The 15th Annual Waste Testing & Quality Assurance Symposium

PROCEEDINGS

July 18-22, 1999

Crystal Gateway Marriott ■ Arlington, VA

WTQA '99

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The Fifteenth Annual

Waste Testing & Quality Assurance Symposium (WTQA '99)

July 18-22, 1999

Crystal Gateway Marriott
Arlington, VA

HIGHLIGHTS

15th Annual Waste Testing & Quality Assurance Symposium (WTQA '99) Preparing for Change Under PBMS

WTQA '99 is sponsored by the Waste Policy Institute under a cooperative agreement with the U.S. Environmental Protection Agency. Co-Sponsors include ACIL, ACS Division of Environmental Chemistry, Virginia Tech Chemistry Department, and EnviroAnalysis.

Highlights

The theme of WTQA '99 is "Preparing for Change Under PBMS." Performance Based Measurement System (PBMS) is a new approach to compliance monitoring that has been initiated by EPA. PBMS will allow facilities to use any scientifically valid technologies or methods to demonstrate compliance, rather than require EPA-approved methods. PBMS' aims include reducing costs incurred by regulated entities that must demonstrate regulatory compliance, and helping laboratories to improve their productivity. Although PBMS will add flexibility to the data gathering process, it also mandates that all methods yield accurate compliance determinations. Some of those in the environmental community who will be affected by PBMS include permit writers, state and federal enforcement officials, and regulated entities. WTQA '99 will provide the latest information on the implementation of PBMS.

PBMS Status and Issues Session

The latest information on PBMS implementation from the RCRA, CERCLA, CWA, SDWA and CAA programs will be presented. In addition reports from NELAC, ELAB, ACS, and the interagency Methods and Data Comparability Board will be provided. This session will bring together the latest updates on who is doing what with PBMS and when it will happen.

Environmental Business in the PBMS Paradigm Session

Features sub-sessions on Contracting (including frameworks for contracting under PBMS, changes in Superfund contracting, and a model agreement) and Laboratory Management Issues (including managing labs under PBMS, laboratory performance expectations, consensus standards roles, and more).

PBMS Implementation Session

Features sub-sessions on Ensuring Scientific and Legal Defensibility (including an overview of EPA's approach, the Comparable Fuels Rule as a model, and perspectives on quality assurance, private laboratories, legal and enforcement issues) and Field and Laboratory Implementation Issues (including how to develop DQOs, developing project-specific MQOs, moving MQOs into commercial laboratories, and balancing error sources for project planning).

Laboratory Auditing and Accreditation under PBMS

Highlights new roles of auditing and accreditation, laboratory compliance programs, changes in state auditor's roles, documentation requirements, community issues, and expectations of government laboratories.

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HISTORICAL PERSPECTIVE OF PERFORMANCE-BASED MEASUREMENT SYSTEMS (PBMS) AT ROCKY MOUNTAIN ARSENAL (RMA)

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ABSTRACT

Compliance monitoring under a performance-based measurement systems (PBMS) is an on-going process at the Rocky Mountain Arsenal (RMA) in Commerce City, CO. RMA is a Superfund site where disposal of industrial and military chemical wastes in unlined basins over a period of approximately 10 years during and following World War II resulted in widespread contamination of soil and both surface and ground waters. The United States Army, along with Shell Oil Company and the U.S. Fish and Wildlife Service, are in the process of remediating RMA. The remediation effort involves the analysis of various matrices for a wide variety of analytes, some of which are unique to RMA, and standard analytical methodologies are either not available or are not adequate to fulfill regulatory requirements in certain instances. Hence the requirement to develop methods which are specific to the RMA and are performance-based.

In response to these site specific requirements and utilizing the Army Environmental Agency Guidelines, RMA developed the RMA Chemical Quality Assurance Plan (CQAP), which addresses all activities from planning to data verification related to the remediation of RMA. Compliance with the CQAP ensures that data produced are legally defensible, cost effective, and scientifically sound. A strict proficiency demonstration process for methods is prescribed by the CQAP to validate both standard and new or unproven methods.

Recently the Environmental Laboratory Advisory Board (ELAB) defined five critical elements for PBMS implementation. As recommended by ELAB, the data produced by laboratories should be legally defensible, cost effective, scientifically sound, demonstrate good performance criteria, and achieve regulatory compliance monitoring requirements. Historically, analogous criteria have been applied to the analytical work performed by laboratories supporting the RMA remediation effort. ELAB has also recommended essential elements for PBMS implementation. This presentation discusses the analytical program at RMA, under the Comprehensive Analytical Laboratory Services (CALS) contract (CALS contractor URS Greiner Woodward Clyde), in the context of these elements. Utilizing the performance criteria, regulatory development, and analytical methods specific to RMA, the remediation of RMA has progressed at an accelerated rate.

INTRODUCTION

RMA was established in 1942 during World War II. It is located ten miles northeast of downtown Denver and occupies 27 square miles. The U.S. Army manufactured military chemical weapons at the Arsenal until the 1960's. Also, during that time and through the early 1980's chemical weapons were destroyed. Following World War II, in an effort to increase economic growth in the area, offset costs, and maintain the facilities for national security, private industry leased the facilities at RMA. One of the manufacturers operating under the lease program was Julius Hyman and Company which produced pesticides. In 1952, Shell Chemical Company acquired Julius Hyman and Company and continued to produce pesticides until 1982. Most of RMA was placed on the National Priorities List (NPL) in 1987. As such, RMA is subject to compliance with CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act, also know as Superfund).

The Remediation Venture Office (RVO), formed in October 1996 to expedite the implementation of the remediation, is an innovative triparty arrangement consisting of personnel from the Army, Shell Chemical, and the Fish and Wildlife Service. Members of the RVO work together to coordinate and provide oversight of the remediation management based on best value concepts, including but not limited to, quality assurance (QA), health and safety, regulatory compliance, fiscal monitoring, and community involvement. Today there is no manufacturing, weapons production, or storage at RMA. As a Superfund site, RMA's only mission is environmental cleanup.

DISCUSSION

The production of the military chemical weapons, pesticides, insecticides, and herbicides generated many waste streams. These wastes were disposed of using widely accepted practices of the time. Efforts to contain liquid wastes began soon after the discovery that contaminated groundwater was causing damage to crops north of RMA in the mid1950s. The Army and Shell Chemical began a systematic investigation into the contamination problems at

RMA. Beginning in 1974, Interim Response Actions (IRA) were implemented to protect offsite human health and the environment from RMA pollution.

The United States Environmental Protection Agency (USEPA) has defined PBMS as "a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effect manner."[1] The unusual matrices and analytes routinely found at RMA pose unique problems for the regulators and the analytical laboratories. Analyses for analytes in matrices for which no standard method exists have been required. This has necessitated the modification of existing approved standard methods, thus the formation of a PBMS at RMA.

The RMA Chemical Quality Assurance Plan (CQAP) was developed from the Army Environmental Agency Guidelines and provides the written guidance for operating the RMA QA program. The purpose of the RMA CQAP is to provide for consistent generation of analytical data, establish standard practices which permit interlaboratory comparisons of data, establish procedures for demonstrating that analytical systems are in control, and ensure that the data produced by the laboratories is not only of highest quality, but scientifically and legally defensible.

The remediation efforts at RMA pose unique problems for project site evaluations as they are being defined. The unusual matrices, along with analytes of raw chemicals, by-products, and break-down products cause unique problems for project site specifications. The regulatory agencies, along with the RVO, meet and determine the goals for the remediation effort, the critical health care risks, the analytes of interest, and the reporting limits for those analytes.

The data quality objectives (DQO) are written detailing a clear objective of the project site evaluation, defining the most appropriate type of data to collect and the most appropriate conditions from which to collect data, and specifying acceptable levels of decision errors that will be used to establish the quantity and quality of data needed to support the decision.

The DQOs may include analytes or matrices that may or may not have specific methods available to produce the required analytical results. The laboratories, after reviewing the project site specified requirements select the appropriate method, or, if needed, modify an existing method to analyze the samples. The specifications within the CQAP allow the laboratories the flexibility to use their expertise to modify existing methods to achieve regulatory compliance.

Laboratory standard operating procedures (SOP) provide specific instructions for the performance-based method analysis. The SOPs include a summary of the performance-based method with information about the matrix, analytes, and a short description of the procedure. The application of the method is stated along with tested concentration range, instrument response, detection/reporting limits, interferences, and analysis rate. Other aspects that are covered in SOPs are safety considerations, apparatus and reagents. Detailed and specific procedures are stated for the preparation of standards including initial and daily calibration standards, instrument mass tuning criteria and performance, and the analysis of calibration data. Acceptance criteria for all standards along with corrective actions if criteria are not met are specified. A description of sample collection and storage conditions is given. Also stated is a detailed procedure of the analytical process, including acceptance criteria for sample analysis, calculations, and the preparation and analysis of quality control samples. The function of quality control charts and acceptance criteria for controlling the method is outlined. Finally, references are given on which the performance-based methods are based. The performance-based method SOPs prescribe strict quality control (QC) and analytical requirements, ensuring that data generated are legally defensible, scientifically sound, and meets good performance criteria based on historical laboratory performance.

A capacity/capabilities visit (CCV) is performed by the CALS contractor to determine whether the laboratory will be able to support RVO with the analyses that are needed. Personnel from URS Greiner Woodward Clyde will visit the laboratories to inspect the laboratory statement of qualifications, training files, facilities and equipment, data management systems, analytical capabilities, and SOPs. The program and contract requirements of RMA are discussed in detail during the visit. These requirements include performance audits, performance-based method proficiency demonstration for analytical methods, participation in the Analytical Laboratory Performance Evaluation System (ALPES), development of performance-based method SOPs, laboratory QA plan, laboratory QC plan, a data management plan, quality systems audits, and attendance at QA meetings as required .

Contract laboratories before performing analytical work, in support of the CALS contract, must demonstrate their competence in meeting RVO specific QA/QC requirements through a performance-based method proficiency

demonstration. The purpose of performance-based method proficiency demonstration is to: a) establish the lowest concentration at which a result may be reliably reported, b) define the working range of the analytical process, and c) provide initial performance-based quality control acceptance criteria which will be used to control the analytical process during sample analysis. Performance-based method proficiency demonstration provides evidence that a laboratory is able to meet RVO DQOs.

CALS provides to the contract laboratories a reference method (if available), target analyte lists, and the target reporting limits (TRLs). The TRLs are the reporting limits needed by RVO to support remediation goals. The TRL information is used by the laboratories during the performance-based method proficiency demonstration to determine the dynamic concentration range of the method. The performance-based method proficiency demonstration consists of three parts:

- Instrument calibration
- Preparation and analysis of proficiency samples
- Calculation of method reporting limits (MRL)

INSTRUMENT CALIBRATION

The performance-based method requires an initial calibration, prior to the analysis of samples. The initial calibration sequence includes, at a minimum, five calibration standards and a zero standard. The standards will bracket the working range of the measurement system. The acceptability of the initial calibration will be reviewed using appropriate QC criteria. Upon completion of an acceptable initial calibration, the laboratory proceeds with the analysis of the proficiency samples.

PREPARATION AND ANALYSIS OF PROFICIENCY SAMPLES

RMA standard matrix, which includes RMA standard soil, standard water (ASTM Type II water, plus 100 milligrams per liter of sulfate and chloride), or other matrices specific to RMA, must be used during the performance-based method proficiency demonstration. Spiking solutions are prepared that are independent of the calibration stock solutions. A minimum of five concentrations of the target analytes is prepared in the RMA standard matrix plus a preparation blank sample. The concentrations of the target analytes are evenly distributed throughout the dynamic concentration range. Two sets of performance-based method proficiency samples are prepared and analyzed according to the specified performance-based method SOP. The proficiency samples are prepared and analyzed on two separate days to introduce day-to-day laboratory variability.

CALCULATION OF MRLS

After the analysis of the performance-based method proficiency samples, the results of the analysis is evaluated for the determination of the MRLs. The found concentrations of the target analytes for each spiking concentration, including the blank sample, is entered into the MRL computer program. The MRL is extracted using confidence bands as described by Habaux and Vos using 2-tail 90% confidence bands. The software program: a) plots the found versus target concentration data, b) determines the confidence band about the resultant linear regression curve, and c) calculates the MRL.

MRLs are the lowest reportable target analyte concentration in a sample using a specific analytical method. Reporting MRL concentrations as performance-based method target concentrations considers both the measurement precision and the method accuracy. Analyte concentrations in field samples are corrected for method recovery efficiencies determined during the performance-based method proficiency demonstration.

Upon completion of the performance-based method proficiency demonstration, the laboratories will submit the data to RVO for review. Method proficiency data includes the calibration data, sample preparation, sample analysis, MRL calculations, and certificates of analysis for all reference materials assuring the purity and identification of all analytes.

Upon method approval, the RVO will provide the laboratory with the a unique method number to be used when reporting data. The pre-award performance evaluation (PE) sample is shipped to the laboratory ensuring method performance criteria are met. The laboratory will analyze the pre-award PE sample and submit the data to RVO as a RVO-required data package. The data package is reviewed and comments submitted to the laboratory. Corrective action, if necessary, is implemented by the laboratory before the laboratory is awarded a contract by the CALS contractor to perform work for RMA. If necessary, a second pre-award PE sample may be submitted to the laboratory to demonstrate that the corrective actions have been implemented. If the laboratory fails two pre-award PE samples a contract will not be awarded.

While performing analysis of samples, the laboratories analyze QC checks. These include, at a minimum method blanks, laboratory control samples (LCSs), matrix spikes, surrogates, and duplicates (when applicable). The results obtained from the QC samples must be evaluated against acceptance criteria per the laboratory performance-based method SOP and historical laboratory QC performance. The results of the QC checks are included in the electronic data file which is sent to PMRMA with the results of the field sample analysis.

A requirement of each laboratory is to control chart the LCS to demonstrate that the laboratory's process for sample preparation and analysis is in control. The LCS matrix should be comparable to the sample matrix. RVO identifies specific controlling analytes (RMA target analytes) contained in the LCS solution that are control charted for each method. The recoveries of the analytes should be in a state of statistical control. The control charts are used to monitor the variation of the analytical method and provide a mechanism for the laboratories to detect out-of-control situations and to improve the analytical method. When an out-of-control situation is observed the laboratories must investigate the method, determine a cause, and implement corrective action.

The laboratories generating data for RVO prepare data packages that are stand-alone compilations of all data related to the analysis of a single analytical lot. An analytical lot is defined as the number of samples, including QC, that can be processed through the rate limiting step of an analytical method. The data packages contain all information necessary to verify the reported results and to completely document the quality control procedures utilized during the analysis. Any deviations from the performance-based method SOP must be clearly noted in the data package. This ensures that the data generated are accurate, defensible, and meets the project site-specific DQOs.

Information contained in the data packages includes:

- reported sample results and associated MRLs;
- reported QC sample results;
- case narrative that explains deviations during the preparation and analysis of the samples, corrective actions, manual integrations, and other observations identified and noted during the preparation or analysis of the samples;
- standards preparation, including certificates of analyses of the standards;
- sample preparation and extraction;
- initial and continuing calibration information;
- copies of the chain-of -custodies; and
- quantitation reports and chromatograms of the calibration and sample analysis.

As part of the CALS contract, laboratories submit monthly quality assurance status reports (QASR). These reports include: QA/QC changes, method changes, personnel changes, facility changes, data quality indicators (including accuracy, precision, and completeness), revisions of MRLs, and non-conformance occurrences. Each of these areas discuss, acceptance criteria, out-of-control situations, or modifications performed that relate to RMA samples. The QASRs are reviewed by the CALS contractor. During the review the CALS contractor, determines if any out-of-control situations have occurred and if the laboratories have addressed the situations. What caused the situation and the types of corrective actions taken by the laboratories should be noted in the QASRs by the laboratories. The CALS contractor may request additional information concerning the laboratories' corrective actions to more fully understand and evaluate the situation. If the severity of the situation is warranted. The CALS contractor may conduct an unannounced audit or may issue a stop work order until all out-of-control issues have been adequately addressed. This is an on-going performance-based assessment of the laboratories method proficiency, accuracy, and data deliverables.

Audits are an essential part of the PBMS at RMA. The two types of audits performed by the CALS contractor are quality systems audits and performance audits. Quality systems audits are audits of the operational functions of the contract laboratories including the QA program. The performance audits monitor the laboratories' ability to produce accurate analytical measurements of the specific RMA analytes through analysis of PE samples.

Quality systems audits provide RVO a performance-based assessment of the contact laboratories. Quality system audits are either external or internal (self-assessment). The external quality systems audits, through on-site visits, verify that the laboratories are complying with the CQAP's QA/QC requirements and determine if the QA/QC procedures were implemented effectively and suitably to achieve technically sound and defensible analytical data. During the life of the laboratories' contract with the CALS contractor, a minimum of one quality systems audit is conducted every six months. Additional quality system audits may be performed if there are QA/QC concerns, large sample

volumes, PE sample results, changes in laboratory management and/or QA program, and/or results of previous quality systems audits.

During the quality systems audit the CALS audit team will review QA plans and performance-based method SOPs and verify that previous audit findings have been implemented. Specific data packages, both routine and PE samples, will be inspected to verify reported results and verify conformance with QA and program requirements. Interviews will be conducted, if necessary, to clarify concerns, substantiate auditor concerns, or verify the implementation of corrective actions. A walk-through of the laboratory is performed to evaluate the various areas of the laboratory. This may include sample receipt, organic preparation and analysis, inorganic preparation and analysis, data management and review, quality assurance, and training.

A quality systems audit report is prepared by the CALS audit team and submitted to the laboratory detailing the findings and observations of the audit. The laboratory addresses the findings and observations presented in the audit report and submits the response to the CALS contractor. RVO reviews the response and determines whether the laboratory has addressed and implemented corrective actions appropriately.

Internal quality systems audits will be performed by the contract laboratories annually, at a minimum. These audits are conducted by the QA department in order to assess the PBMS used by the laboratories. Any deficiencies observed during the internal audits are documented and corrective actions implemented. Documentation of the quality systems internal audits is retained by the laboratories and is reviewed by the CALS audit team during the external quality systems audit. The corrective actions of the internal quality systems audit must have been satisfactorily implemented or the associated deficiencies will become findings during the external quality systems audit.

ALPES, as an independent QA oversight, administers the performance audits for RVO performance-based methods. These performance audits are conducted semiannually or whenever problems occur. The PE samples may be prepared for special projects or in batches for distribution to multiple laboratories. The batch is submitted in the form of samples ready for analysis. Double-blind PE samples may also be submitted to the laboratories to further monitor the PBMS of the laboratories.

RMA analytes of interest are added to the required matrix to achieve the desired concentration. Matrices used are RMA standard water, soil, quartz filters or passivated summa canisters, or other special matrices such as concrete, waste material, or biota. The laboratories are notified of single-blind PE sample shipment and the expected arrival date. Double-blind PE samples are included in the shipments of field samples. The PE samples are analyzed in accordance with the laboratories' approved performance-based method SOP. A RVO stand-alone data package is generated and submitted for review. The data are reviewed for accuracy and completeness.

