samples with metals concentrations in the range where toxicity is significant.

INTRODUCTION

To be protective of aquatic organisms and human health the US Environmental Protection Agency has established water quality standards[3], which specify safe concentration levels in background waters, for toxic metal species. Regulatory agencies must evaluate the concentrations of analytes in receiving waters and discharges to determine "reasonable potential" for impact to an ecosystem. Reliable methods for measuring trace concentrations of target compounds are essential to developing permit limits on discharges.

As regulatory levels for metals have decreased, sometimes several orders of magnitude, field collection protocols which are practical and applicable to a wide variety of site conditions and personnel must be developed.

The US Geological Survey (USGS) and the US Environmental Protection Agency (USEPA) have made progress in the last two years towards developing widely applicable field and laboratory procedures. The USGS has focused on internal procedures[4] designed to be used by USGS personnel. As a regulatory agency the USEPA has developed procedures[5,6,7,8,9,10,11,12] which can be used by monitoring groups, public agencies, and the regulated community.

The freshwaters appropriate for collection by this method include all surface waters and groundwaters with a specific conductivity of approximately 1000 umhos/cm or less. Appropriate wastewaters include treated effluents (conductivity < 1000 umhos/cm). Saltwaters, brackish waters, highly turbid wastewaters, i.e. landfill leachates, are not appropriate as they require special laboratory preparation and analysis.

The protocols contained in this Standard Operating Procedure are applicable to the compounds listed in Table 1 Target Analytes, Analytical Test Methods. and Detection Limits on page 8.

Additionally this SOP is suitable for freshwater and treated final effluents with concentrations of toxic metals below approximately 200 µg/L. The 200 µg/L threshold should be applied cautiously as this is only a generalization of the effect of contamination. For example, because of well documented contamination problems with copper and zinc, if a final effluent has historically had copper or zinc reported in the 0.2 mg/L range use of this protocol may reveal that the actual concentrations are significantly lower. However if the historical numbers for cadmium, arsenic, or mercury have been in the 0.2 mg/L range use of this protocol may not affect these concentrations. Another factor to consider when determining the applicability of this SOP is that typically the reporting level of historic data is much higher than the lowest concentrations when compared to Water Quality Standards.

For concentrations above approximately 200 µg/L, existing 40 CFR 136 procedures are adequate and contain the necessary Quality Controls (including the requirement to collect blanks) to make reliable measurements in the mg/L range. The United States EPA Region III has prepared extensive guidance for existing and new data which falls into this range.

METHODOLOGY

Improving on a combination of the more salient features from the USGS, USEPA, and others[4,13] the Virginia

Department of Environmental Quality (VADEQ) began a pilot project designed to 1) determine if current technology could be used to accurately measure metal concentrations in water below 1.0 µg/L using clean techniques, 2) develop protocols for wastewater treatment plant effluent collection and analysis which could be incorporated into guidance and, 3) develop freshwater protocols for an ambient water quality monitoring program.

The main design considerations were to develop a system to 1) collect field samples free of contamination and, 2) minimize the level of effort required by field technicians.

When measuring at trace concentrations small amounts of background contamination and interference can be significant. The most likely sources of contamination are:

1. improper sample handling techniques,
2. improperly cleaned sampling equipment and sample containers, and
3. atmospheric dust and debris.

These ideas led to the design of a closed loop sample container which could be filled onsite, transported to the laboratory, prepared, and digested all in the same container. Figure 1 Loop Sample Bottle shows the container used to collect the samples.

Figure 2 Sample Collection Scheme illustrates the closed loop sample collection system. Sample collection is accomplished by pumping water from the sampling zone through a teflon tube, peristaltic tubing, and a capsule filter, directly into the loop sample container.

The entire process consists of the following steps:
1. Sample containers and tubing kits are cleaned and certified in a controlled laboratory environment.
2. The containers and kits are packaged into coolers and shipped to the field.
3. Blank ultra pure water from a blank sample container is processed through the tubing kit to condition and clean the capsule filter.
4. Ultra pure water from the sample container is pumped through the tubing assembly into the empty blank container to produce the field blank.
5. Sample is collected into the empty sample container using the tubing assembly.
6. Blanks and samples are shipped to the laboratory.
7. All samples and blanks are acidified, digested, prepared in the original container.
8. Samples are analyzed accordingly.