Contract laboratories may participate in performance audits conducted and evaluated by outside organizations such as the National Institute of Occupational Safety and Health (NIOSH) Proficiency Testing Program or by state certifications. The laboratories submit to the CALS contractor copies of the PE sample results, the acceptance criteria, and any corrective action taken to address deficiencies. RVO may, after reviewing the corrective actions, perform a quality systems audit.

SUMMARY

Compliance monitoring under the PBMS is an integral part of the analytical program at RMA. The PBMS's flexibility supports RVO's analytical program with methodologies that are scientifically sound, legally defensible, demonstrate good performance criteria and meet regulatory compliance monitoring requirements.

The remediation effort will transform the former military chemical weapons and pesticides manufacturing facility into one of the largest urban wildlife refuges in the country.

FOOTNOTES

1. Federal Register, Vol. 62, No. 193, October 6, 1997, Page 52098

ACKNOWLEDGMENTS

The Comprehensive Analytical Laboratory Services support team at the Rocky Mountain Arsenal comprised of the RVO Support Team, URS Greiner Woodward Clyde, Lockheed Martin, Oak Ridge National Laboratory, and Roybal Corporation. Northglenn and Westminister, CO Public Works and Utilities Departments.

REFERENCES

1. Comprehensive Analytical Laboratory Services, Laboratory Quality Control Plan, April 1999.
2. Comprehensive Analytical Laboratory Services, Quality Assurance Management Plan, April 1999.
3. Environmental Analytical Laboratory, Procurement of an Off-Post Analytical Laboratory in Support of CALS, SOP 107, Rocky Mountain Arsenal, June 1997.
4. Federal Register, Vol. 62, No. 193, October 6, 1997, Page 52098
5. Hubaux, A. and Vos, G., "Decision and Detection Limits for Linear Calibration Curves," Analytical Chemistry, 42 (1970), p. 849.
6. Oak Ridge National Laboratory Analytical Support Group, Office of the Program Manager for Rocky Mountain Arsenal Analytical Laboratory Performance Evaluation System, SOP ALPES-99-LSD-002, February 1999.
7. Program Manager Rocky Mountain Arsenal, Chemical Quality Assurance Plan, April 1996.
8. RVO Analytical Systems Manager, Standard Operating Procedure for Performing ASM Laboratory Audits, SOP 2010, Rocky Mountain Arsenal, Draft 1999.

MAINTAINING CONTROL AT A RAPID RESPONSE FIELD ANALYTICAL SUPPORT PROJECT - A CASE STUDY OF PERFORMANCE-BASED MEASUREMENT SYSTEMS

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ABSTRACT

The Lockheed Martin Field Analytical Support Project (FASP) Team routinely uses performance-based analytical methods to provide rapid results at environmental field sites using mobile laboratories. This work is performed under the Environmental Services Assistance Team (ESAT) contract to the U.S. Environmental Protection Agency (EPA) Region 10. This paper describes a case study for the development, validation, and application of a performance-based analytical field method. An EPA Region 10 removal action project required quick turnaround data to determine the extent of contamination and confirm removal action. Drinking-water wells in an agricultural area were contaminated with high concentrations of the herbicide dinoseb. The source of the dinoseb was adjacent to an agricultural irrigation canal, prompting quick action to avoid additional groundwater contamination. A performance based analytical procedure for the herbicide dinoseb in soil was developed using gas chromatography with electron capture detection. Available EPA methods for dinoseb did not meet the data quality objectives for the project, or were not practical for use in a mobile laboratory. The primary objective was to provide reliable analytical data for two action levels of dinoseb in soil (1.6 µg/Kg and 80 µg/Kg). The FASP team developed a procedure two weeks prior to field deployment. The method used a small quantity of extraction solvent with direct injection of the extract into a gas chromatograph with an electron capture detector. The method was validated prior to field deployment, and quality assurance protocols were developed to assure project data quality objectives were met. Field chemists analyzed a total of 820 soil samples at the field site. Quality control included analyzing extraction blanks, extraction spikes, and matrix spikes. In addition, investigators shipped 10% of the samples to a fixed laboratory for comparison analysis. The results of the quality control show the field method produced reliable data. Overall, performance-based analytical methods for field screening allow for quicker, more cost effective site investigations and remedial actions. This paper provides guidelines for establishing quality control procedures to assure generation of data within project data quality objectives.

INTRODUCTION

On October 19, 1998, the FASP Team was tasked by the EPA to determine the feasibility of providing on-site support for the analysis of the herbicide dinoseb (2-sec-butyl-4,6-dinitrophenol) in soil. The project was to support an emergency removal project starting on November 2, 1998 in central Washington. The Region 10 FASP Team's approach to field analysis is to use laboratory-grade instruments in a well-equipped mobile laboratory to provide data of documented quality. If possible, the FASP Team follows standard operating procedures (SOPs) developed for compounds most likely to be encountered in Region 10. These SOPs contain generalized quality assurance procedures, which may be modified depending upon site-specific data quality requirements. However, no field SOP existed for dinoseb. A performance-based method for dinoseb was quickly developed, with site-specific quality control procedures

incorporated into an SOP before field deployment. This paper describes the analytical method developed, the method validation procedures, quality control procedures, problems encountered, and corrective actions employed during the project.

METHOD DEVELOPMENT

The first step in preparing the analytical protocol was to obtain the data quality objectives for the removal project. The objectives were well defined. Two action levels were defined for dinoseb. All soil having dinoseb concentrations above 1.6 mg/Kg had to be removed. To track potential "hot spots," the investigators wanted detection limits at least ten times lower than the action level, or at 0.16 mg/Kg. The other action level was at 80 mg/Kg. Soil above this limit had to be segregated from lower level contaminated soil for efficient remediation. A quick analytical data turnaround was an important objective, with an analytical capacity of at least 30 samples per day. Although false positive results were not desired, a higher priority was assuring a minimum of false negative results.

Present EPA methods did not meet the data quality objectives of the project, or were not practical for field laboratory use. Dinoseb is listed as an analyte for EPA methods 8041 and 8151. Method 8041 is a gas chromatographic method using a flame ionization detector for soil extracts. However, flame ionization would not meet the detection levels required for the project. Method 8151 uses a derivatization procedure followed by electron capture gas chromatography. Although this procedure produces low detection limits, the derivatization method is not practical for field laboratory use. In addition, fixed-laboratory extraction procedures were not practical for a mobile laboratory. A method was developed to determine dinoseb by analyzing soil extracts without derivatization using electron capture gas chromatography. The extraction procedure selected was the same as used previously for FASP soil extractions using methyl-tert-butyl ether as an extraction solvent. The extraction method had been validated for pentachlorophenol but not for dinoseb, so further validation studies were required for this project.

The gas chromatograph was a Hewlett Packard Model 5890 Series II equipped with an electron capture detector. The column was a 30-meter J&W™ DB5-MS with a 0.53 mm ID and a 1.5 micron film. Helium was used for the carrier gas at a constant flow of 7.0 milliliters per minute. The initial oven temperature was 100ºC for three minutes, ramped at 12ºC per minute to 300ºC, then held for 5.0 minutes. The injector temperature was 200ºC and two microliter injections were made in the splitless mode. The detector temperature was 340ºC with 5% methane/argon used as the make-up gas. Soil was extracted in disposable glass culture tubes with PTFE-lined screw caps. Five grams of soil were extracted twice with five milliliters of methyl tert-butyl ether. Before adding the solvent, the soil was spiked with a surrogate compound, and acidified with phosphoric acid. The extraction was performed using a multi-tube vortexer followed by centrifuging to separate the phases.

METHOD VALIDATION

The FASP team follows a set of guidelines for method validation before field deployment, although the specific validation steps depend upon project goals and historical method performance. As a minimum, method validation includes verifying instrument response and linearity over the concentration range of interest for the target compounds. In addition, method extraction blanks must show no interfering compounds and spiked matrix extracts must demonstrate good recovery of target compounds.

Since the method developed for dinoseb was a new procedure, additional quality assurance validation was performed. The precision of the method near the detection limit was found by analyzing a series of spiked soils. These results were compared with a precision study using the EPA method 8151 laboratory procedure. Although a thorough check for possible interfering compounds could not be done because of time limitations, several chlorinated pesticides and herbicides were found not to interfere. The definitive validation procedure was analyzing samples collected from the site using the developed method. These samples were also analyzed by a commercial laboratory. The results of the split samples had to agree before the mobile laboratory deployment.

FIELD QUALITY CONTROL

Quality control protocols used in the field laboratory are generally the same as those used in fixed laboratories, with the difference that criteria used in the field are not as strict as those used in fixed laboratories. This greater flexibility allows sample analyses to continue thus avoiding project slowdowns without adversely affecting data quality objectives.

The initial instrument calibration was performed with a minimum of five calibration levels. The calibration was successful if concentrations were found within $\pm$ 25% of the expected value and with a regression correlation coefficient (r^2) greater than 0.995. A calibration verification standard was analyzed once every 12 hours at a level near the

lower action value for dinoseb. The acceptance criterion was the result being within ± 35% of expected value, or a new calibration curve was prepared. Retention time windows for dinoseb standards and spikes were established to be within ± 0.4% of the initial calibration retention time. Matrix spike and matrix spike duplicates were analyzed once per 20 samples. The acceptance criterion was recovery between 50% and 150% and the relative percent difference (RPD) less than or equal to 30%. Surrogate spike control limits were set at a recovery between 50% and 150%. Reagent extraction blanks and spikes were analyzed once per day.

In addition, a minimum of 10% of the samples analyzed on site were shipped to a commercial laboratory for confirmation analysis by EPA Method 8151. Duplicate field samples were submitted blindly to the field laboratory. Quality assurance included a peer review of all documentation, chromatograms, and results before reporting to the site investigator.

RESULTS AND DISCUSSION

Method validation experiments before field deployment displayed to site investigators that the performance-based method would meet the data quality objectives of the project. A method detection limit and precision study was performed by spiking a soil sample with dinoseb at a level near the desired lower detection limit. A series of seven replicate soil samples spiked at 0.2 mg/Kg was analyzed. The results showed a mean concentration of 0.24 mg/Kg with a standard deviation of 0.018 mg/Kg, or a percent relative standard deviation of 7.3%. The minimum detection limit was set at 0.10 mg/Kg, which was below the objective of 0.16 mg/Kg. The field method was compared with EPA method 8151 by extracting a series of seven soil samples spiked at 0.2 mg/Kg, then methylating the extract as specified in the EPA method. Although the methylated dinoseb has a greater response with sharper peaks, the precision was poorer using Method 8151 (a resulting mean concentration of 0.195 mg/Kg with a standard deviation of 0.97 mg/Kg). The primary method validation was the comparison of 40 samples from the site analyzed by the field method compared to split samples sent to a commercial laboratory for quick-turnaround analysis by Method 8151. Of the 40 samples, 33 samples showed non-detects for dinoseb in each methods. The seven samples with dinoseb showed good comparison, with an average percent difference of nine percent between the two methods.

The only problem encountered during the method validation was poor recovery of the surrogate compound. The surrogate selected for the method was 2,4,6-tribromophenol. This surrogate had successfully been used in previous projects as a surrogate for pentachlorophenol analyses. However, for the analysis of the 40 soil samples from the site, nearly all recoveries were less than 50%. It was felt that the problem was due to a matrix effect specific to the surrogate but not the dinoseb. The dinoseb recoveries from spiked site samples were good, and the confirmation results for the dinoseb agreed with dinoseb results from the field method. Another compound (2,4,5,6-tetrachloro-m-xylene) was selected as the surrogate, with this surrogate showing good recoveries from the on-site samples.

After validation results verified the performance-based method would meet the project objectives, the mobile laboratory was immediately moved to the site location, where 820 samples were analyzed over a six-week period. Nearly all of the quality control samples were within the acceptance criteria established for the project; however, one problem developed during the project. Four days into sample analyses, two batches of samples had many surrogate recoveries below the target value of 50%, 24 of the 62 samples. The problem was believed to be due to a high concentration of carbonates in the soil matrix. The extraction procedure called for adding acid to the soil prior to extraction, to assure the dinoseb analyte (a weak acid) was extracted with the organic solvent. Upon adding acid to some of the soil samples, a vigorous reaction was observed, producing excessive foaming suggesting a high concentration of lime in the matrix. The first step of corrective action was to discuss the problem with the project managers. The decision was made to continue with the sampling and analyses, with low surrogate results flagged to assist with selection of samples for confirmation analyses. The other corrective action was to modify the method, using a weaker buffering solution. The modified method was tested by analyzing six samples containing high carbonate levels in duplicate, one set analyzed with the original buffer and the second set analyzed with the weaker buffer. All six samples showed good surrogate recoveries using the modified procedure. The new buffer solution was incorporated into the procedure, with acceptable surrogate recoveries found afterwards.

CONCLUSION

Performance-based analytical methods are practical and useful means to analyze environmental samples in the field. Analytical methods can be optimized for the analytes of interest with quality control protocols specific for project data quality objectives. For this project, quality control included continuing calibration levels and matrix spike levels near the removal action defined for the cleanup, providing on-site investigators estimates of analytical precision and accuracy. Verification of performance-based method results with laboratory-based methods is an important

component of quality assurance. Typically, 10 percent of the field samples are shipped to an off-site laboratory for analysis. Confirmation results not only verify the results of the field project, but can be used to direct method improvement.

SUGGESTIONS FOR REDUCTION OF ANALYTICAL COSTS BY ELIMINATION OF UNNECESSARY QUALITY CONTROL (QC) SAMPLES

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ABSTRACT
A rationale is presented for collecting fewer QC samples for hazardous-waste projects and to encourage project managers and quality assurance project officers to question the need for every QC sample or activity. Many field QC samples can be eliminated from hazardous waste site investigations, resulting in significant analytical cost savings, without any effect on the quality of the overall investigation. The categories of QC samples or analyses which could be reduced include second column confirmations, field blanks, matrix spike and matrix spike duplicates, and duplicate samples. Additional cost reductions could be realized through careful selection of analytical methods and the use of on-site methods, where feasible.

INTRODUCTION
Many field QC samples can be eliminated from hazardous waste site investigations with no effect on the quality of the overall investigation. The QA/QC requirements for environmental investigations were derived under CERCLA and RCRA with the purpose of generating legally defensible results. "The EPA Contract Laboratory Program (CLP) is intended to provide analytical services for Superfund waste site samples. As discussed in the User's Guide to the Contract Laboratory Program (EPA 1988), the program was developed to fill the need for legally defensible results supported by a high level of quality assurance (i.e., data of known quality) and documentation."[1] All analyses performed for CERCLA (Superfund) investigations were initially required to be conducted at DQO Level IV (CLP). The initial (discovery) stage of a site investigation should be conducted at Level III or IV. Once the origin and responsibilities are established for a site, the purpose of QA/QC should be adjusted to new DQOs. Determining the extent of contamination, conducting RI/FS, and monitoring remediations may be successfully accomplished with field screening methods, on-site Level II analyses, and fixed laboratory Level II, with some samples (generally 10%) confirmed at Level III or Level IV.

Significant analytical cost reductions could be realized by eliminating unnecessary second column confirmations, field blanks, matrix spike and matrix spike duplicates, and duplicate samples. Second column confirmations, field blanks, matrix spikes/spike duplicates, and field duplicates can, in most cases, be reduced or eliminated. This should result in a reduction in the number of QC samples, a better understanding of the effect of QC on the data, and reduced costs in time and money for the work.

QUALITY CONTROL SAMPLES AND PROCEDURES
SECOND-COLUMN CONFIRMATIONS
Second column confirmations apply to organic analyses using GC methods, such as SW846 methods SW8010, SW8020, SW8021, SW8080, SW8081 and SW8280. A second column confirmation often is billed by the laboratory as a separate sample analysis. Method 8000A of SW846 states in Paragraph 7.6.9.1 "Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses."[2] Methods SW8010B, SW8011, SW8015A, SW8020B, SW8021A, and SW8030A, include the statement "if analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended."

Many projects have specified that all positive results for GC methods will be confirmed by second column confirmation only because the SW846 method provides for it. Many more projects have suffered from inflated analytical costs because second column confirmations were not discussed in the work plan or the QAPP and the laboratory performed these analyses because they were called for by the SW846 method. The large number of confirmations resulting from this protocol is excessive and often results in an unnecessary inflation of the analytical cost. If good historical data exists, the only analytes requiring confirmation are compounds not previously detected and confirmed. For example, if benzene was detected and confirmed by method SW8240 (a GC/MS method) or by method SW8020 with second column confirmation during Superfund investigations, a positive result for benzene in the RI/FS investigation does not need to be confirmed. Positive results less than Quantitation Limits, MCLs, ARARs, or cleanup levels should not be confirmed. Sampling efforts involving numerous samples at each site, e.g. grid sampling, should include only enough confirmations to confirm the identity of each analyte found at the site.

BLANKS

The field blanks collected at a site could include trip blanks, ambient blanks, bottle blanks, source water blanks, and equipment rinseate blanks. The reason for analyzing different types of blanks is to be able to trace the origin of contamination in order to take corrective action. This requires that the results be available as field work is being conducted. Generally, blank results are not available before the sample results are reported, which can be many weeks after the field effort is completed. A multiplicity of blanks may be justified, but the project manager should develop good reasons for them. Long-term programs involving numerous separate projects could benefit from different types of blanks, since corrective action can be taken between projects. If on-site analytical equipment is available, analysis of blanks on-site would allow corrective action to be taken rapidly and these are generally much less expensive than fixed-base laboratory analyses. On-site analysis of blanks must be conducted with methods which are analyte-specific, have quantitation limits lower than the action levels, and documented calibrations and detection limits. Many of the blanks submitted to laboratories for analysis are probably not necessary.

In many cases, two or more blanks could be combined; e.g., an equipment rinseate blank taken to the sampling site serves as an ambient blank and a bottle blank, and if this blank is shipped in a cooler with VOA analyses, it also serves as a trip blank. Another approach might be to collect a full set of field blanks and analyze only the most comprehensive (the equipment rinsate). As stated by Dr. Keith[3], "Sample analysis is often expensive. Sometimes it is prudent to collect a full suite of blanks but only analyze the field blanks. If the field blanks indicate no problems, the other blanks may be discarded or stored as necessary. If a problem is discovered, the individual blanks can be analyzed to determine its source. Resampling will still likely be necessary."

Data validation guidelines state that if a compound is found in any blank, positive sample results greater than the quantitation limit and less than five times the blank concentration are qualified as not detected (U or ND) at a quantitation limit (QL) equal to the sample result. If this adjusted QL is above the action level, it cannot be used to demonstrate a concentration below the action level. There is no difference between a positive sample result greater than an action level and a blank qualified result with a quantitation limit greater than the action level when the purpose is to demonstrate a concentration below the action level. Thus, if the purpose of sampling is to demonstrate that ARARs, MCLs, or cleanup levels have been met, or for monitoring remediation efforts, there may be no reason to take any field blanks. Since the resulting corrective action (i.e., resampling) based on a sample result above the action level is the same with or without blanks, the blanks are not necessary.

MATRIX SPIKE/MATRIX SPIKE DUPLICATES

It has been estimated that up to 90 percent of all environmental measurement variability can be attributed to the sampling process.[6] The matrix spiking protocol assumes that one sample out of a batch of twenty is adequate to assess the effect of the matrix on accuracy and precision. Much of the variability of the sampling process is due to the variability of environmental media and the contaminants within that media; likewise, the matrix effect is as variable as each medium and its contaminants. To be effective in defining method accuracy and precision, matrix spiking would have to be done for all samples.

Since data validation based on MS/MSD results is applied only to the sample spiked, the QA/QC value of MS/MSD samples is much lower than the value of surrogate recoveries and of laboratory control sample/laboratory control sample duplicate results (LCS/LCSD). Surrogates are added to every sample analyzed for organics and are the best measure of accuracy and matrix effects for an individual sample. LCS/LCSD results for each batch and the laboratory control charts are the best measure of laboratory accuracy and precision for organic analyses. The LCS/LCSD program is also the best measure of accuracy and precision for metals analyses. Laboratories do not charge for surrogates or LCS samples. The digestion procedure for metals virtually destroys the matrix so that the

only interferences normally encountered in ICP and atomic absorption methods are from high concentrations of other metals. Elimination of MS/MSD samples could reduce analytical costs by 10%. For a project with analytical costs of $50,000, this represents a savings of $5,000.

FIELD DUPLICATES

The two types of Field Duplicates are split samples and co-located samples. A split sample is a sample which has been thoroughly blended and split between two containers. Often, the split samples are sent to different laboratories. Split samples are intended to measure the precision of the whole sampling and analysis procedure. Most often, if they contain anything to measure, split samples are a measure of how thoroughly the sample was blended before being split. There is no way to determine an effect on the rest of the samples at the site. Co-located samples are samples taken in the same location but not blended. The intent of co-located samples is to measure sampling precision or the variability of the matrix.

> "When designing experiments or procedures, it is important to keep in mind that the overall objective is accuracy. It naturally follows that those in charge of a project should ask whether additional measurements really contribute to the accuracy of a method, or simply to its precision.
>
> In today's business world cost is very important, and each extra measurement adds to the cost of a project. We all know that precision is important, but we need to take a closer look at the costs and benefits to the customer when expenses are increased for the sake of improving precision without necessarily increasing accuracy."[7]

Often, the stated purpose of field duplicates is to measure the precision of the complete process from sampling through analysis. This is nice-sounding phraseology in a work plan, but what can you do with the results? Due to the potentially large variability inherent in the media being sampled particularly for soils and sediments, one sample location out of twenty probably will not represent the sampling or matrix variability. The result is that these measurements are often reported as measures of "precision", but they have no effect on the flagging or the use of the data. As stated above, the source of the greatest variation in environmental analytical results is the variability of the media. Comparable results (<40% RPD) are seldom achieved from co-located duplicate soil samples, even with the best efforts of the best sampling technicians available. A statistical evaluation of all sample results at a site should be used to measure the precision and representativeness of the sampling program. These statistical measures may provide confidence intervals for establishing extent of contamination in a medium.

SUMMARY

Since the purpose of this paper is to encourage the use of performance-based criteria to the selection of QC samples, the recommended guidelines listed in this section should not be used as a prescriptive set of guidelines. Any and all QC which contributes to the quality of the data or are required for other reasons should be included regardless of arguments presented in this paper. For each QC sample or analysis proposed, Project Managers (PMs) and Quality Assurance Project Officers (QAPOs) should ask what that determination contributes to the quality of the data and whether it helps meet the project DQOs. If a QC sample contributes nothing toward the DQOs, an argument should be made against incurring the cost for that sample.

RECOMMENDATIONS

The following are recommended guidelines and uses for QA/QC samples:

Second-Column Confirmations

1. If historical data exist, the laboratory should be directed to conduct second-column confirmations only for compounds not previously detected. When second-column confirmations are deemed necessary, the laboratory should confer with the PM or the QAPO.

2. Positive results less than Quantitation Limits, MCLs, ARARs, or cleanup levels should not be confirmed.

3 . Sampling efforts involving numerous samples at each site, e.g. grid sampling, should have a limited number of confirmations.

Blanks

1. For sampling efforts undertaken to demonstrate that ARARs, MCLs, or cleanup levels have been met, eliminate all field blanks.
2. For projects which require blanks, use the following criteria for determining the frequency and type of blanks to take:

1. Ambient blanks - Collect only in the event that the field team observes nearby activities that could contaminate VOC samples.

2. Equipment blanks - Collect rinseates on bailers used to collect groundwater samples. Collect equipment rinseates for each decontamination event. Do not collect rinseate blanks for soil or sediment samples.

3. Combine blanks (Equipment Rinseate, Ambient, and Trip Blanks) wherever possible. When equipment rinseate or ambient blanks are taken, eliminate trip blanks and ship all sample VOCs in the same cooler as the blank.

4. If sampling of multiple types of blanks cannot be avoided, analyze only the equipment rinseate. If a problem is found, then analyze the remainder of the blanks.

5. If corrective actions are possible, submit source blanks as needed to implement those corrective actions. During long-term programs, submit source water blanks from water purification systems either to a fixed base laboratory or to an on-site chemist to maintain quality control of that system.

Matrix Spike/Matrix Spike Duplicates

1. Use surrogate recoveries to measure matrix effects for organic analyses.

2. Use Laboratory Control Spikes/Duplicates (LCS/LCSD) rather than MS/MSDs for determining precision and accuracy.

3. Use control charts for warning and control limits on precision and accuracy.

4. Avoid MS/MSD for metal analyses; metal analyses do not generally require a measure of matrix effects since the digestion and analytical methods destroy the matrix.

Field Duplicates

1. Collect and analyze field duplicates for Level IV (CLP) projects only. Eliminate or greatly reduce the requirements for field duplicates for Levels I, II, and III projects, unless it is necessary to establish statistical measures of uncertainty in the definition of extent of contamination.

LIST OF REFERENCES

1. EPA, *Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual (PartA),* p. 5-5, EPA/540/1-89/002, December 1989.
2. EPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update 1,* November 1990.
3. Keith, Lawrence H., Ph.D., *Environmental Sampling and Analysis, A Practical Guide,* Lewis Publishers, Inc., 1992.
4. Taylor, John K., Ph.D., *Quality Assurance of Chemical Measurements,* Lewis Publishers, Inc., 1990.
5. USEPA Contract Laboratory Program, *National Functional Guidelines for Organic Data Review,* June, 1991.
6. Homsher, M.T.; Haeberer, Fred; Marsden, Paul J.; Mitchum, R.K.; Neptune, Dean; and Warren, John, *Performance Based Criteria, A Panel Discussion,* Environmental Lab, October/November 1991.
7. Phifer, Lyle H., *Accuracy Versus Precision,* Environmental Testing & Analysis, March/April 1995.
8. EPA, *Data Quality Objectives Process for Superfund, Interim Final Guidance,* p. 42, EPA540-R-93-071, September 1993.

ASSESSMENT OF THE PERFORMANCE OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN WASTE DRUM HEADSPACE

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ABSTRACT

Since the 1970's, the Department of Energy (DOE) has retrievably stored transuranic (TRU) radioactive wastes in drums. Most of these drums are destined for final disposition in the Waste Isolation Pilot Plant (WIPP) in New Mexico. Prior to transportation to and acceptance into the WIPP, each drum must meet a set of criteria, one of which is to demonstrate that a set of volatile organic compounds (VOCs) do not exceed a specified concentration in the headspace of the waste drum. Because of the large number of drums that must be sampled and the high cost in time and money associated with sampling each drum and sending the sample to a laboratory for analysis, a Fourier transform infrared spectroscopic (FTIRS) method was developed to provide near-real-time analysis of waste drums as they are being processed through various facilities. Specifically, the method quantitatively determines 29 target VOCs, methane, and 12 other interfering inorganic and organic compounds that have been found real TRU waste drum headspace. These 42 analytes are quantitatively determined from each sample spectrum using the method of partial least squares (PLS). A single calibration for each analyte of interest was performed using a set of 190 spectra and these calibrations transferred to each of the deployed instruments. The implementations of the FTIRS method have been in accordance with the WIPP Quality Assurance Program Plan (QAPP), including participation in the Performance Demonstration Program (PDP).

Overall, the method has been demonstrated to perform adequately via the PDP, control samples, method performance samples and direct comparison to gas chromatography-mass spectrometry (GC/MS) analyses of duplicate samples. Precision and accuracy are within the respective ±25% and ±30% precision and accuracy requirements of the QAPP. The long term precision is ±5%. The FTIRS method consistently achieves an overall score of 90±5% and a score of 97±3% for a set of 8 critical target compounds in the PDP. Both of these scores are sufficient to pass the PDP. The major errors encountered are primarily associated with analytes at low concentrations in the presence of other analytes or interferences at high concentrations.

INTRODUCTION

For nearly 30 years, the DOE has been retrievably storing TRU wastes in metal drums at its various facilities. These drums are destined for final disposal at the WIPP in New Mexico. Before these drums may be sent to the WIPP it must be determined that they comply with certain transportation requirements and the WIPP Waste Acceptance Criteria (WAC). The headspace of each drum must be sampled and analyzed for a number of volatile organic compounds (VOCs) and hydrogen to determine if the drum meets the WAC or these compounds. Normally, this involves manual sampling the drum headspace with a SUMMA canister, transport of the canister to a laboratory and subsequent analysis by gas chromatography/mass spectrometry. Due to the large number of drums that must be sampled, a more cost effective and timely sampling and analysis alternative was needed that could be used alone or readily interfaced with existing field equipment for drum venting and headspace sampling.

To meet the need for a rapid and cost effective method for at-line waste drum headspace analysis of VOCs, a method employing Fourier transform infrared spectroscopy (FTIRS) was developed at the Idaho National Engineering Laboratory (INEEL)[1]. Since that time, an FTIRS based VOC analysis system has been incorporated into the Drum Vent Facility (DVF) at INEEL's Radioactive Waste Management Complex (RWMC) and a similar mobile gas analysis system (MGAS) was fabricated which has been deployed to several field locations.

Fourier transform infrared spectroscopy was selected as a reasonable alternative to at-line GC/MS instrumentation for several reasons. Very rugged FTIRS instrumentation is commercially available and has been used for several on-line applications[2,3]. Analysis times with FTIRS are generally in the range of seconds to minutes while GC/MS analysis times are typically 10's of minutes. Most VOCs and many other compounds can be analyzed by FTIRS. Furthermore, like GC/MS, the FTIR spectrum of a sample contains a historical record of the composition of the sample. As methods improve, or as new analytes or interferences are identified, the FTIR spectra of all the previous samples can be reanalyzed. The very nature of absorption spectroscopy makes this possible. It also makes the instrument calibrations/standardizations universal within certain limits, i.e. once a calibration/ standardization is

established it is possible to transfer that calibration to another instrument[4].

EXPERIMENTAL

Instrumentation. The wall-mounted FTIRS system at the RWMC was supplied by Bomem, Inc. (Québec, Québec Canada) according to the specification supplied by the INEEL. This is a "turn-key" FTIR system that is located in the DVF in a potential contamination area near the containment silo where waste drums are vented. To minimize the possibility of damage to the instrument and the possibility of radioactive contamination of the hardware, the instrument is housed in a NEMA 12 enclosure (48 in. tall x 36 in. wide x 16 in. deep). In the NEMA 12 enclosure, a Bomem MB 100 series FTIRS is vertically mounted with a small manifold to control the gas handling operations necessary for the FTIRS analysis. The FTIRS is equipped with a specially designed top plate with an Axiom Analytical 1 meter pathlength LFT series gas cell and an EG&G Judson microcooler motor cooled MCT detector. The gas cell has an internal volume of only 50 mL and is essentially a gold plated light pipe with zinc selenide windows. This cell and the sample handling manifold within the NEMA 12 enclosure are heated to 110°C to minimize carryover problems and evacuation times between samples. The optical bench is purged with hydrocarbon and CO_2 free dry air that is vented into the NEMA 12 enclosure to help maintain a slight positive pressure within the enclosure. Transducers are mounted in the cell to record the temperature and pressure of each sample. Because of the heat load supplied by the instrumentation, heated gas cell and manifold components, the NEMA 12 enclosure is cooled to ~28 C with a closed cycle air conditioner mounted directly to the cabinet. Operation of the gas handling equipment and the FTIR are controlled via RS422 from a personal computer located in the DVF control room over 60 feet away. Vacuum is supplied by a direct connection to the DVF facility vacuum manifold.

A complete description of the computerized DVF operations is beyond scope of this paper, however a brief description of how the FTIRS interacts with this system follows. When the computer controlling the DVF operations is ready for an FTIRS analysis, it sends an analog trigger signal to the FTIRS computer. The FTIRS computer then initiates a sequence to evacuate the internal manifold and gas cell up to an external valve on the main sampling manifold controlled by the DVF computer. When the cell and internal manifold are evacuated, the FTIRS computer signals the DVF computer to open the valve and allow the sample to flow into the FTIRS cell. When a stable pressure is reached in the gas cell, the FTIRS sends another analog signal telling the DVF computer that it has the sample and then begins to collect the first spectrum of 48 coadded scans. This spectrum is then evaluated using individual PLS methods for each of the analytes. The spectral residuals are used as an indicator of a potential problem. If the spectral residual is above a preset value for any of the analyte methods, then the cell pressure is reduced and a second, "diluted" sample spectrum is acquired and analyzed for the analytes that triggered the dilution. A report is generated which is stored on the hard disk of the FTIRS computer, sent to the printer and sent to the DVF computer hard disk via a local area network connection. Total analysis time is 4 to 6 minutes, depending upon the need for dilution.

The MGAS was supplied by Applied Automation, Inc. (Bartlesville, OK) according the specifications supplied by the INEEL. This system contains a Bomem MB 100 series FTIR with an identical top plate as in the wall mounted system described above, a VG Gaslab 300 quadrapole residual gas analyzer (RGA) for hydrogen analysis, a gas handling manifold, and a vacuum pump. These components are housed in a specially designed stainless steel cart. One compartment on this cart contains the controlling computers and associated electronics. Another contains the vertically mounted FTIRS. A third contains the vacuum pumps, the RGA, and a cooling fan pulling air through a HEPA filter and then dispersing it to the various cart compartments. A fourth compartment is an oven containing the gas-handling manifold. A compartment with a lid that opens up contains the keyboards and computer screens for the user interface. The oven and transfer lines within the cart are also maintained at 100°C. Sample collection and analysis proceeds similar to that described for the wall mounted system.

Quantitative analysis methods. The wall-mounted FTIRS at the RWMC and the FTIRS in the MGAS use the same quantitative analysis methods. These methods are based upon the partial least squares (PLS) algorithm[5] and were generated using Galactic Industries PLSplus add-on package to Grams/386 or Grams/32. Each analyte has its own PLS method so that the spectral region can be optimized for that analyte. Table 1 lists the target analytes and the PLS method parameters for each analyte. The calibration set consists of over 190 spectra collected on different instruments with different detectors and cells. The first group consisted of pure component spectra of the 30 target analytes, carbon dioxide, ethane and propane collected on a MB 100 FTIRS by Bomem using a 20 cm cell and a DTGS detector. This set of spectra was later expanded with spectra to represent interfering compounds actually found in waste drum headspace by FTIRS analysis. These spectra of hydrocarbons >C6, trimethylamine, nitrous oxide, ammonia, high concentrations of carbon dioxide, carbon monoxide, and methane were collected using a 20 cm cell and a DTGS detector on the wall-mounted FTIRS at the RWMC. Others of mixed standards, ethanol, isopropanol, perfluorotributylamine, and 1,4-dioxane were collected using a 1 meter cell with an MCT detector with either the FTIRS at the RWMC or on the MGAS. Artificial spectra containing offsets and sloping lines were also added to

Table 1. Target analytes, PLS methods and QAOs[7] for waste drum headspace analysis by FTIRS. Precision and accuracy QAOs for all analytes are ±25% and ±30%, respectively.

							QAOs	
Analyte	Spectral Region(s)	Points	Spectra	PLS Factors	SECV	R^2	MDL[a]	PRQL[b]
Acetone	1262-1160	212	191	19	3.6	0.989	50	100
Benzene	712-670	88	187	15	0.6	0.999	5	10
Bromoform	1170-1120	105	191	9	1.9	0.991	5	10
1-Butanol	1156-900	266	191	26	7.4	0.919	50	100
MEK	1240-1130	115	191	24	2.0	0.994	50	100
	1820-1670	156						
Carbon Tetrachloride	820-775	95	191	12	1.6	0.996	5	10
Chlorobenzene	1105-988	337	191	21	2.6	0.983	5	10
Chloroform	806-731	157	191	34	0.6	0.999	5	10
	1255-1181	155						
Cyclohexane	2987-2825	337	185	29	0.4	1.000	5	10
11-Dichloroethane	1106-950	325	191	21	4.5	0.965	5	10
12-Dichloroethane	717-695	47	192	28	3.5	0.994	5	10
	750-722	59						
	1260-1200	125						
11-Dichloroethene	912-825	181	191	25	3.4	0.986	5	10
	1169-1049	249						
c-12-Dichlorothene	882-827	115	191	14	0.9	0.998	5	10
Ethylbenzene	830-680	156	183	23	7.7	0.868	10	20
	3140-3020	125						
Ethyl Ether	1225-1020	214	191	25	1.2	0.997	5	10
Methanol	1100-935	343	191	24	1.5	0.998	50	100
Methylene Chloride	784-744	84	191	25	1.9	0.995	5	10
	1296-1237	124						
Methyl isobutyl ketone	1407-1330	81	191	12	3.4	0.983	50	100
	1815-1703	117						
1122-Tetrachloroethane	845-742	214	191	21	2.8	0.980	5	10
Tetrachloroethene	940-870	147	191	14	0.7	0.999	5	10
Toluene	775-689	179	191	31	1.8	0.996	5	10
	1129-1003	132						
111-Trichloroethane	1134-1040	196	191	17	2.0	0.999	5	10
Trichloroethene	968-920	101	191	17	1.7	0.998	5	10
	864-830	74						
Freon 113	1240-996	507	191	31	1.2	0.998	5	10
124-Trimethylbenzene	834-774	126	191	13	3.2	0.976	5	10
135-Trimethylbenzene	860-811	103	191	14	0.9	0.998	5	10
o-Xylene	773-700	152	191	23	2.3	0.987	5	10
m-Xylene	810-730	167	191	21	2.5	0.984	5	10
p-Xylene	840-710	270	191	32	2.8	0.981	5	10
Methane	3026-3000	55	181	13	5.9	1.000	500	1000
	1310-1291	41						

[a]MDL=Method detection limit
[b]PRQL=Program required quantitation limit

the set for simple background factor definition. The frequency regions for each analyte were selected after evaluating the correlation spectra for that component calculated by a development aid in the PLSplus package and the actual spectrum of the analyte. An optimum number of factors for each analyte method were selected from the evaluation of the predicted residual error sum of squares (PRESS) values determined using the cross-validation procedure in the PLSplus package.

RESULTS AND DISCUSSION

To date, the FTIRS method has been applied to the analysis of VOCs in the headspace of over 600 actual waste drums. Prior to performing these analyses, the methodology was demonstrated to meet the WIPP quality assurance objectives (QAOs) outlined in the Quality Assurance Program Plan (QAPP)[6,7]. The QAOs essentially consist of ±25% precision, ±30% accuracy, 90% completeness, and the MDLs and PRQLs listed in Table 1. Table 2 lists the quality control samples used to demonstrate that the QAOs are being met. An on-line batch is defined as a 12-hour period whereas an analytical batch would represent a set of 20 samples.