The advantage of this design is that field technicians receive the sample containers and equipment ready to use. Other than filter conditioning[14,15] there are no cleaning steps required and no need to preserve the samples other than icing. The sample containers include the water to be used for field blank collection with the blank collection exactly duplicating the site conditions of the sample collection. All the plasticware is inexpensive and can be discarded after single use.

DISCUSSION

Ambient Sample Collection Protocol

1. Locate an area where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.
2. Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.
3. Cover the work area with a large piece of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.
4. Remove a tubing kit, two sample containers, and a bridge bottle from the cooler and place on the plastic near the pump.
5. Remove a pack of sample gloves from the storage container and place on the plastic.
6. Remove the plastic sample caddie from the storage box and place it on the sample processing area near the pump. Secure the two sample bottles in the caddie.

Bridge Bottle Filling

1 . Locate the sample weights for connection to the BRIDGE BOTTLE.
2. Locate the polypropylene sampling rope spool, cut a sufficient length of rope to allow for deployment, and place on plastic.
3. Don one or two pairs of vinyl gloves using clean precautions.
4. Tie one end of the sampling rope to the five pound weight leaving approximately a 1' long end for connection to the BRIDGE BOTTLE.
5. Untie or open by tearing the top of the outer plastic bag containing the BRIDGE BOTTLE.
6. Reach into the outer bag and untie or tear the inner bag near the handle connection. Check the configuration of the tubing to ensure that proper filling will occur. While the bottle is still in the inner bag it is acceptable to remove the top fitting to check the inner sipper tube. Adjust all fittings appropriately.
7. When the fittings have been properly secured and adjusted remove the BRIDGE BOTTLE from the inner bag and lay on the plastic film. Tie the weighted end of the rope onto the handle of the bottle leaving about 6" of line between the bottle and the weight.
8. Proceed to the sampling location with the BRIDGE BOTTLE apparatus. If appropriate carry several extra pairs of gloves to the site to facilitate bridge bottle handling.
9. When deploying from bridges with moderate to low stream velocities collect the sample upstream of the bridge by lowering the assembly into the water. Ensure that the assembly does not contact any structures or other objects as it is lowered into the water.
10. Once in the water the weight will partially submerge the BRIDGE BOTTLE which will begin to fill. Check to insure the air release tube is above the water level and not obstructed. When the bottle is first submerged a good indication it is filling properly is a small slug of water may be expelled from the air vent tube. The bottle will fill quickly if it has been properly adjusted.
11. Problems with filling from bridges can occur when stream velocities are high. Sampling on the downstream side of bridges is acceptable to avoid the risk of losing the assembly due to the current sweeping it under a bridge or other obstruction. When stream velocities are high an additional 7.5 pounds of weight will aid in sample collection. The added weight will cause the container to sink lower when partially filled which may submerge the vent tube. The vent tube can be extended past the bottom of the bottle to prevent filling with water when the weight is heavy or the water is rough.
12. Other problems with filling can occur when the inlet tube is clogged, the vent tube contains a slug of water or other obstruction, the vent tube is below the surface of the water, the weight is not positioned close enough to the bottle, or the vent tube or inlet tube has become disconnected from the bottle.
13. When the BRIDGE BOTTLE is approximately 1/3 to 1/2 full retrieve the bottle and return to the sample processing area. Ensure that the assembly does not contact any structures or other objects as it is retrieved.
14. When deploying while wading or from a small craft the BRIDGE BOTTLE can be submerged by hand without the weights.
15. When the water level at the sample site is very shallow it may be difficult to submerge the BRIDGE BOTTLE deep enough to begin siphoning. The alternative is to use the effluent sample configuration where the stream sample is pumped directly into the loop sample container. Sampling in this manner requires the pump assembly to be transported to the site. This is best accomplished by attaching the pump assembly to a backpack.
16. Once the BRIDGE BOTTLE has been brought back to the sample processing area set it next to the pump and remove the weight. With the inlet and vent tubing properly configured the BRIDGE BOTTLE can remain on the plastic outside of a bag without any danger of atmospheric contamination.