Table 2. Summary of quality control samples for FTIRS based VOC analysis.

QC Sample	Minimum Frequency	Acceptance Criteria
Method performance samples	Seven initially and four semiannually	Meets Table 1 QAOs
Laboratory or on-line duplicates	One per analytical or on-line batch	RPD = 25%
Laboratory or on-line blanks	One per analytical or on-line batch prior sample analysis	< PRQL
Laboratory or on-line control samples	One per analytical or on-line batch prior to sample analysis	±100±30% Recovery
GC/MS comparison sample	One per analytical or on-line batch	RPD = 25%
Blind audit samples	Controlled by PDP Plan	Specified in Gas PDP Plan

Because the nature of the FTIRS analysis is a multivariate analysis where each analyte is quantitated from a highly overlapped spectrum, using a single standard with all analytes in it is not really appropriate since very rarely are more than 3-6 analytes ever found in a single sample. Therefore, the method performance samples consisted of a set of six certified standards with 1-9 analytes. The concentration of each analyte in these standards was at the PRQL for that analyte. Table 3 lists the data used to establish that performance of the wall-mounted FTIRS at the RWMC met the basic QAOs. The detection limits were simply calculated as three times the standard deviation of the mean result of the seven replicate measurements on that particular standard sample. Similar results were obtained for the FTIRS on the MGAS.

Prior to beginning the sample analysis on any given day, a single beam reference spectrum is collected to which each single beam spectrum will be ratioed to calculate the absorbance spectrum for that sample. When the reference spectrum has been collected the blank and control samples are analyzed. The control sample contains the 10 most common, or representative, analytes generally encountered in actual sample analysis. If the blank and control sample results meet the Table 2 acceptance criteria then samples can be analyzed. If these criteria are not met, a new reference spectrum is acquired and the blank and control samples reanalyzed. Table 4 summarizes 61 measurements of the same control sample covering operation of the MGAS FTIRS in three months. In May of 1998, the MGAS was at Entropy, Inc. in North Carolina where it was installed in a trailer and operators were trained. It was then transported to the Nevada Test Site and put in operation actually sampling drums from October through the end of November of 1998. Many of the reference sample spectra were collected during warmup periods and are not associated with any actual waste drum analyses. When these analyses are eliminated the RSDs range are reduced to 2.8-4.5% but the accuracy remains the same. The accuracy and precision are well within the QAOs and demonstrate the long term stability of the instrumentation and reproducibility of the technique. Similar results are routinely obtained with the FTIRS at the RWMC.

Participation in the Performance Demonstration Program (PDP)[8] is mandatory to fully meet the QAO's for headspace analysis. An overall score of 75% and a score of 95% for a specified list of critical target compounds (CTCs) is required to pass. The CTCs are acetone, carbon tetrachloride, cyclohexane, 1,2-dichloroethane, dichloromethane, 1,1,1-trichloroethane, trichloroethene, and o-xylene. Five points are awarded for each positive identification, each relative standard deviation (RSD) within ±25%, each relative percent difference on the duplicate samples within ±25%, and each accuracy within ±30%. One point is subtracted for each false positive. The CTCs, remaining VOCs,

Table 3. Results from the initial analysis of replicate analyses of the method performance samples with the RWMC FTIRS.

		Concentration (ppmv)					ppmv
Analyte	**Cylinder**	**True**	**Mean**	**SD**	**%RSD**	**% Error**	**DL**
Acetone	AAL13812	100.2	98.6	0.9	1.0	-1.5	2.8
Benzene	ALM46028	10.1	11.3	0.1	0.6	11.5	0.2
Bromoform	ALM46028	9.9	9.1	0.5	5.2	-8.5	1.4
1-Butanol	ALM47039	101.0	89.5	3.7	4.1	-11.4	11.1
Methyl Ethyl Ketone	AAL13812	100.2	97.3	1.2	1.2	-2.8	3.6
Carbon Tetrachloride	ALM49467	9.9	9.8	0.0	0.5	-0.6	0.1
Chlorobenzene	ALM50465	9.9	9.5	0.6	6.1	-4.3	1.7
Chloroform	AAL13812	9.9	10.0	0.1	1.3	1.2	0.4
Cyclohexane	ALM50465	9.7	9.7	0.0	0.4	0.3	0.1
1,1-Dichloroethane	AAL13812	10.1	8.1	0.6	7.4	-19.1	1.8
1,2-Dichloroethane	ALM49467	9.9	11.7	0.6	5.0	18.1	1.8
1,1-Dichloroethene	ALM50465	9.9	9.2	0.2	2.2	-6.6	0.6
c-1,2-Dichloroethene	ALM46028	9.9	10.0	0.2	2.0	1.0	0.6
Ethylbenzene	ALM46028	19.9	18.0	0.5	3.0	-9.7	1.6
Ethyl Ether	ALM49467	10.2	10.5	0.1	1.0	3.1	0.3
Methanol	AAL7127	100.0	98.5	3.2	3.2	-1.5	9.5
Dichloromethane	ALM50465	9.9	9.3	0.1	1.5	-6.3	0.4
Methyl Isobutyl Ketone	ALM49467	99.5	88.1	1.2	1.3	-11.4	3.5
1,1,2,2-Tetrachloroethane	ALM49467	9.9	12.3	0.7	5.4	24.3	2.0
Tetrachloroethene	ALM50465	9.8	9.8	0.2	2.3	-0.2	0.7
Toluene	AAL13812	10.1	9.7	0.3	3.1	-3.0	0.9
1,1,1-Trichloroethane	AAL7127	10.1	9.7	0.4	4.1	-4.0	1.2
Trichloroethene	ALM46028	10.0	10.1	0.2	2.2	1.0	0.7
Freon-113	ALM50465	10.2	10.2	0.1	0.7	-0.4	0.2
1,2,4-Trimethylbenzene	ALM50465	9.9	9.8	0.6	5.6	-1.0	1.7
1,3,5-Trimethylbenzene	AAL13812	10.0	8.9	0.7	8.1	-10.8	2.2
o-Xylene	ALM49467	9.9	9.9	0.3	3.4	-0.2	1.0
m-Xylene	AAL13812	10.1	9.7	0.5	5.5	-3.9	1.6
p-Xylene	ALM50465	9.8	11.5	0.7	6.3	16.9	2.2
Methane	ALM50465	997.0	996.2	1.1	0.1	-0.1	3.3

and methane are scored independantly. Both FTIRS instruments have passed multiple PDP cycles with an average CTC score of 97±3% and an overall score of 90±5%. The PDP samples are among the most difficult samples analyzed by the FTIRS method to date. These samples can contain several 10's of thousands of ppmv of carbon dioxide and may have several thousand ppmv of methane in the same sample along with 5 to 10 VOC analytes. Not only is having more than 5 analytes unusual, but carbon dioxide and methane at these high concentrations, and in the same sample is somewhat unusual. An analysis of the data from 231 unvented drums[9] indicate that the higher levels of methane and of carbon dioxide usually found in the PDP samples represent only about 10±5% of the drums and there was no correlation between the them. Of the drums analyzed so far with the FTIRS method, the frequency at which carbon dioxide at these levels occurs appears to be about right but methane has only rarely been noted, and then only at low concentrations. Carbon dioxide and methane at these high concentrations may be significant interferences for many analytes at low concentrations in the same sample. In particular, very high concentrations of carbon dioxide can significantly affect the results for the target aromatic VOCs. The result is either a false positive or negative with an elevated detection limit caused by the high spectral residual forced dilution. A more complete

calibration set which includes many of the nonlinearities which result in these errors may help to minimize this problem. Even with this issue, the performance of the FTIRS method in the PDP is quite good.

Table 4. Summary of 61 measurements of the same on-line control sample by the MGAS FTIRS in May, October and November of 1998 when it was in operation.

	Concentration (ppmv)				
Analyte	True	Mean	SD	%RSD	% Error
Acetone	101.0	100.8	5.6	5.6	-0.2
Carbon Tetrachloride	100.0	101.8	4.7	4.6	1.8
Chloroform	100.0	100.3	4.7	4.7	0.3
1,1-Dichloroethane	99.2	96.7	4.2	4.3	-2.5
Dichloromethane	98.9	96.9	4.3	4.4	-2.0
Toluene	100.0	101.6	5.1	5.0	1.6
1,1,1-Trichloroethane	199.0	200.0	9.7	4.9	0.5
Trichloroethene	99.2	100.4	5.0	5.0	1.2
Freon-113	100.0	97.5	4.2	4.3	-2.5
Methane	1000.0	1024.0	46.0	4.5	2.4

An additional requirement of the method is that there is some method by which unexpected compounds can be identified. One of the additional advantages of this method is that as new compounds are encountered, they generally show up as interferences causing an increase in the spectral residual. Evaluation of the spectra will reveal the infrared spectrum of the unknown compound that can be identified by comparison to a spectral library or by manual interpretation. In this way, 1,4,-dioxane, ethanol, isopropanol, trimethylamine, ammonia, nitrous oxide, and perfluorotributylamine have been identified. More recently acetylene, ethylene, acetaldehyde and carbonyl sulfide have been identified. Once appropriate spectra of the new compound are added to the calibration set and new calibration methods are generated, they are used to reanalyze the spectra from all previous suspect samples.

SUMMARY

The determination of VOCs and methane in TRU waste drum headspace with FTIRS has been demonstrated to be generally a fast and reliable method. Accuracy and precision are well within the QAOs defined in the WIPP QAPP. The ability of the method to meet the PRQL and MDL for each analyte has also been demonstrated. The major problems encountered with the method occur when very high concentrations of a compound or interference are present in the sample. This forces the need for a dilution and subsequently raises the detection limits for the sample and causes inaccuracies due to high spectral residuals. Unknown compounds can be identified when encountered, the calibrations adjusted accordingly and all previous samples can be reanalyzed.

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REFERENCES

1. Bauer, W.F.; Connolly, M.J.; Rilling, A.; Gravel, D.; Perry, S., *Evaluation of Fourier transform infrared spectroscopy for the determination of volatile organic compounds in transuranic waste drum headspace*, Idaho National Engineering Laboratory, INEL-95/-332, September 7, **1995**.
2. Cronin, J.T. *Spectroscopy* **1992,** *7*, 33-39.
3. Russworm, G.M.; Kagann, R.H.; Simpson, O.A.; McClenny, W.A.; Hergot, W.F. *Journal of the Air and Waste Management Association* **1991,** *41*, 1062-1066.
4. Wang, Y.; Lysaght, M.J.; Kowalski, B.R.K. *Analytical Chemistry* **1992,** *64*, 562-564.
5. Haaland, D.M.; Thomas, E.V.T. *Analytical Chemistry* **1988,** *60*, 1193-1201.
6. USDOE, *Transuranic Waste Characterization Quality Assurance Program Plan*, USDOE-Carlsbad Area Office, CAO-94-1010, April 30, **1995**.
7. USDOE, *Transuranic Waste Characterization Quality Assurance Program Plan*, US DOE Carlsbad Area Office, Interim Guidance, February, **1996**.

8. USDOE, *Performance Demonstration Program Plan for the Analysis of Simulated Headspace Gases for the TRU Waste Characterization Program*, USDOE-Carlsbad Area Office, CAO-95-1077, June, **1995**.
9. Clements, T.L.J.; Kudera, D.E., *TRU Waste Sampling Program: Volume 1--Waste Characterization*, Idaho National Engineering Laboratory, EGG-WM-6503, September, **1985**.

COMPARISON OF LABORATORY DUPLICATE, MATRIX SPIKE, AND FIELD DUPLICATE RESULTS FOR MERCURY IN A LARGE MULTI-STATE PIPELINE INVESTIGATION

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ABSTRACT
The collection, preparation, and analysis of laboratory duplicate, matrix spike, and field duplicate samples have historically been considered important quality control measures to be used by the laboratory in the performance of analyses for various environmental investigations. For an on-going pipeline investigation, involving the collection of thousands of samples across six states, a significant number of laboratory duplicate, matrix spike, and field duplicate samples have been collected by several sampling consultants for the characterization of mercury. The analyses of field duplicates as well as the preparation and analysis of laboratory duplicates and matrix spikes for the subject investigation have been performed by several commercial environmental laboratories. A formal description of the comparative study of the statistical trends observed among the results of the field-prepared duplicate samples, the laboratory-prepared duplicate samples, and the laboratory-prepared matrix spike samples for mercury will be presented.

INTRODUCTION
As data quality indicators, laboratory duplicate, matrix spike, and field duplicate samples provide information to data users relative to analytical precision, field sample collection precision, and perhaps, to a lesser extent, sample representativeness. These quality control measures, when used in conjunction, can provide valuable information specifically pertaining to how the analytical method may or may not be working for sample analysis. The careful collection, preparation, and analysis of meaningful laboratory duplicate, matrix spike, and field duplicate samples have historically been a challenge for environmental investigators.

Typically, investigators routinely collect a sufficient sample mass/volume, thoroughly homogenize the sample in the field, and place the sample in laboratory-supplied bottleware for shipment to the laboratory for analysis. In the case of single-blind field duplicates, a larger aliquot of sample form one location is homogenized; the aliquot is subsequently split between two separate sets of fictitiously labeled bottles for shipment to the laboratory for analysis. The preparation of laboratory duplicate and matrix spike samples may involve homogenizing the received sample (to varying degrees) and subsequently splitting the sample into separate aliquots for the preparation and analysis of background, laboratory duplicate, and matrix spike samples.

The sample data utilized for this study was collected as part of on-going natural gas pipeline investigations. Approximately 1,100 solid and 30 aqueous sample collection events occurred from August 1996 to January 1999 as part of this pipeline investigation. These sample collection events were performed in six states (Ohio, West Virginia, Virginia, Maryland, Delaware, and Pennsylvania). The solid samples were mostly shallow borings or surface samples. The aqueous samples were mostly monitoring well samples.

PROCEDURE
A quality control sample utilized by almost all analytical methods to evaluate the accuracy of the analytical procedure is a matrix spike sample. A matrix spike sample is an aliquot of a matrix (e.g., water or solid) fortified (spiked) with known quantities of specific analytes and subjected to the entire analytical procedure. The percent recovery for the matrix spike is calculated using the equation:

%Recovery = (Matrix Spike Sample Concentration – Sample Concentration)/(Spike Added Concentration) x 100

The recovery of the analyte provides the user with information about the effectiveness of the analytical procedure in terms of the accuracy in determining the qualitative presence and quantitative concentration of the analyte in the sample matrix being analyzed. The "true" recovery of the analyte can be inherently impacted by the effectiveness (precision) of the sample collection, preparation, and analytical procedures, as demonstrated by the results of laboratory and field duplicate analyses described below. The project-specified matrix spike recovery criteria for mercury are 75-125% in solid and aqueous matrices.

During the evaluation of the matrix spike analyses, the concentration of the background sample in relation to the concentration of the spike added was used to determine the usability of the matrix spike recoveries. The national US EPA data evaluation guidelines indicate that a recovery from a matrix spike analysis is not considered meaningful if four-times the concentration of spike added is less than the observed concentration in the background sample. For this study, only matrix spike results where the concentration of the sample was less than or equal to four-times the concentration of spike added were evaluated.

A quality control sample utilized to assess the precision of the method is the laboratory duplicate sample. A laboratory duplicate is a second aliquot of a sample that is treated in the same manner as the original sample in order to determine the precision of the method (not withstanding any confounding effects of sample homogeneity). The duplicate precision is expressed as the relative percent difference (RPD) and is calculated by the following equation:

%RPD = (Sample Concentration – Laboratory Duplicate Concentration)/[(Sample Concentration + Laboratory Duplicate Concentration)/2] x 100

The concentration of an analyte in the laboratory duplicate sample is compared to the concentration of that analyte in the original sample to assess the precision between the results. The precision between the laboratory duplicate results provides the data user with information regarding the homogeneity of the sample matrix and effectiveness of the sample preparation and analysis procedures.

During the evaluation of the laboratory duplicate analyses, the concentrations of the background and laboratory duplicate results were used to determine the precision criterion utilized. If both results were greater than or equal to five-times the sample-specific project required detection limit (PRDL), the project laboratory duplicate precision criterion for mercury in a solid matrix was the RPD between the results must be less than or equal to 35%. If at least one of the results was less than five-times the sample-specific PRDL, the project laboratory duplicate precision criterion for mercury in a solid matrix was the difference between the results must be less than or equal to twice the sample-specific PRDL. If both results were greater than or equal to five-times the sample-specific PRDL, the project laboratory duplicate precision criterion for mercury in an aqueous matrix was the RPD between the results must be less than or equal to 20%. If at least one of the results was less than five-times the sample-specific PRDL, the project laboratory duplicate precision criterion for mercury in an aqueous matrix was the difference between the results must be less than or equal to the sample-specific PRDL.

A quality control sample that can be utilized to measure the precision of the field sampling and analytical method is the field duplicate sample. A field duplicate sample is a sample that is thoroughly homogenized in the field, split between two sets of bottleware, and submitted to the laboratory as two discrete samples. The duplicate precision is expressed as the RPD and is calculated by the following equation:

%RPD = (Sample Concentration – Field Duplicate Concentration)/[(Sample Concentration + Field Duplicate Concentration)/2] x 100

The concentration of an analyte in the field duplicate sample is compared to the concentration of that analyte in the original sample to assess the precision between the results. The precision between the field duplicate results provides the data user with information regarding the homogeneity of the sample matrix and effectiveness of the sample collection and analysis procedures.

During the evaluation of the field duplicate analyses, the concentrations of the background and field duplicate results were used to determine the precision criterion utilized. If both results were greater than or equal to five-times the sample-specific PRDL, the project field duplicate precision criterion for mercury in a solid matrix was the RPD

between the results must be less than or equal to 35%. If at least one of the results was less than five-times the sample-specific PRDL, the project field duplicate precision criterion for mercury in a solid matrix was the difference between the results must be less than or equal to twice the sample-specific PRDL. If both results were greater than or equal to five-times the sample-specific PRDL, the project field duplicate precision criterion for mercury in an aqueous matrix was the RPD between the results must be less than or equal to 20%. If at least one of the results was less than five-times the sample-specific PRDL, the project field duplicate precision criterion for mercury in an aqueous matrix was the difference between the results must be less than or equal to the sample-specific PRDL.

RESULTS

All of the matrix spike analyses performed on project samples were initially evaluated. Tables 1 and 2 summarize the matrix spike recovery data.

Table 1. Solid Matrix Spike Results

Analyte	Low Recovery (<75%)	Acceptable Recovery	High Recovery (>125%)
Mercury	427 (36%)	505 (43%)	254 (21%)

Table 2. Aqueous Matrix Spike Results

Analyte	Low Recovery (<75%)	Acceptable Recovery	High Recovery (>125%)
Mercury	0 (0%)	26 (96%)	1 (4%)

The data for the aqueous matrix spike analyses demonstrate that the sample collection, preparation, and analytical procedures utilized were acceptable for the vast majority of the samples collected for mercury. A small portion of the aqueous matrix spike analyses displayed unacceptable recoveries indicating possible problems with the matrix, homogeneity, collection, preparation, and analysis. The matrix spike recoveries are graphically presented in Figure 1.

All of the laboratory duplicate analyses performed on project samples were initially evaluated. Tables 3 and 4 summarize the laboratory duplicate precision data.

Table 3. Solid Laboratory Duplicate Results

Analyte	Acceptable Precision	Unacceptable Precision
Mercury	1022 (86%)	164 (14%)

Table 4. Aqueous Laboratory Duplicate Results

Analyte	Acceptable Precision	Unacceptable Precision
Mercury	27 (100%)	0 (0%)

The data for the solid and aqueous laboratory duplicate analyses demonstrate that the sample collection, preparation, and analytical procedures utilized were acceptable for the vast majority of the samples collected for mercury. A small portion of the solid laboratory duplicate analyses displayed unacceptable recoveries indicating possible problems with sample homogeneity, collection, preparation, and analysis. The laboratory duplicate results are graphically presented in Figure 2.

All of the field duplicate analyses performed on project samples were initially evaluated. Tables 5 and 6 summarize the field duplicate precision data.

Table 5. Solid Field Duplicate Results

Analyte	Acceptable Precision	Unacceptable Precision
Mercury	857 (76%)	278 (24%)

Table 6. Aqueous Field Duplicate Results

Analyte	Acceptable Precision	Unacceptable Precision
Mercury	27 (96%)	1 (4%)

The data for the solid and aqueous field duplicate analyses demonstrates that the sample collection and analytical procedures utilized were acceptable for the majority of the samples collected for mercury. A portion of the solid field duplicate analyses displayed unacceptable recoveries indicating possible problems with sample homogeneity, collection, and analysis. The field duplicate results are graphically presented in Figure 3.

In order to determine the most likely cause or causes for matrix spike recovery failures, laboratory duplicate failures, and field duplicate precision failures, the correlation between the matrix spike recoveries, the laboratory duplicate precision, and the field duplicate precision was evaluated. The correlation of the matrix spike, laboratory duplicate, and field duplicate samples required that each of these quality control samples was present in the sample collection event or sample delivery group (SDG). The project sample collection scheme was not developed to collect all of the quality control samples with each SDG. Therefore, a limited number of SDGs contained all of these quality control samples. Tables 7 and 8 summarize the correlation of the quality control data.

Table 7. Solid Results Comparison

Mercury	LD In/FD In	LD In/FD Out	LD Out/FD In	LD Out/FD Out
MS Low	220 (19.2%)	96 (8.4%)	63 (5.5%)	34 (3.0%)
MS Acceptable	376 (32.9%)	77 (6.7%)	25 (2.2%)	4 (0.3%)
MS High	152 (13.3%)	59 (5.2%)	22 (1.9%)	16 (1.4%)

Table 8. Aqueous Results Comparison

Mercury	LD In/FD In	LD In/FD Out	LD Out/FD In	LD Out/FD Out
MS Low	0 (0.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)
MS Acceptable	25 (96.2%)	0 (0.0%)	0 (0.0%)	0 (0.0%)
MS High	1 (3.8%)	0 (0.0%)	0 (0.0%)	0 (0.0%)

The correlation of the solid quality control results has been graphically presented in Figure 4. The correlation of the aqueous quality control results is graphically presented in Figure 5.

DISCUSSION

The individual quality control samples provide pieces of information about sample matrix, homogeneity, collection, preparation, and analysis. In order to garner the most information about the project samples, the data user must collectively utilize the information generated by the analyses of the quality control samples. The correlation of the quality control samples placed each SDG into one of 12 categories. The data user can infer certain information from each of the 12 categories.

An SDG is placed in Category A if the matrix spike (MS) recovery, laboratory duplicate (LD) precision, and field duplicate (FD) precision are acceptable (In). In this case, all procedures are acceptable.

An SDG is placed in Category B if the MS recovery is low (Low) and the LD and FD precision are acceptable (In). In this case, it may be inferred the sample matrix is binding the analyte (inhibiting the digestion procedure from liberating the analyte for analysis), the sample matrix is inhibiting the instrumental sensitivity or instrument response, or an error during the matrix spike sample preparation may have occurred.

An SDG is placed in Category C if the MS recovery is high (High) and the LD and FD precision are acceptable (In). In this case, it may be inferred the sample matrix is potentially positively influencing the instrument sensitivity or an error during the matrix spike sample preparation may have occurred.

An SDG is placed in Category D if the MS recovery and LD precision are acceptable (In) and the FD precision is unacceptable (Out). In this case, it may be inferred the sample collection procedure did not adequately homogenize the sample prior to submission to the laboratory or the sample matrix does not allow for adequate homogenization of the sample matrix.

An SDG is placed in Category E if the MS recovery is low (Low), the LD precision is acceptable (In), and the FD precision is unacceptable (Out). In this case, it may be inferred the low matrix spike recovery may be attributed to sample homogeneity problems. The inferences previously made for Categories B and D may also apply.

An SDG is placed in Category F if the MS recovery is high (High), the LD precision is acceptable (In), and the FD precision is unacceptable (Out). As is the case with Category E, it may be inferred the low matrix spike recovery may be attributed to sample homogeneity problems. The inferences previously made for Categories C and D may also apply.

An SDG is placed in Category G if the MS recovery is acceptable (In), the LD precision is unacceptable (Out), and the FD precision is acceptable (In). In this case, it may be inferred the sample preparation procedure did not adequately homogenize the sample prior to sample analysis or the sample matrix does not allow for adequate homogenization of the sample matrix.

An SDG is placed in Category H if the MS recovery is low (Low), the LD precision is unacceptable (Out), and the FD precision is acceptable (In). As is the case with Categories D and E, it may be inferred the low matrix spike recovery may be attributed to sample homogeneity problems. The inferences previously made for Categories B and G may also apply.

An SDG is placed in Category I if the MS recovery is high (High), the LD precision is unacceptable (Out), and the FD precision is acceptable (In). As is the case with Categories D, E, and H, it may be inferred the low matrix spike recovery may be attributed to sample homogeneity problems. The inferences previously made for Categories C and G may also apply.

An SDG is placed in Category J if the MS recovery is acceptable (In), the LD precision is unacceptable (Out), and the FD precision is unacceptable (Out). In this case, it may be inferred the sample collection and sample preparation procedures do not adequately homogenize the sample prior to analysis or the sample matrix does not allow for adequate homogenization of the sample matrix.

An SDG is placed in Category K if the MS recovery is low (Low), the LD precision is unacceptable (Out), and the FD precision is unacceptable (Out). In this case, it may be inferred the low matrix spike recovery may be attributed to sample homogeneity problems, the sample collection and sample preparation procedures do not adequately homogenize the sample prior to analysis, or the sample matrix does not allow for adequate homogenization of the sample matrix.

An SDG is placed in Category L if the MS recovery is high (High), the LD precision is unacceptable (Out), and the FD precision is unacceptable (Out). In this case, it may be inferred the high matrix spike recovery may be attributed to sample homogeneity problems, the sample collection and sample preparation procedures do not adequately homogenize the sample prior to analysis, or the sample matrix does not allow for adequate homogenization of the sample matrix.

SUMMARY

The individual quality control analysis provides an indication of the sample collection, preparation, and analysis procedures as well as the sample matrix. When more than one type of quality control sample is utilized, the data user gains a better insight into the performance of the procedures used for collection and analysis of the sample matrix. As demonstrated by the data presented, the vast majority of the aqueous data collected and a portion of the solid data collected indicate that the procedures utilized were acceptable for the sample matrices collected. In almost one-half of the solid sample SDGs, matrix effects interfered with analysis. As a result, sample matrices were not adequately analyzed or the sample collection and analysis procedures were not adequately performed. Also, in several solid sample SDGs, the sample collection and analysis procedures were not adequately performed or sample matrices were not adequately analyzed due to sample homogeneity complications.

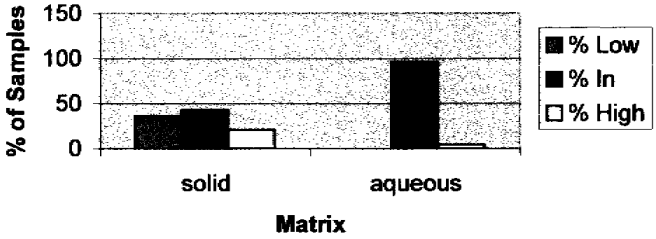

Figure 1. Matrix Spike Recoveries

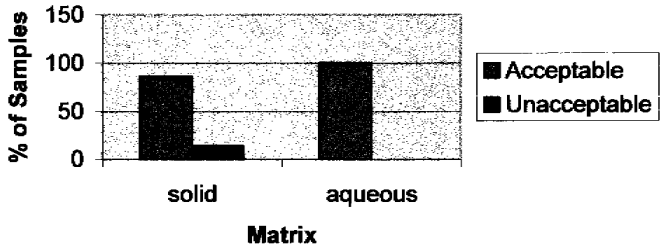

Figure 2. Laboratory Duplicate Results

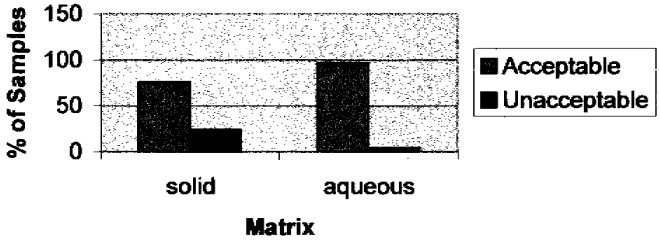

Figure 3. Field Duplicate Results

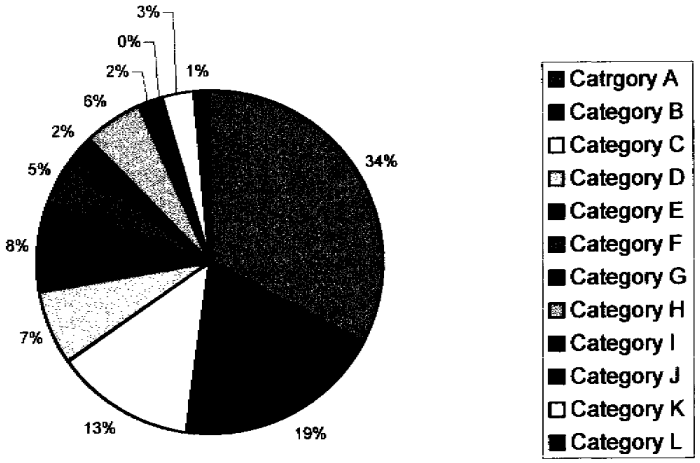

Figure 4. Comparison - Mercury in Solid Samples

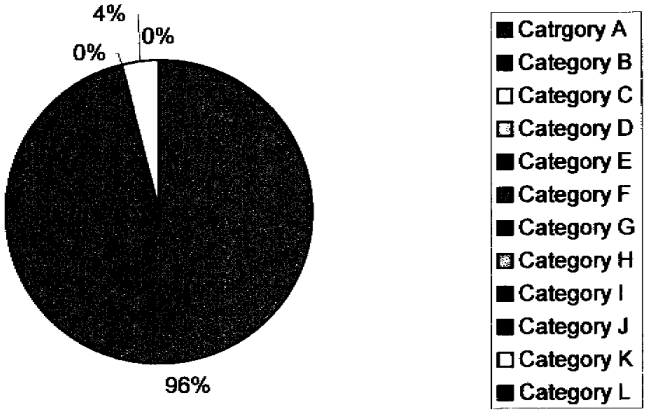

Figure 5. Comparison - Mercury in Aqueous Samples

CURRENT ACTIVITIES IN ENVIRONMENTAL STANDARD REFERENCE MATERIALS FOR TRACE ORGANIC CONTAMINANTS

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ABSTRACT

In the past five years the National Institute of Standards and Technology (NIST) has issued several new environmental matrix Standard Reference Materials (SRMs) with certified concentrations of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides. These materials include air and diesel particulate matter, sediments, mussel tissues, and cod liver oil. The certified values for these materials are presented.

INTRODUCTION

Since 1980 the National Institute of Standards and Technology (NIST) has issued a number of Standard Reference Materials (SRMs) for use in the determination of organic contaminants in environmental samples[1]. These SRMs include simple calibration solutions that contain a number of analytes and are useful for calibrating the measurement system and natural matrix materials that are useful for validating the complete analytical procedure and providing quality control of routine analyses. The recent natural matrix SRMs are described briefly below with a summary of the certified values for several of these materials.

RESULTS AND DISCUSSION

The typical mode used for certification of natural matrix SRMs for organic contaminants has been the analysis of the material using two or more "chemically independent" analytical techniques. The results of these multiple technique analyses, if in agreement, are used to determine the "certified" concentrations for the measured analytes. When results are obtained from only one analytical technique, the concentrations are typically reported as reference values (previously denoted as noncertified values). A summary of the natural environmental matrix SRMs for organic contaminants that have been issued by NIST during the past five years is provided in Table 1. The recent natural matrix SRM activities have focused primarily on: (1) updating the certified and reference values on existing materials (ie., recertification), (2) replacing materials that are no longer available (i.e., renewals), and (3) producing new matrix materials. Tables 2-5 summarize the certified values for PAHs and PCB congeners in several of these SRMs. The concentrations listed in Tables are the certified concentrations or reference concentrations (denoted in parentheses) as determined by statistically combining the results from the different analytical methods. For each SRM the method used for combining the data and the definition of the associated uncertainties are given in detail in the Certificate of Analysis.

Several of the SRMs issued during the past 20 years have been reanalyzed (i.e., a new certification of the same material) to provide certified and reference values for additional analytes. Environmental matrix SRMs need to be updated or recertified as analytical measurement capabilities improve and/or as the need for more analytes increases. The SRMs recently recertified are listed in Table 6 and include SRM 1588a, SRM 1939a, SRM 1649a, and SRM 1650a. The number of certified and reference values for PAHs, PCBs, and pesticides determined in the original certification are compared to those in the recertification. An excellent example of the need to update and recertify an existing SRM is SRM 1649, Urban Dust/Organics. SRM 1649, the first particle-based natural matrix material developed by NIST for organic contaminants, was issued in 1992 with certified concentration values for only five PAHs and reference concentrations for nine additional PAHs. Since 1982 NIST has developed and implemented improved analytical methods for the measurement and certification of a significantly greater number of PAHs, as well as PCBs and pesticides, in environmental matrix SRMs. The recertified air particulate material was reissued recently as SRM 1649a, Urban Dust, and the updated certificate lists certified values for 22 PAHs, 35 PCB congeners, and 8 chlorinated pesticides, as well as reference values for 22 PAHs, 1 chlorinated pesticide, 17 congeners of 2,3,7,8-polychlorinated dibenzo-p-dioxins and dibenzofurans, 32 inorganic constituents, mutagenic activity, particle-size characteristics, total organic carbon, total extractable material, and carbon composition. The certified concentrations for selected PAHs and PCB congeners in SRM 1649a are shown in Tables 2 and 4, respectively.

Two renewal materials, SRM 1941a (Organics in Marine Sediment) and SRM 1974a (Organics in Mussel Tissue), were issued in 1994 and 1995 after the first issue of these materials was depleted after five years. As a complement to the frozen mussel tissue (SRM 1974a), three freeze-dried mussel tissue materials are available: SRM 2974, which is a freeze-dried version of the same mussel tissue homogenate used for SRM 1974a; RM 8045, which has similar concentrations of contaminants as SRM 2974; and SRM 2977, which has contaminant concentrations 2-5 times

lower than SRM 2974 (see Tables 3 and 5). A new marine sediment, SRM 1944 (NY/NJ Waterway Sediment) was recently completed with concentrations of PAHs, PCB congeners, and chlorinated pesticides that are approximately 10 times higher than in SRM 1941a (see Tables 2 and 4). SRM 1944 will also be the first NIST SRM with values assigned for selected dibenzo-p-dioxin and dibenzofuran congeners. Two new diesel particulate-related SRMs are available with certified values for PAHs, i.e., SRM 2975 Diesel Particulate Matter (Industrial Forklift) and SRM 1975 Diesel Particulate Extract, which is a dichloromethane extract of the diesel particulate material used in SRM 2975. The certification of a fish tissue material, SRM 1946 (Lake Superior Fish Tissue) is in progress and will be issued as a frozen tissue homogenate (similar to SRM 1974a and 1945) with certified values for PCBs, pesticides, and methylmercury.

REFERENCES

1. S.A. Wise., and M.M. Schantz, in R. Clement and M. Sin (editors), *Reference Materials for Environmental Analysis: Making and Using Them,* Lewis Publishers, Boca Raton, FL, 1997, 143-186.

Table 1. Recent NIST Natural Matrix SRMs for the Determination of Organic Contaminants in the Environmental Samples

SRM No.	Title	Date Issued	Certified Constituents	Reference (Noncertified) Constituents
1588a	Organics in Cod Liver Oil	1998[a]	PCBs (24); Pesticides (14)	PCBs (34); Pesticides (3); PCDDs/PCDFs (7)
1649a	Urban Dust	1998[b]	PAHs (22), PCBs (35); Pesticides (8)	PAHs (22); Pesticide (1); PCDDs/PCDFs (17)
1650a	Diesel Particulate Matter	1999[c]	PAHs (19); Nitro-PAHs (1)	PAHs (25); Nitro-PAHs (3)
1939a	PCBs in River Sediment	1998[d]	PCBs (20); Pesticides (3)	PCBs (4)
1941a	Organics in Marine Sediment	1994	PAHs (23) PCBs (21); Pesticides (6)	PAHs (14); PCBs (7); Pesticides (4); Trace Elements (27)
1944	NY/NJ Waterway Sediment	1999	PAHs (24); PCBs (35); Pesticides (4); Trace Elements (9)	PAHs (32); PCDDs/PCDFs (17); Pesticides (7); Trace Elements (20)
1945	Organics in Whale Blubber	1994	PCBs (27); Pesticides (15)	PCBs (2); Pesticides (2)
1974a	Organics in Mussel Tissue	1999	PAHs (15); PCBs (20); Pesticides (7); Methyl-Hg	PAHs (18); PCBs (4); Pesticides (4); Trace Elements (32)
1975	Diesel Particulate Extract	1999	PAHs (8)	PAHs (~28); Nitro-PAHs (15)
2974	Organics in Freeze-Dried Mussel Tissue	1997	PAHs (14); PCBs (20)	PAHs (17); PCBs (4); Pesticides (4); Trace Elements (32)
2975	Diesel Particulate Matter (Industrial Forklisft)	1999	PAHs (11)	PAHs (~25)
2977	Mussel Tissue (Organic Contaminants and Trace Elements)	1999	PAHs (14); PCBs (25); Trace Elements (8)	PAHs (16); Trace Elements (8)
8045	Mussel Tissue (Raritan Bay, NJ)	1999	PAHs (17); PCBs (24); Pesticides (12)	PAHs (10)

[a]Originally issued in 1989; same material recertified in 1998.
[b]Originally issued in 1982; same material recertified in 1998.
[c]Originally issued in 1985; same material recertified in 1999.
[d]Originally issued in 1990; same material recertified in 1998.