Ambient Dissolved Grab Blank

1 . Refer to Figure 2 Sample Collection Scheme for the schematic of the field sampling equipment used to process blanks and samples.
2. Determine which tech will be clean hands and which will be dirty hands.
3. Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag.
4. Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.
5. Clean hands disconnects one side of the sample loop on a sample container. Clean hands connects the end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.
6. Dirty hands connects the peristaltic tubing at approximately the mid-point of the length to the field pump, clean hands inverts the sample container, and dirty hands switches on the pump.

7. Process the entire contents, 1000 mls, of the sample container through the tubing and filter apparatus at a flow rate of 500 mls/min. (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter. After the last noticeable air bubbles have been expelled from the filter it can be oriented in any direction during the rinsing. When the sample container is nearing empty orient the capsule filter with the arrow down. Once the sample container is empty continue processing until the free water in the tubing and filter has been expelled.
8. Dirty hands turns off the pump. This step is a rinse of the filter which cleans and conditions the media. The rinse can be pumped directly to waste.
9. Use the same flow and orientation scheme throughout all sample and blank processing.

Field Blank

1. Clean hands removes the pump tubing from the empty bottle and connects the capsule filter to the empty container via the sample loop tubing. Remove one side of the loop fitting from a second sample container and connect the free end of the tubing to the container. Remember that this second bottle is full of clean water from the lab. Invert the container, dirty hands switches on the pump. Process the entire contents, approximately 1000 mls, of the sample container through the tubing and filter apparatus into the first sample container.
2. Dirty hands switches off the pump when the filter has been emptied. Clean hands disconnects the outlet tubing from the blank sample container and immediately reconnects the loop tubing, seals the inner bag and places inside the outer bag. Dirty hands identifies this as a blank by recording the ULTRA # as the CONTAINER ID, seals the outer bags, and places on ice in a sample cooler.
3. Clean hands immediately (immediately means the sooner the switch is made the less likely contamination can adhere to the end of an open tube, immediately means less than one minute) disconnects the tubing from the sample container and then connects the free end containing the filter, which was just removed from the blank sample container, to the empty sample container. Clean hands then disconnects the vent tubing from the BRIDGE BOTTLE and connects the pump tubing in place of the vent tubing.
4. The field blank collected in this manner is a comprehensive blank because it is collected in the same equipment as the sample and it is processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

Ambient Dissolved Grab

1. In a field notebook dirty hands records the sample container identification number, date, time. Clean hands secures the sample container in the sample caddie.
2. While keeping the BRIDGE BOTTLE near level dirty hands holds the bottle at the midsection or lower and shakes the vessel to ensure mixing. Dirty hands switches on the pump and clean hands collects a full sample container while following the filter orientation scheme. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.
3 Once the sample container is full, dirty hands switches off the pump. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies the sample by recording the ULTRA # as the CONTAINER ID, seals the outer bags, and places on ice in a sample cooler.
4. The clean protocol is complete at this step and field parameters can now be taken from the remaining water in the BRIDGE BOTTLE. Suggested field parameters include pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the solid series and total organic carbon should be prepared; group code SOLIDS, catalog number 190-243, and group code NME10. catalog number 190-25.
5. When finished with the BRIDGE BOTTLE seal the apparatus in a plastic bag and return to the cooler for recycling back to DCLS. DCLS will reclean, certify, and repackage for reuse.
6. Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.

Effluent Sample Collection Protocol

Equipment Setup

1 Locate an area near the final effluent sampling location where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.
2. Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.
3. Cover the work area with a large pick of plastic film. Set out the pump and connect the battery. Switch pump

on for a quick burst to check that it is working. Dial the pump speed to 5.
4. Remove a tubing kit and two sample containers from the cooler and place on the plastic near the pump.
5. Remove a pack of sample gloves from the storage container and place on the plastic. Refer to, for the schematic of the field sampling equipment used to collect treatment plant grab samples.
6. Remove the plastic sample caddie from the storage box and place it on the sample processing area near the pump.
7. Locate the sample wand used for positioning the teflon sample tubing in the effluent.