Table 2. Certified and Reference Concentrations of Selected PAHs in Sediment, Air Particulate, and Diesel Particulate SRMs[a]

	SRM 1941a (µg/kg)	SRM 1944 (mg/kg)	SRM 1649a (mg/kg)	SRM 1650a (µg/kg)
Naphthalene	1010 ± 140	1.65 ± 0.31		
Phenanthrene	489 ± 23	5.27 ± 0.22	4.14 ± 0.37	68.4 ± 8.5
Anthracene	184 ± 14	1.77 ± 0.33	0.432 ± 0.082	(1.50 ± 0.63)
Fluoranthene	981 ± 78	8.92 ± 0.32	6.45 ± 0.18	49.9 ± 2.7
Pyrene	811 ± 24	9.70 ± 0.42	5.29 ± 0.25	47.5 ± 2.7
Benzo[*c*]phenathrene	(80 ± 39)	0.76 ± 0.10	0.46 ± 0.03	2.75 ± 0.64
Benz[*a*]nthracene	427 ± 25	4.72 ± 0.11	2.21 ± 0.073	6.33 ± 0.77
Chrysene	380 ± 24	4.86 ± 0.10	3.049 ± 0.060	14.4 ± 0.8
Triphenylene	197 ± 11	1.04 ± 0.27	1.357 ± 0.054	11.4 ± 1.6
Benzo[*b*]fluoranthene	740 ± 110	3.87 ± 0.42	6.45 ± 0.64	8.81 ± 0.60
Benzo[*j*]fluoranthene	341 ± 22	2.09 ± 0.44	(1.5 ± 0.4)	3.52 ± 0.40
Benzo[*k*]fluoranthene	361 ± 18	2.30 ± 0.20	1.913 ± 0.031	2.64 ± 0.31
Benzo[*a*]fluoranthene	118 ± 11	0.78 ± 0.12	0.409 ± 0.035	
Benzo[*e*]pyrene	553 ± 59	3.28 ± 0.11	3.09 ± 0.19	7.44 ± 0.53
Benzo[*a*]pyrene	628 ± 52	4.30 ± 0.13	2.509 ± 0.087	1.33 ± 0.35
Perylene	452 ± 58	1.17 ± 0.24	0.646 ± 0.075	(0.16 ± 0.04)
Benzo[*ghi*]perylene	525 ± 67	2.84 ± 0.10	4.01 ± 0.91	6.50 ± 0.94
Indeno [1,2,3-*cd*]pyrene	501 ± 72	2.78 ± 0.10	3.18 ± 0.72	5.62 ± 0.53
Dibenz[*a*,*j*]anthracene	74.3 ± 6.8	0.500 ± 0.044	0.310 ± 0.034	0.52 ± 0.10
Dibenz[*a*,*c*] anthracene	43.1 ± 3.7	0.335 ± 0.013	0.200 ± 0.025	0.500 ± 0.063
Dibenz[*a*,*h*] anthracene	73.9 ± 9.7	0.424 ± 0.069	0.288 ± 0.023	0.890 ± 0.21
Pentaphene	42 ± 12	0.288 ± 0.026	0.151 ± 0.035	(0.24 ± 0.11)
Benzo[*b*]chrysene	99 ± 20	0.63 ± 0.10	0.315 ± 0.013	0.316 ± 0.038
Picene	80.0 ± 9.0	0.518 ± 0.093	0.426 ± 0.022	0.620 ± 0.081

[a]All concentrations are certified values except those in parentheses, which are reference values.

Table 3. Certified and Reference Concentrations of PAHs in Mussel Tissue SRMs[a]

	SRM 1974a (µg/kg wet)	SRM 2974 (µg/kg)	RM 8045 (µg/kg)	SRM 2977 (µg/kg)
Naphthalene	2.68 ± 0.50	(9.63 ± 0.61)	31.4 ± 6.0	18.8 ± 4.8
Phenanthrene	2.53 ± 0.28	22.2 ± 2.5	73.7 ± 7.0	35.1 ± 3.8
Anthracene	0.69 ± 0.20	6.1 ± 1.7		8.1 ± 4.2
Fluoranthene	18.6 ± 1.0	163.7 ± 10.3	166 ± 12	38.7 ± 1.0
Pyrene	17.26 ± 0.74	151.6 ± 8.0	256 ± 21	78.9 ± 3.5
Benz[*a*]nthracene	3.71 ± 0.54	32.5 ± 4.8	25.3 ± 2.3	20.3 ± 0.8
Chrysene	5.04 ± 0.26	44.2 ± 2.7	59 ± 10	(49 ± 2)
Triphenylene	5.77 ± 0.67	50.7 ± 6.1	63.1 ± 8.8	(38 ± 1)
Benzo[*b*]fluoranthene	5.28 ± 0.42	46.4 ± 4.0	58 ± 15	11.0 ± 0.3
Benzo[*j*]fluoranthene	(2.33 ± 0.20)	(20.5 ± 1.8)	23.4 ± 1.5	(4.6 ± 0.2)
Benzo[*k*]fluoranthene	2.30 ± 0.10	20.2 ± 1.0	24.1 ± 3.4	(4 ± 1)

Table 3. (Continued)

	SRM 1974a (µg/kg wet)	SRM 2974 (µg/kg)	RM 8045 (µg/kg)	SRM 2977 (µg/kg)
Benzo[*e*]pyrene	9.56 ± 0.21	84.0 ± 3.2	89.3 ± 6.3	13.1 ± 1.1
Benzo[*a*]pyrene	1.780 ± 0.073	15.63 ± 0.80	(6.7 ± 2.6)	8.35 ± 0.72
Perylene	0.874 ± 0.030	7.68 ± 0.35	4.08 ± 0.32	3.50 ± 0.76
Benzo[*ghi*]perylene	2.50 ± 0.25	22.0 ± 2.3	19.7 ± 4.4	9.53 ± 0.43
Indeno [1,2,3-*cd*]pyrene	1.62 ± 0.32	14.2 ± 2.8	12.2 ± 2.9	4.84 ± 0.81
Anthanthrene	(0.131 ± 0.036)	1.15 ± 0.31		
Dibenz[*a,j*]anthracene	(0.142 ± 0.010)	(1.247 ± 0.084)		
Dibenz[*a,c* + *a,h*] anthracene	(0.342 ± 0.022)	(3.00 ± 0.22)	3.51 M 0.49	2.0 ± 0.2
Dibenz[*a,h*] anthracene				1.41 ± 0.19
Benzo[*b*]chrysene	(0.182 ± 0.016)	(1.60 ± 0.16)	2.05 ± 0.37	1.07 ± 0.15
Picene			4.50 ± 0.45	2.29 ± 0.27

[a]All concentrations are certified values except those in parentheses, which are reference values.

Table 4. Certified and Reference Concentrations for Selected PCBs in Sediment, Air Particulate, and Cod Liver Oil SRMs[a]

	SRM 1941a (µg/kg)	SRM 1944 (µg/kg)	SRM 1939a (µg/kg)	SRM 1649a (µg/kg)	SRM 1588a (µg/kg)
PCB 28	(9.8 ± 3.7)	80.8 ± 2.7	(2461 ± 78)	18.5 ± 1.2	28.32 ± 0.55)
PCB 31	(6.2 ± 2.4)	78.7 ± 1.6	(6440 ± 490)	17.3 ± 1.4	8.33 ± 0.28
PCB 44	4.80 ± 0.62	60.2 ± 2.0	1131 ± 74	15.4 ± 1.6	35.1 ± 1.4
PCB 49	9.5 ± 2.1	53.0 ± 1.7	3740 ± 280	12.2 ± 1.5	29.90 ± 0.84
PCB 52	6.89 ± 0.56	79.4 ± 2.0	4320 ± 130	24.65 ± 0.97	83.3 ± 2.3
PCB 66	6.8 ± 1.4	71.9 ± 4.3	840 ± 130	65 ± 0.12	54.7 ± 1.5
PCB 95	7.5 ± 1.1	65.0 ± 8.9	(1210 ± 420)	51.6 ± 4.2	63.5 ± 1.1
PCB 87	6.70 ± 0.37	29.9 ± 4.3		10.65 ± 0.62	56.3 ± 1.1
PCB 99	4.17 ± 0.51	37.5 ± 2.4	380 ± 96	9.58 ± 0.69	
PCB 101/90	11.0 ± 1.6	73.4 ± 2.5		52.9 ± 1.0	126.5 ± 4.3
PCB 105	3.65 ± 0.27	24.5 ± 1.1	201 ± 28	8.63 ± 0.80	60.2 ± 2.3
PCB 110	9.47 ± 0.85	63.5 ± 4.7	1068 ± 70	26.6 ± 1.6	76.0 ± 2.0
PCB 118	10.0 ± 1.1	58.0 ± 4.3	423 ± 88	25.7 ± 1.5	176.3 ± 3.8
PCB 128	1.87 ± 0.32	8.47 ± 0.28	91.2 ± 8.48	6.35 ± 0.69	47.0 ± 2.4
PCB 38/163/164	13.38 ± 0.97	62.1 ± 3.0	258.1 ± 6.9	69.7 ± 7.5	263.5 ± 9.1
PCB 149	9.2 ± 1.1	49.7 ± 1.2	427 ± 47	75.7 ± 1.3	105.7 ± 3.6
PCB 151	(2.62 ± 0.22)	16.93 ± 0.36	192.1 ± 2.6	34.3 ± 3.9	54.8 ± 2.1
PCB 153	17.6 ± 1.9	74.0 ± 2.9	297 ± 19	82.5 ± 8.0	273.8 ± 7.7
PCB 156	0.93 ± 0.14	6.52 ± 0.66	37.0 ± 6.6	16.25 ± 0.77	27.3 ± 1.8
PCB 170/190	3.00 ± 0.46	22.6 ± 1.4	107 ± 17	30.8 ± 2.2	46.5 ± 1.1
PCB 180	5.83 ± 0.58	44.3 ± 1.2	140.3 ± 6.1	78.7 ± 8.2	105.0 ± 5.2
PCB 183	(1.63 ± 0.15)	12.19 ± 0.57	47.3 ± 2.3	20.34 ± 0.95	31.21 ± 0.62
PCB 187/159/182	(7.0 ± 2.6)	25.1 ± 1.0	156.4 ± 2.6	40.1 ± 2.5	35.23 ± 0.83
PCB 194	1.78 ± 0.23	11.2 ± 1.4	35.5 ± 4.1	28.9 ± 3.6	15.37 ± 0.61
PCB 206	3.67 ± 0.87	9.21 ± 0.51	29.7 ± 5.6	20.6 ± 4.6	

[a]All concentrations are certified values except those in parentheses, which are reference values.

Table 5. Certified and Reference Concentrations for Selected PCBs in Mussel Tissue and Whale Blubber SRMs[a]

	SRM 1974a (µg/kg wet)	SRM 2974 (µg/kg)	RM 8045 (µg/kg)	SRM 2977 (µg/kg)	SRM 1945 (µg/kg)
PCB 28	(9.0 ± 1.7)	(79 ± 15)	7.91 ± 0.90	5.37 ± 0.44	(14.1 ± 1.4)
PCB 31	(8.6 ± 2.4)	(76 ± 21)	21.4 ± 0.20	3.92 ± 0.24	(3.12 ± 0.69)
PCB 44	8.28 ± 0.84	72.7 ± 7.7	11.8 ± 0.64	3.25 ± 0.63	12.2 ± 1.4
PCB 49	10.12 ± 0.59	88.8 ± 5.7	16.9 ± 0.9		20.8 ± 2.8
PCB 52	13.1 ± 1.3	115 ± 12	17.7 ± 2.8	8.37 ± 0.54	43.6 ± 2.5
PCB 66	11.54 ± 0.50	101.4 ± 5.4	18.4 ± 1.5	3.65 ± 0.32	23.6 ± 1.6
PCB 95	9.5 ± 1.9	83 ± 17	20.8 ± 2.1	5.39 ± 0.59	33.8 ± 1.7
PCB 87	(6.1 ± 1.6)	(54 ± 14)	10.2 ± 0.3	2.15 ± 0.08	16.7 ± 1.4
PCB 99	8.08 ± 0.46	70.9 ± 4.56	18.85 ± 0.44	1.59 ± 0.20	45.4 ± 5.44
PCB 101/90	14.6 ± 1.1	128 ± 10.1	35.9 ± 1.6	11.2 ± 1.2	65.2 ± 5.6
PCB 105	6.04 ± 0.39	53.0 ± 3.8.39	10.9 ± 0.5	3.76 ± 0.49	30.1 ± 2.3
PCB 110	14.5 ± 1.0	127.3 ± 9.4	35.3 ± 0.5	4.03 ± 0.20	23.3 ± 4.0
PCB 118	14.90 ± 0.40	130.8 ± 5.3	35.1 ± 1.0	10.51 ± 0.81	74.6 ± 5.1
PCB 128	2.50 ± 0.39	22.0 ± 3.5	5.24 ± 0.17	2.49 ± 0.28	23.7 ± 1.7
PCB 138/163/164	15.2 ± 1.1	134 ± 10	35.7 ± 1.5	16.6 ± 1.6	131.5 ± 7.4
PCB 149	9.98 ± 0.27	87.6 ± 3.5	34.7 ± 0.4	9.23 ± 0.12	106.6 ± 8.4
PCB 151	2.91 ± 0.40	25.6 ± 3.6	10.9 ± 0.3		28.7 ± 5.2
PCB 153	16.54 ± 0.86	145.2 ± 8.8	56.9 ± 3.5	14.1 ± 1.0	213 ± 19
PCB 156	0.85 ± 0.11	7.4 ± 1.011	1.97 ± 0.11	0.96 ± 0.08	10.3 ± 1.1
PCB 170/190	0.63 ± 0.12	5.5 ± 1.4	2.37 ± 0.56	2.95 ± 0.23	40.6 ± 2.6
PCB 180	1.95 ± 0.43	17.1 ± 3.83	7.81 ± 0.63	6.79 ± 0.67	106.7 ± 5.3
PCB 183	1.82 ± 0.27	16.0 ± 2.47	5.25 ± 0.14	1.33 ± 0.10	36.6 ± 4.1
PCB 187/159/182	3.87 ± 0.27	34.0 ± 2.57	16.9 ± 1.3	4.76 ± 0.38	105.1 ± 9.1
PCB 194				28.9 ± 3.6	39.6 ± 2.5
PCB 195				9.63 ± 0.37	17.7 ± 4.3

[a]All concentrations are certified values except those in parentheses, which are reference values.

Table 6. Recertifications and Renewals of Previous Environmental Matrix SRMs

	Original Certification			New Certification		
	PAHs[a]	PCBs	Pesticides[a]	PAHs[a]	PCBs	Pesticides[a]
Recertifications						
SRM 1588a (1989 - 1998)[b]	0	5	10	0	25	14
SRM 1649a (1982 - 1998)	5 (9)	0	0	22 (22)	35	8(1)
SRM 1650a (1985 - 1999)	5 (6)	0	0	19 (25)	0	0
SRM 1939a (1990 - 1998)	-5	3 (12)	0	0	20 (4)	3
Renewals						
SRM 1941a (1989 - 1994)[c]	11 (24)	0 (15)	0 (7)	23 (14)	21 (7)	6 (4)
SRM 1974a (1990 - 1995)	9 (19)	0 (13)	0 (12)	15 (18)	20 (4)	7 (4)

[a]The first number indicates the number of certified constituents; the number in parenthesis indicates the number of noncertified or reference values.

[b]The first date indicate the year of the original certification and the second date is the year of the reissue of the material after recertification.

[c]The first date indicate the year of the original certification and the second date is the year of the issue of the renewal material.

REACTIVE SULFIDE ANALYSIS: A CASE STUDY IN AUDITING WASTE CHARACTERIZATION METHODOLOGIES

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ABSTRACT

The preparation and analysis of waste samples for reactive sulfides is defined in Chapter 7 of SW-846 as a "method-defined parameter where the analytical result is wholly dependent on the process used to make the measurement. ... Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods." Changes made to the analytical preparation or analysis method may result in improper waste characterization and disposal.

The study involved the evaluation of eight commercial laboratories providing waste stream characterization support for several industrial clientele. These laboratories received extensive full-day audits which included an evaluation of both method compliance and the actual step-by-step analyst techniques used for the sample preparation and analysis of reactive sulfides. Audits of the reactive sulfide methods revealed both significant method deviations and analyst error. Upon completion of the audits, a single-blind performance evaluation (PE) study was conducted to determine the accuracy of the laboratory-reported results when compared to known values.

The PE study was conducted for reactive sulfide using both an aqueous phase and a solid sulfide salt as PE samples. The PE study included a review of the reactive sulfide tests performed by SW-846 Chapter 7 preparation and analysis by Method 9034. The results of this study exhibited a wide range of reactive sulfide concentrations, some of which would have represented incorrect waste characterization if the PE samples were actual waste stream samples.

This paper will focus on a discussion of the laboratory audit results, method compliance issues, analyst technique, and a review of the PE sample results from these case studies.

INTRODUCTION

In an article in *Chemical and Engineering News* (July 20, 1998), it was announced that the US EPA is considering omitting reactivity from the regulatory requirements associated with waste characterization. Significant historical problems with the analytical methodology was cited as a reason for consideration of this action. The reactivity tests are currently performed by preparation of waste samples using the reaction procedure detailed in SW-846 Chapter 7. Upon completion of the reaction step, reactive sulfides are analyzed using SW-846 Method 9034 and reactive cyanides are analyzed using SW-846 Method 9012. Analytical results obtained for reactive sulfides are compared against the interim guideline of 500 mg/kg for total releasable sulfide. Concentrations of reactive sulfides in a waste sample that are greater than the interim guideline are considered hazardous, and disposal costs are significantly greater than those for wastes with concentrations less than the guidelines which are classified as non-hazardous.

A study was conducted by the authors that involved the evaluation of eight commercial laboratories providing waste stream characterization support for several industrial clientele. The first case study involved the remediation of a sludge basin at an industrial facility. Results of waste samples collected and submitted to several laboratories resulted in a significant disparity among the reported results. This study involved detailed on-site audits of three laboratories. The auditors witnessed the preparation and analysis of thoroughly homogenized split sludge samples at each of the three laboratories and noted significant differences in the method performed and varying degrees of compliance with the analytical methods. The second case study involved on-site audits of five commercial laboratories which are evaluated on a yearly basis as part of a corporate environmental laboratory program for waste characterization. In addition, these laboratories participated in a single-blind performance evaluation (PE) study which was performed to determine the accuracy of the laboratory-reported results when compared to known values.

PRELIMINARY CASE STUDY PREPARATION

Prior to conducting these case studies, detailed step-by-step auditing checklists were created based on a thorough review of the SW-846 Chapter 7 reaction method and SW-846 Method 9034. Since reactivity is defined in SW-846

Chapter 7 as a "a method-defined parameter," variances and interpretation afforded other SW-846 methodologies are not permitted. Therefore, these procedures require absolute compliance by the analytical laboratories and the auditors remained stringent to this requirement during the auditing process.

CASE STUDY NUMBER ONE: SLUDGE BASIN

On a recent project involving the remediation of a sludge basin at a large industrial facility, the authors were requested to identify the reasons for the significant disparity observed among split sample reactive sulfide results from several laboratories. For split sludge samples submitted to one laboratory, reactive sulfide results were consistently greater than 500 mg/kg (up to 2000 mg/kg). For split sludge samples submitted to another laboratory, reactive sulfide results were consistently less than 30 mg/kg. For the same sludge samples submitted to a third laboratory, reactive sulfide results were 300-600 mg/kg.

Because of the significant cost ramification of the hazardous classification due to reactive sulfides, it was important to identify the reasons for the discrepancies. Through detailed on-site audits of all three laboratories and witnessing the analysis of thoroughly homogenized split sludge samples at each of the three laboratories, a number of very interesting observations resulted. The reaction set-up for all three laboratories varied significantly for the supposedly "method-defined" parameter. The second laboratory, while performing the analysis adequately, was observed to have a low-bias for sulfide due to poor technique. One laboratory had not obtained a positive result for reactive sulfide from 1995 until the day of the on-site audit and witnessing of split sample analysis. On the day of the on-site audit, after implementing changes suggested by the auditor, this laboratory obtained results of 700-800 mg/kg; these results were comparable to the results obtained by the first laboratory on the same samples. Once these technique problems were resolved, the third laboratory's reactive sulfide results were comparable with the results of the other two laboratories.

The following method non-compliance issues were noted during the audits of these facilities.

Laboratory #1

Deviation from SW-846 Chapter 7.3.4

- The laboratory does not use a rotometer to monitor and control 60 mL/min of nitrogen, as stipulated in Chapter 7 of SW-846.

Laboratory #2

Deviations from SW-846 Chapter 7.3.4

- The laboratory utilizes 50 mL of 2.5N NaOH scrubber solution. SW-846 Chapter 7 stipulates 50 mL of 0.25N NaOH scrubber solution.
- The laboratory does not use a rotometer to monitor and control 60 mL/min of nitrogen, as stipulated in Chapter 7 of SW-846.

Deviations from SW-846 Method 9034

- For the "Standard Iodine Solution," the laboratory's SOP stipulates dissolving 20 to 25 g of KI and 3.2 g of iodine to 1 liter of reagent water. SW-846 Method 9034 stipulates the addition of 10 mL of 6N hydrochloric acid (HCl) to this reagent. The laboratory did not add HCl to the iodine solution.
- The laboratory utilized the prepared iodine solution in a reagent blank to perform the iodine standardization; however, SW-846 Method 9034 (Section 5.6) stipulates a very specific reagent to be prepared for the iodine solution standardization .
- The laboratory acidified the 100 mL of scrubber solution with 6N HCl and then poured the acidified scrubber on top of the iodine solution. SW-846 Method 9034 stipulates "[pipetting] the gas scrubber solution…keeping the end of the pipette below the surface of the iodine solution."

Laboratory #3

Deviations from SW-846 Chapter 7.3.4

- The laboratory utilizes 300 mL of 0.25N NaOH scrubber solution. SW-846 Chapter 7 stipulates 50 mL of 0.25N NaOH scrubber solution.
- The laboratory did not use a rotometer to monitor and control 60 mL/min of nitrogen, as stipulated in Chapter 7 of SW-846.
- The laboratory utilized 500 mL of 0.01N H_2SO_4 for sulfide reaction. SW-846 Chapter 7 stipulates adding "enough sulfuric acid to fill the (500 mL boiling) flask half full" (250 mL).

- The laboratory utilized SW-846 Method 9030 as the sulfide determinative step. SW-846, Chapter 7, stipulates the use of SW-846 Method 9034 exclusively.

Deviations from SW-846 Method 9034

- The analyst stated that the hydrogen sulfide standard solution is typically prepared every two months and stored in opaque brown plastic bottles at 4°C. SW-846, Method 9034, Section 5.7 states, "These standards are unstable and should be prepared daily." The analyst also indicated that he does not verify the hydrogen sulfide standard solution by direct titration techniques, and the true value is assumed to be the theoretical value. Similarly, the analyst indicated that he does not empirically determine the normality of the iodine solution; this determination is stipulated as a requirement in both SW-846 and the laboratory SOP.
- For the "Standard Iodine Solution," the laboratory's SOP stipulates dissolving 20 to 25 g of KI and 3.2 g of iodine to 1 liter of deionized water. SW-846 Method 9034 stipulates the addition of 10 mL of 6N HCl to this reagent. The laboratory does not add HCl to the standard iodine solution.
- The laboratory SOP does not include the preparation of the sodium sulfide nonanhydrate stock solution stipulated in Section 5.7 of SW-846 Method 9034.
- For titration, the laboratory utilized 200 mL of scrubber solution, 20 mL of iodine solution, and 8 mL of 6 N HCl (total of approximately 228 mL). SW-846 Method 9034 requires that after combining the aforementioned scrubber solutions and reagents the laboratories should "add enough reagent water to bring the volume to 100 mL."
- The laboratory poured the scrubber on top of the combined iodine/6N HCl solution. SW-846 stipulates "[pipetting] the gas scrubber solution…keeping the end of the pipette below the surface of the iodine solution."

ANALYST TECHNIQUE REVIEW

As previously discussed, method deviations may cause significant variances in obtaining results that are comparable among laboratories and quantitatively accurate based on the prescribed analytical methods. However, the actual laboratory techniques and procedures used by the analyst (which may not be method-defined) are as important as method compliance in obtaining quantitative results. Improper techniques can be the cause of significant problems when evaluating the comparability and usability of reactive sulfide data. Since these audits were performed when samples were actually being prepared and analyzed, the authors were able to evaluate each analyst's techniques in a step-by-step fashion.

The following are notable techniques observed during the audits of these facilities.

- Examination of one of the reaction glassware set-ups revealed a broken acid drop funnel connection which was Teflon®-taped at the glassware break.
- The analyst proceeded to add 10 mL of reagent water for the method blank and 5 mL of the sulfide spike solution (for the blank spike) to the respective open boiling flasks. At this point, the sodium hydroxide scrubber solution and 0.01N sulfuric acid had not been measured and poured into the appropriate vessels, nor had any glassware connections been made to minimize the time that samples would be exposed to the ambient air.
- The sample was mostly free liquids and the analyst used a stainless steel spatula to administer approximately 0.5 g at a time into the boiling flask which was positioned on its side. After achieving a weight of 13.3 g, it was apparent that a great deal of sample was adhering to the side walls of the boiling flask. This is problematic since the portion of sample coating the boiling flask walls does not directly react with the 0.01N sulfuric acid.
- It was noted that the stirring bars were already rigorously stirring the method blank, the blank spike, and sample, without any glassware connections having been made. As evident by the smell of sulfide, laboratory personnel acknowledged that the stirring bars should not be rotating until the system is closed and the sulfuric acid is dropped (also as specified in Section 7.5 of Chapter 7).
- The nitrogen gas flow was manually adjusted through the fritted glass connections immersed in the 50-mL scrubber solutions. (Another of the laboratories maintained on approximate rate of 90-0.25 inch N_2 gas bubble per minute.) Once the flow was adjusted, a vacuum pump was placed on the exit air connection. The observed pressure resulted in some of the glass connections separating to release pressure build-up. When the glassware joint connections appeared secure, the sulfuric acid was slowly dropped into the boiling flasks. Once the drop funnels were empty, final adjustments were made to the stirring bar and nitrogen flow, again resulting in pressure build-up and some of the glass connections separating to release pressure build-up. The separation resulted in loss of reaction gas for some of the reactions. In addition, one of the gas losses was observed to be from a cracked piece of glassware that clearly had observable gas bubbles being released from the crack. The analyst taped the cracked glassware with Teflon® tape to minimize the continued loss of reaction gas. Finally, it was observed that both samples coated the side-walls of the boiling flask.

- In the process of coordinating the shut-off of the nitrogen gas and the vacuum applied to the exit valve, the scrubber solution for one sample backed up into the reaction boiling flask.
- The samples were removed and diluted to volume with reagent water in volumetric flasks. The sealed flasks were inverted repeatedly to mix the solutions but in the process the scrubber solutions were purged with the oxygen present in the neck of the flasks. Each of the 500-mL aerated scrubber solutions were then poured into labeled disposable wide-mouth, 120-mL sludge cups, each with 1/4 - 1/2 inch of headspace, capped, and stored at 4°C until titration. The auditors noted that the excessive aeration of these final solutions caused a loss of sulfides, as evidence by the strong sulfide smell.

Titration of the Scrubber Solutions

- For the direct titration of the sulfide standard solution to empirically determine the "true" value of the prepared sulfide stock solution (without being processed through the reaction procedure), the analyst removed 5 mL of the stock standard and diluted this aliquot to 500 mL with reagent water. The analyst utilized a squirt bottle for this dilution and squirted the reagent with a fast stream directly down the center of the neck of the volumetric flask and directly into the sulfide standard/reagent water mixture. The fast stream of reagent water into the solution resulted in the generation of large purging bubbles that formed at the bottom of the open flask. The Laboratory QA Director also observed this procedure (as well as the evident smell of sulfides) in the ambient air.
- The analyst performing the titration opened one of the sludge cups containing the reagent blank and measured 100 mL of the solution using a glass graduated cylinder. The 100-mL of solution was then poured into a second fresh 120-mL wide-mouth sludge cup and acidified with 6N HCl (the sample is not pipetted under the surface of the iodine as required in Method 9034, Section 7.3.3).
- For all of the titrations, the rotation of the stirring bar applied by the analyst with the acidified, diluted scrubber solutions imparted a notably significant aerating vortex. For some of the sample titrations, the distinct smell of sulfide was noticeable prior to the actual titration of the acidified, diluted, vortexing scrubber solutions. Loss of sulfide gas prior to titration was clearly evident.
- Once each sample to be titrated was placed on the stirring plate and the stirring bar was rigorously rotated, the analyst added the starch indicator solution. This is not compliant with Method 9034, Section 7.3.6 which requires the titration of the scrubber solutions "...until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears."
- Upon addition of the scrubber solution into the initial 3 mL of iodine, it was observed that the iodine was totally consumed (the scrubber solutions went completely clear). For these samples, an additional 3 mL of iodine was added directly to the diluted acidified scrubber solutions. The additional iodine aliquots imparted a medium yellow color to the samples; however, the solutions were still not amber and additional iodine should have been added. (Method 9034, Section 7.3.3 requires iodine to be added until the amber color remains.)

ANALYTICAL RESULTS COMPARISON

The analysis for two site samples for reactive sulfides was performed by Laboratories #1 and #2 within a holding time of 7 days from sample collection. A quantitative comparison of the reported results is as follows:

Field Sample Designation	Laboratory #1 Results	Laboratory #2 Results
Sample A	968 mg/kg	449 mg/kg
Sample B	857 mg/kg	415 mg/kg

Regarding Laboratory #2's analysis of samples A and B, the results of the blank spike (13.9%) and the matrix spike (optimally, 17.6%) are clearly indicative of a reactive sulfide loss. The observed glassware reaction set-up, the observed unrefined laboratory sample handling techniques, and the numerous unnecessary scrubber solution agitations and transfers clearly demonstrated many opportunities for the loss of reactive sulfide during both the preparatory and determinative procedures applied by Laboratory #2

A second group of samples were analyzed by Laboratories #1 and #3. This sample analyses included the analysis of both raw sample provided to Laboratories #1 and #3 and analysis of several scrubber solutions previously prepared by Laboratory #1. This approach was conceived to determine at which point (during the reaction or titration step) reactive sulfide was being lost.

Field Sample Designation	Laboratory #1 Results of Raw Samples	Laboratory #3 Results of Raw Samples	Laboratory #3 Results of Scrubber Solutions
Sample C	1070 mg/kg	565 mg/kg	780 mg/kg
Sample C (Duplicate)	860 mg/kg	N/A	660 mg/kg

Regarding Laboratory #3's analysis of sample C, the results of the blank spike (66%) are clearly indicative of a reactive sulfide loss. The observations and discoveries made during the audit provide compelling evidence by which conclusions may be drawn. On the day of the audit of Laboratory #3 when the analyst prepared every reagent fresh (with the authors correcting the incorrect preparation of certain reagents) and performed the entire method step-by-step with the auditors present, the laboratory obtained its first reactive sulfide results >500 mg/kg since 1995 which were comparable to laboratory #1's results. These reactive sulfide results were obtained on investigative samples characterized by other laboratories to have been in excess of 500 mg/kg of reactive sulfide.

CASE STUDY NUMBER TWO: CORPORATE LABORATORY PROGRAM

The second case study involved the review of five commercial laboratories which are evaluated on a yearly basis as part of a Corporate Environmental Laboratory program. These laboratories also underwent detailed on-site audits. In addition, these laboratories participated in a single-blind performance evaluation (PE) study which was performed to determine the accuracy of the laboratory-reported results when compared to known values. Since these audits were not specific to the analysis of reactive sulfide as detailed in Case Study #1, analyst technique could not be evaluated on a step-by-step basis. However, method deviations were present at each laboratory audited. A summary of these finding is presented below.

SUMMARY OF AUDIT FINDINGS

- The volumes and concentrations of sodium hydroxide scrubber solution and sulfuric acid were not method compliant.
- The flow rate of nitrogen was not monitored to 60 mL/min using a rotometer, and the size of the bubbles varied between laboratories.
- The standardization of the potassium iodide solution and preparation of reagents used in the determinative step were not documented for each titration batch.
- Method detection limit studies were not previously performed.
- A method blank, MS/MSD, and an LCS were not performed with each batch of 20 samples.
- Hydrogen sulfide standards must be prepared (and documented) daily. Several laboratories were preparing the standard annually and preserving the solutions with zinc acetate.
- Several of the laboratories were not using the correct determinative step for analysis of reactive sulfides. Reactivity must be performed by SW-846 Method 9034 for sulfides.
- For titration of the reactive sulfides, the laboratory preserved the scrubber solution with zinc acetate. This preservation step is not a requirement of Method 9034.
- The analyst indicated that the scrubber solution is added to the flask for titration and the standardized iodine solution is pipetted on top of the solution. This procedure is not method-compliant.
- The analyst indicated that the starch solution is added prior to beginning the titration. This procedure is not method-compliant.
- Several of the analysts appeared to be improperly trained or to lack the knowledge and analytical techniques to adequately perform the analytical method.

As an additional step, the authors conducted a single-blind performance evaluation (PE) study to monitor laboratory performance. Single-blind PE samples were simultaneously submitted to the five participating laboratories being evaluated under this program. The PE samples were analyzed by each laboratory for reactive sulfide by SW-846 Chapter 7 preparation followed by analysis by Method 9034.

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 know the PE sample's true concentrations or results. A single-blind sample permits the data user to better understand a laboratory's accuracy and precision capabilities and to draw conclusions about the accuracy and precision of actual waste sample results.

The actual pure compounds used for the PE samples were chosen and prepared by Environmental Resource Associates (ERA) of Arvada, Colorado. Two PE samples were chosen for the analysis of reactive sulfide. One of the reactive sulfide samples was provided as an aqueous solution and the second reactive sulfide PE sample was provided as a gravimetrically determined sulfide salt contained in gelatin capsules. The capsule was to be placed in the reaction vessel and would dissolve in the weak acid solution used as a reagent in the SW-846 Chapter 7 reaction/preparation method. The expected concentrations were calculated by ERA based on the assumed 10-gram sample weight used for solid sample preparation and analysis.

A review of reactive sulfide results for all laboratories, except for Laboratory B, exhibited low to very low recoveries. It was noted in the laboratory audit reports for all participating laboratories that significant issues relating to method compliance were found by the authors during the on-site audits. Two laboratories are currently performing method certification studies; the PE samples arrived during this method certification period. The authors directed the laboratories to analyze the PE samples using the methods being certified with the understanding that the methods may not be fully implemented by the laboratory. Additional correspondence received from one laboratory indicated that the current reaction vessels being used are not of sufficient quality to maintain a leak tight seal under the pressure requirements of the methods; the lack of a tight seal results in the loss of reactive sulfide.

It should be noted that the recoveries of reactive sulfide reported by Laboratory C are extremely low and may represent a significant method or technique error by the analyst. The recoveries reported by Laboratory B appear to be bias very high and it is recommended that the laboratory review the calculations to determine if a reporting error occurred.

		Laboratory A		**Laboratory B**		**Laboratory C**		**Laboratory D**		**Laboratory E**	
Compound/ Analyte	***True Value***	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
Reactive Sulfide #1 (mg/l)	794	265	33.38%	1,250	157.43%	ND	o%	452	56.93%	520	65.49%
Reactive Sulfide #2 (mg/kg)											
Laboratory A	1,010	265	26.24%								
Laboratory B	984			1,870	190.04%						
Laboratory C	976					81.5					
Laboratory D	1,050							520	49.52%		
Laboratory E	1,010									690	68.32%

CONCLUSIONS

Based on the information obtained in these two case studies, it is evident that reactive sulfide analysis is being performed by some commercial laboratories in a manner that is not compliant as mandated in a "method-defined parameter." Laboratories that maintain strict adherence to the method, utilize correct techniques, and provide adequate training can obtain acceptable results for reactive sulfide. Based on the collective studies, it was observed that the analysis for reactive sulfides performed by one of the eight laboratories was method-compliant and that this laboratory had demonstrated the capability of producing high quality reactive sulfide data.

REFERENCES

United States Environmental Protection Agency. "Chapter Seven: Characteristics Introduction and Regulatory Definitions." Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, Update III, Office of Solid Waste, December 1996.

United States Environmental Protection Agency. "Method 9034: Titrimetric Procedure for Acid-Soluble and Acid Insoluble Sulfides." Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, Update III, Office of Solid.

LESSONS LEARNED FROM PERFORMANCE EVALUATION STUDIES

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ABSTRACT
Performance Evaluation (PE) samples are routinely utilized by both the regulatory and regulated communities to demonstrate a laboratory's proficiency in performing a given analytical method. PE samples are submitted to laboratories for a wide variety of regulatory programs and are typically prepared in deionized water, clean soil, or other prepared media. The laboratory's reported results are compared to the known identities and concentrations of target analytes in the PE samples. The evaluation of the laboratory's performance is typically based upon the percentage of analytes the laboratory successfully recovered within a defined range of acceptance limits. However, typically executed PE studies do not provide an indication of the laboratory's ability to successfully identify and quantitate target analytes in a complex matrix or test other non-analytical aspects of the laboratory's operation.

This presentation will focus on the authors' experience in conducting PE studies for a multi-state pipeline project and will present the findings relative to these studies. Information gleaned from the PE studies relative to the evaluation of the laboratory's performance will be discussed. Furthermore, observations regarding the laboratories' performance in analyzing multi-phasic samples will be presented.

INTRODUCTION
Performance Evaluation (PE) samples are test samples that are prepared by spiking known concentrations of select analytes into a well-characterized matrix. Typically, PE samples are made in a single matrix such as an aqueous, solid, or an oil matrix. PE samples can be distributed as single-blind or as double-blind samples. For single-blind PE samples, the laboratory is informed that they will be receiving a test sample. In the case of double-blind PE samples, the test samples are given fictitious sample identifications and are submitted concurrently with other project samples to the laboratory. That is, for double-blind PEs samples, the laboratory does not know that the fictitiously labeled PE sample is a test sample. Typically, PE samples are utilized to determine a laboratory's accuracy as it relates to the execution of a particular analytical methodology.

The authors have participated in the maintenance of a number of corporate laboratory programs in the capacity of performing quality assurance/quality control (QA/QC) oversight for these programs. In these roles, the authors have had experience in procuring, distributing, and evaluating the results from PE studies. However, this paper will focus on the lessons learned from one particular project.