Effluent Dissolved Grab Blank

1. Refer to Figure 2 Sample Collection Scheme for the schematic of the field sampling equipment used to process blanks and samples.
2. Determine which tech will be clean hands and which will be dirty hands.
3. Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag.
4. Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.
5. Clean hands disconnects one side of the sample loop on a sample container. Clean hands connects the teflon end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.
6. Dirty hands connects the peristaltic tubing to the field pump on the end of the pump tubing closest to the connection with the teflon tubing. This allows for slack on the filter end of the pump tubing. Clean hands inverts the sample container, and dirty hands switches on the pump.
7. Process the entire contents, 1000 mls, of the sample container through the tubing and filter apparatus at a flow rate of 500 mls/min. (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter. After the last noticeable air bubbles have been expelled from the filter it can be oriented in any direction during the rinsing. When the sample container is nearing empty orient the capsule filter with the arrow down. Once the sample container is empty continue processing until the free water in the tubing and filter has been expelled.
8. Dirty hands turns off the pump. This step is a rinse of the filter which cleans and conditions the media. The rinse can be pumped directly to waste.
9. Use the same flow and orientation scheme throughout all sample and blank processing.
10. Clean hands removes the teflon tubing from the empty bottle and connects the capsule filter to the empty container via the sample loop tubing. Remove one side of the loop fitting from a second sample container and connect the teflon end of the tubing to the container. Remember that this second bottle is full of clean water from the lab. Clean hands inverts the container, and dirty hands switches on the pump. Process the entire contents, approximately 1000 mls, of the sample container through the tubing and filter apparatus into the first sample container.
11. Dirty hands switches off the pump when the filter has been emptied as evidenced by air bubbles in the system. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies this as a blank, seals the outer bags, and places on ice in a sample cooler.
12. This is a comprehensive blank because it is collected in the same equipment as the sample and it is processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

Effluent Dissolved Grab

1. In a field notebook dirty hands records the sample container identification number, date, time. Clean hands secures the sample container in the sample caddie.
2. Clean hands connects the filter to the empty sample container. Clean hands presents a section of the Teflon tubing just past the inlet to dirty hands who then attaches the tubing to the sample wand.
3. The entire assembly: sample caddie containing the empty sample container, sample tubing, pump/battery, and sample wand are transported to the effluent sampling location.
4. Dirty hands places the sample wand sample collection zone taking precaution not to touch the tip of the sampling tube on any items. Once the sample tube is located in the effluent take precaution not to let the tip contact anything but water.
5. Dirty hands switches on the pump and clean hands collects a full sample container while following the filter orientation scheme. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.

6. Once the sample container is full dirty hands switches off the pump. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies the sample, seals the outer bags, and places on ice in a sample cooler.
7. The clean protocol is complete at this step and field parameters can now be taken directly from the effluent. Suggested field parameters include pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the solid series and total organic carbon should be prepared; group code SOLIDS, catalog number 190-243, and group code NME10, catalog number 190-25.

CONCLUSIONS

Using these clean procedures to collect more than two hundred samples the data indicate that collection of contaminant free samples at trace concentrations is possible. State regulatory agencies should be encouraged to move forward in promulgating guidance for trace element wastewater characterizations and ambient water quality monitoring. The careful application of the techniques developed by the U.S. Geological Survey and the U.S. Environmental Protection Agency can produce high quality data, satisfactory for regulatory decision making. By adopting the system of field procedures proposed here, investigations of water quality can be performed simply and cost effectively.

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Table 1. Target Analytes, Analytical Test Methods, and Detection Limits

Parameter	CAS Number	Method Detection Limits, µg/L				
		ICPMS USN	ICPMS USN TR	ICPMS	ICP AES USN	CVAA
Aluminium	7429-90-6		0.04	0.37		
Antimony	7440-36-0	0.05	0.03	0.33		
Arsenic	7440-38-2	0.07	0.03	0.24	5.37	
Cadmium	7440-43-9	0.06	0.04	1.72	2.37	
Calcium	7440-70-2				0.08	
Chromium	7440-47-3	0.02	0.04		2.27	
Copper	7440-50-8	0.02	0.06	0.87	4.98	
Iron	7439-89-6				2.3	
Lead	7439-92-1	0.17	0.03	0.28		
Magnesium	7439-95-4				0	
Manganese	7439-96-5	0.02	0.03	1.32	0.58	
Mercury	7439-97-6			0.12		0.07
Nickel	7440-02-0	0.04	0.02	0.39	1.71	
Selenium	7782-49-2		0.06	0.77		
Silver	7440-22-4	0.19	0.03	0.15		
Zinc	7440-66-6	0.26	0.03	2.18	1395	

ICPMS USN inductively coupled plasma mass spectrometry sample introduction by ultrasonic nebulization
ICPMS USN TR inductively coupled plasma mass spectrometry sample introduction by ultrasonic nebulization total recoverable
ICPMS inductively coupled plasma mass spectrometry
ICP AES USN inductively coupled plasma atomic emission spectrometry sample introduction by ultrasonic nebulization
CVAA cold vapor atomic absorption spectrometry

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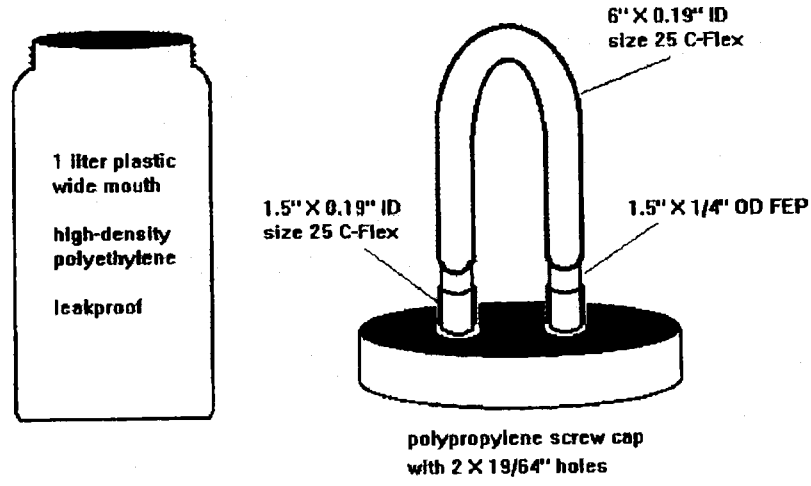

Figure 1. Loop Sample Bottle

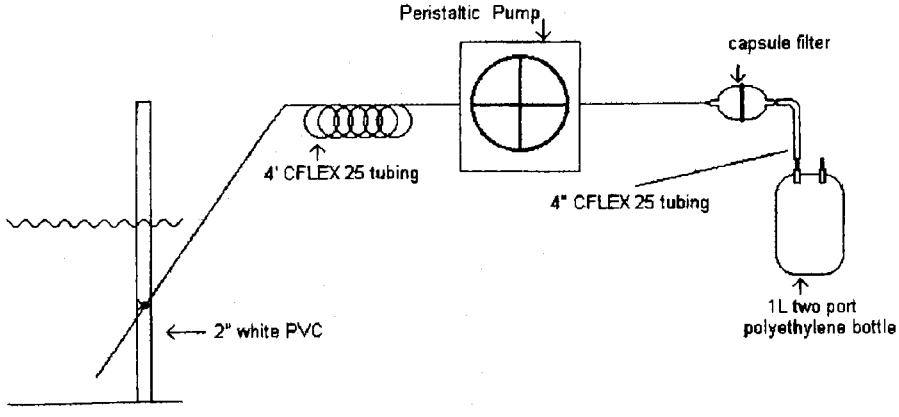

Figure 2. Sample Collection Scheme

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