As the QA/QC oversight contractor on a 19,000 mile pipeline that stretches across nine of the United States, quarterly PE samples have been submitted to the seven project laboratories for approximately three years. At the onset of the project, a laboratory specification manual was prepared that identified prescribed SW-846 preparative and analytical methods for the program execution. Where method ambiguities existed, program-specific method requirements were established. In addition, the laboratory specification manual listed the target analytes, associated reporting limits, QC requirements (including frequency, QC limits, acceptance criteria and corrective action), and data deliverable specifications (electronic and hard copy). By establishing a corporate laboratory specification manual that all seven project laboratories were required to follow, data inconsistencies were minimized and data comparability was enhanced.

Typically, PE samples are utilized to demonstrate method proficiency based upon the accuracy of the laboratory-reported results compared to the known certified values. However, more information can be gleaned from a PE study than a laboratory's demonstration of method proficiency, particularly in the case when a laboratory specification manual is utilized for a laboratory program and when full data package deliverables are requested to substantiate the reported analytical results. Information relative to the evaluation of the laboratory's technical and administrative services, sample login and receipt, data package preparation, method compliance, and quality assurance can also be evaluated.[1] In addition, in this particular project, the authors were able to utilize the ongoing PE studies to identify laboratory specific trends, program specific trends, and to determine overall precision amongst the project laboratories.[2] These trends have been utilized to provide feedback to the project laboratories to enhance their overall performance.

Careful consideration was given to the preparation of the PE samples for the subject project. The intent was to test the project laboratories' ability to analyze samples that were similar in matrix and composition to the project samples for the analyses of interest. As such, the PE samples were custom-prepared by a reputable PE vendor for the analytes of interest (volatiles, polyaromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and metals [including mercury]). The PE samples were soil samples that were carefully manufactured by mixing clay and sand in proper proportion and sieve size such that the real world matrix would be stable, homogeneous, and suitable for application of the spiked analytes. The PE samples were also moistened with deionized water to make a multi-phasic test sample (*viz*., moist soil). The analytes were spiked into the PE samples at a concentration roughly three to five times the reporting limits. The project reporting limits were based upon state cleanup action levels.

Since the PE samples were custom-made for the subject project, verification of the manufacturing process was important. Prior to distribution, the PE vendor verified (at their own production facility) that the recoveries of the spiked analytes in the PE samples were acceptable for distribution to the project laboratories. In addition to the distribution of the custom-made pre-moistened soil PE samples to the project laboratories, the PE samples were submitted to three referee laboratories, with one of these referee laboratories receiving the PE samples in triplicate. Use of the referee laboratories allowed for additional independent verification of the manufacturing process. It should be noted that the project laboratory specification manual was distributed to the referee laboratories to prescriptively follow for the analysis of the PE samples.

All PE samples were carefully shipped to the project laboratories and referee laboratories simultaneously. The PE samples were shipped via overnight courier in an iced cooler, under Chain-of-Custody. For single-blind PE sample rounds, the bottleware for the PE samples was provided by the PE provider. For double-blind PE sample rounds, the bottleware for the PE samples originated from the project laboratory via a request from the project sampling teams.

PE sample results are typically evaluated by comparing the laboratory-reported result to the certified true value and determining the accuracy of the reported analytical results as a percentage relative to the true or certified value. For the subject project, the PE sample results were evaluated in this manner and in two other ways. The first way was to compare the laboratory-reported result to the mean result of the referee laboratories and determine a percentage. The second way was to compare the laboratory-reported result to the historical average result and determine a percentage. The historical average result was based upon the large database of results obtained from the PE supplier for the analyte of interest from previous PE samples that they prepared and distributed in a similar manner.

The limits utilized for evaluating the PE samples were comparable to matrix spike limits typically observed for the analytical methods. That is, for the volatile organic analysis, the recovery limits of 70-130% were utilized. For the PAH analysis, recovery acceptance limits of 30-130% were utilized. For the PCB fraction, recovery acceptance limits of 60-130% were utilized. For the metals fraction, recovery acceptance limits of 75-125% were utilized. Finally, for the mercury fraction, recovery acceptance limits of 80-120% were utilized.

RESULTS

During the last two quarters of 1998, two single-blind PE sample studies were conducted for the subject project. The results for the two studies are tabulated as follows. The first table in each of the two PE studies is a comparison of the laboratory-reported results against the certified true value. The second set of tables in each of the two PE studies is a comparison of the laboratory-reported results against the mean referee-reported results. The third set of tables in each of the two PE studies is a comparison of the laboratory-reported results against the historical average (as previously discussed).

ROUND 1. Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	*True Value*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
benzene (µg/kg)	50	43	86.00%	51	102.00%	21	42.00%	26	52.00%	63	126.00%	37	74.00%	50	100.00%
1,1,1-trichloroethane (µg/kg)	75	62	82.67%	75	100.00%	29	38.67%	33	44.00%	79	105.33%	ND		27	36.00%
1,1,2,2-tetrachloro-ethane (µg/kg)	97	40	41.24%	92	94.85%	53	54.64%	76	78.35%	3		110	113.40%	45	46.39%
carbon tetrachloride (µg/kg)	79	53	67.09%	71	89.87%	30	37.97%	32	40.51%	63	79.75%	53	67.09%	33	41.77%
chlorobenzene (µg/kg)	63	58	92.06%	77	122.22%	27	42.86%	43	68.25%	72	114.29%	82	130.16%	59	93.65%
ethylbenzene (µg/kg)	25	24	96.00%	23	92.00%	10	40.00%	16	64.00%	31	124.00%	30	120.00%	24	96.00%
4-methyl-2-pentanone (µg/kg)	247	170	68.83%	230	93.12%	190	76.92%	110	44.53%	230	93.12%	290	117.41%	82	33.20%
tetrachloroethene (µg/kg)	44	45	102.27%	48	109.09%	18	40.91%	18	40.91%	51	115.91%	49	111.36%	48	109.09%
trichloroethene (µg/kg)	35	38	108.57%	57	162.86%	21	60.00%	20	57.14%	69	197.14%	31	88.57%	33	94.29%
total xylenes (µg/kg)	198	190	95.96%	260	131.31%	85	42.93%	130	65.66%	230	116.16%	267	134.85%	210	106.06%
Aroclor 1248 (µg/kg)	342	55	16.08%	310	90.64%	240	70.18%	200	58.48%	270	78.95%	329	96.20%	264	77.19%
anthracene (µg/kg)	3,510	71		880	25.07%	820	23.36%	82		500	14.25%	470	13.39%	1,300	37.04%
chrysene (µg/kg)	2,040	490	24.02%	1,300	63.73%	560	27.45%	170		840	41.18%	1,300	63.73%	1,500	73.53%
benzo(k)fluoranthene (µg/kg)	2,610	590	22.61%	1,700	65.13%	660	25.29%	160		1,400	53.64%	1,800	68.97%	2,100	80.46%
benzo(a)pyrene (µg/kg)	4,370	380		1,200	27.46%	750	17.16%	180		1,400	32.04%	1,000	22.88%	2,000	45.77%
indeno(1,2,3-cd)pyrene (µg/kg)	2,880	380	13.19%	1,100	38.19%	690	23.96%	180		710	24.65%	1,800	62.50%	2,000	69.44%
fluoranthene (µg/kg)	3,720	780	20.97%	2,000	53.76%	900	24.19%	370		1,100	29.57%	2,400	64.52%	2,600	69.89%
naphthalene (µg/kg)	4,600	1,300	28.26%	2,400	52.17%	1,500	32.61%	980	21.30%	1,800	39.13%	1,500	32.61%	2,700	58.70%
antimony (mg/kg)	135	32.0	23.70%	46.9	34.74%	57.5	42.59%	66.1	48.96%	31.3	23.19%	68.4	50.67%	47.0	34.81%
arsenic (mg/kg)	14.5	9.7	66.90%	14.7	101.38%	10.9	75.17%	14.5	100.00%	14.6	100.69%	16.4	113.10%	14.4	99.31%
barium (mg/kg)	496	280	56.45%	451	90.93%	359	72.38%	406	81.85%	348	70.16%	476	95.97%	401	80.85%
beryllium (mg/kg)	6.06	4.1	67.66%	5.8	95.71%	4.7	77.56%	5.9	97.36%	5.5	90.76%	6.3	103.96%	5.6	92.41%
cadmium (mg/kg)	21.3	12	56.34%	20.5	96.24%	14.3	67.14%	18.6	87.32%	10.4	48.83%	21.0	98.59%	17.5	82.16%
chromium (mg/kg)	234	150	64.10%	225	96.15%	182	77.78%	229	97.86%	204	87.18%	255	108.97%	220	94.02%
lead (mg/kg)	543	340	62.62%	505	93.00%	372	68.51%	501	92.27%	442	81.40%	555	102.21%	472	86.92%
mercury (mg/kg)	36.5	28.0	76.71%	21.6	59.18%	20.0	54.79%	34.3	93.97%	30.7	84.11%	34.5	94.52%	30.4	83.29%
nickel (mg/kg)	292	150	51.37%	269	92.12%	186	63.70%	241	82.53%	186	63.70%	273	93.49%	239	81.85%
silver (mg/kg)	413	140	33.90%	114	27.60%	275	66.59%	344	83.29%	275	66.59%	428	103.63%	233	56.42%

ROUND 1 (Cont.) Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	*Referee Mean*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
benzene (µg/kg)	28	43	153.57%	51	182.14%	21	75.00%	26	92.86%	63	225.00%	37	132.14%	50	178.57%
1,1,1-trichloroethane (µg/kg)	39	62	158.97%	75	192.31%	29	74.36%	33	84.62%	79	202.56%	ND		27	69.23%
1,1,2,2-tetrachloro-ethane (µg/kg)	51	40	77.97%	92	179.34%	53	103.31%	76	148.15%	3		110	214.42%	45	87.72%
carbon tetrachloride (µg/kg)	39	53	136.95%	71	183.46%	30	77.52%	32	82.69%	63	162.79%	53	136.95%	33	85.27%
chlorobenzene (µg/kg)	40	58	143.92%	77	191.07%	27	67.00%	43	106.70%	72	178.66%	82	203.47%	59	146.40%
ethylbenzene (µg/kg)	16	24	150.00%	23	143.75%	10	62.50%	16	100.00%	31	193.75%	30	187.50%	24	150.00%
4-methyl-2-pentanone (µg/kg)	90	170	188.89%	230	255.56%	190	211.11%	110	122.22%	230	255.56%	290	322.22%	82	91.11%
tetrachloroethene (µg/kg)	24	45	189.87%	48	202.53%	18	75.95%	18	75.95%	51	215.19%	49	206.75%	48	202.53%
trichloroethene (µg/kg)	21	38	183.57%	57	275.36%	21	101.45%	20	96.62%	69	333.33%	31	149.76%	33	159.42%
total xylenes (µg/kg)	138	190	137.98%	260	188.82%	85	61.73%	130	94.41%	230	167.03%	267	193.90%	210	152.51%
Aroclor 1248 (µg/kg)	242	55	22.73%	310	128.10%	240	99.17%	200	82.64%	270	111.57%	329	135.95%	264	109.09%
anthracene (µg/kg)	820	71		880	107.32%	820	100.00%	82	10.00%	500	60.98%	470	57.32%	1,300	158.54%
chrysene (µg/kg)	1,447	490	33.86%	1,300	89.84%	560	38.70%	170	11.75%	840	58.05%	1,300	89.84%	1,500	103.66%
benzo(k)fluoranthene (µg/kg)	1,737	590	33.97%	1,700	97.87%	660	38.00%	160		1,400	80.60%	1,800	103.63%	2,100	120.90%
benzo(a)pyrene (µg/kg)	1,755	380	21.65%	1,200	68.38%	750	42.74%	180	10.26%	1,400	79.77%	1,000	56.98%	2,000	113.96%
indeno(1,2,3-cd)pyrene (µg/kg)	1,575	380	24.13%	1,100	69.84%	690	43.81%	180	11.43%	710	45.08%	1,800	114.29%	2,000	126.98%
fluoranthene (µg/kg)	2,250	780	34.67%	2,000	88.89%	900	40.00%	370	16.44%	1,100	48.89%	2,400	106.67%	2,600	115.56%
naphthalene (µg/kg)	2,325	1,300	55.91%	2,400	103.23%	1,500	64.52%	980	42.15%	1,800	77.42%	1,500	64.52%	2,700	116.13%
antimony (mg/kg)	47	32.0	68.09%	46.9	99.79%	57.5	122.34%	66.1	140.64%	31.3	66.60%	68.4	145.53%	47.0	100.00%
arsenic (mg/kg)	12.1	9.7	80.17%	14.7	121.49%	10.9	90.08%	14.5	119.83%	14.6	120.66%	16.4	135.54%	14.4	119.01%
barium (mg/kg)	402	280	69.65%	451	112.19%	359	89.30%	406	101.00%	348	86.57%	476	118.41%	401	99.75%
beryllium (mg/kg)	5.40	4.1	75.93%	5.8	107.41%	4.7	87.04%	5.9	109.26%	5.5	101.85%	6.3	116.67%	5.6	103.70%
cadmium (mg/kg)	15.2	12	78.95%	20.5	134.87%	14.3	94.08%	18.6	122.37%	10.4	68.42%	21.0	138.16%	17.5	115.13%
chromium (mg/kg)	194	150	77.32%	225	115.98%	182	93.81%	229	118.04%	204	105.15%	255	131.44%	220	113.40%
lead (mg/kg)	476	340	71.37%	505	106.00%	372	78.09%	501	105.16%	442	92.78%	555	116.50%	472	99.08%
mercury (mg/kg)	34.5	28.0	81.16%	21.6	62.61%	20.0	57.97%	34.3	99.42%	30.7	88.99%	34.5	100.00%	30.4	88.12%
nickel (mg/kg)	208	150	72.18%	269	129.45%	186	89.51%	241	115.98%	186	89.51%	273	131.38%	239	115.01%
silver (mg/kg)	190	140	73.53%	114	59.87%	275	144.43%	344	180.67%	275	144.43%	428	224.79%	233	122.37%

NOTE:

ND - Not Detected.

ROUND 1 (Cont.) Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	*Historical Average*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
benzene (µg/kg)	51	43	84.81%	51	100.59%	21	41.42%	26	51.28%	63	124.26%	37	72.98%	50	98.62%
1,1,1-trichloroethane (µg/kg)	76	62	82.01%	75	99.21%	29	38.36%	33	43.65%	79	104.50%	ND		27	35.71%
1,1,2,2-tetrachloro-ethane (µg/kg)	100	40	40.20%	92	92.46%	53	53.27%	76	76.38%	3		110	110.55%	45	45.23%
carbon tetrachloride (µg/kg)	80	53	66.08%	71	88.53%	30	37.41%	32	39.90%	63	78.55%	53	66.08%	33	41.15%
chlorobenzene (µg/kg)	65	58	89.37%	77	118.64%	27	41.60%	43	66.26%	72	110.94%	82	126.35%	59	90.91%
ethylbenzene (µg/kg)	26	24	92.66%	23	88.80%	10	38.61%	16	61.78%	31	119.69%	30	115.83%	24	92.66%
4-methyl-2-pentanone (µg/kg)	264	170	64.39%	230	87.12%	190	71.97%	110	41.67%	230	87.12%	290	109.85%	82	31.06%
tetrachloroethene (µg/kg)	45	45	99.12%	48	105.73%	18	39.65%	18	39.65%	51	112.33%	49	107.93%	48	105.73%
trichloroethene (µg/kg)	34	38	111.44%	57	167.16%	21	61.58%	20	58.65%	69	202.35%	31	90.91%	33	96.77%
total xylenes (µg/kg)	207	190	91.79%	260	125.60%	85	41.06%	130	62.80%	230	111.11%	267	128.99%	210	101.45%
Aroclor 1248 (µg/kg)	287	55	19.16%	310	108.01%	240	83.62%	200	69.69%	270	94.08%	329	114.63%	264	91.99%
anthracene (µg/kg)	1,820	71		880	48.35%	820	45.05%	82		500	27.47%	470	25.82%	1,300	71.43%
chrysene (µg/kg)	1,510	490	32.45%	1,300	86.09%	560	37.09%	170	11.26%	840	55.63%	1,300	86.09%	1,500	99.34%
benzo(k)fluoranthene (µg/kg)	1,920	590	30.73%	1,700	88.54%	660	34.38%	160		1,400	72.92%	1,800	93.75%	2,100	109.38%
benzo(a)pyrene (µg/kg)	2,590	380	14.67%	1,200	46.33%	750	28.96%	180		1,400	54.05%	1,000	38.61%	2,000	77.22%
indeno(1,2,3-cd)pyrene (µg/kg)	2,330	380	16.31%	1,100	47.21%	690	29.61%	180		710	30.47%	1,800	77.25%	2,000	85.84%
fluoranthene (µg/kg)	2,610	780	29.89%	2,000	76.63%	900	34.48%	370	14.18%	1,100	42.15%	2,400	91.95%	2,600	99.62%
naphthalene (µg/kg)	2,460	1,300	52.85%	2,400	97.56%	1,500	60.98%	980	39.84%	1,800	73.17%	1,500	60.98%	2,700	109.76%
antimony (mg/kg)	42	32.0	76.19%	46.9	111.67%	57.5	136.90%	66.1	157.38%	31.3	74.52%	68.4	162.86%	47.0	111.90%
arsenic (mg/kg)	12.0	9.7	80.83%	14.7	122.50%	10.9	90.83%	14.5	120.83%	14.6	121.67%	16.4	136.67%	14.4	120.00%
barium (mg/kg)	451	280	62.08%	451	100.00%	359	79.60%	406	90.02%	348	77.16%	476	105.54%	401	88.91%
beryllium (mg/kg)	5.01	4.1	81.84%	5.8	115.77%	4.7	93.81%	5.9	117.76%	5.5	109.78%	6.3	125.75%	5.6	111.78%
cadmium (mg/kg)	18.1	12	66.30%	20.5	113.26%	14.3	79.01%	18.6	102.76%	10.4	57.46%	21.0	116.02%	17.5	96.69%
chromium (mg/kg)	220	150	68.18%	225	102.27%	182	82.73%	229	104.09%	204	92.73%	255	115.91%	220	100.00%
lead (mg/kg)	479	340	70.98%	505	105.43%	372	77.66%	501	104.59%	442	92.28%	555	115.87%	472	98.54%
mercury (mg/kg)	28.0	28.0	100.00%	21.6	77.14%	20.0	71.43%	34.3	122.50%	30.7	109.64%	34.5	123.21%	30.4	108.57%
nickel (mg/kg)	249	150	60.24%	269	108.03%	186	74.70%	241	96.79%	186	74.70%	273	109.64%	239	95.98%
silver (mg/kg)	340	140	41.18%	114	33.53%	275	80.88%	344	101.18%	275	80.88%	428	125.88%	233	68.53%

NOTE:

ND - Not Detected.

ROUND 2. Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	***True Value***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***	***Reported Value***	***Recovery***
benzene (µg/kg)	149	100	67.11%	84	56.38%	46	30.87%	110	73.83%	120	80.54%	76	51.01%	88	59.06%
chlorobenzene (µg/kg)	44	38	85.78%	31	69.98%	24	54.18%	36	81.26%	37	83.52%	28	63.21%	32	72.23%
1,2-dichloroethane (µg/kg)	78	68	87.63%	51	65.72%	34	43.81%	68	87.63%	74	95.36%	51	65.72%	54	69.59%
ethylbenzene (µg/kg)	108	87	80.56%	67	62.04%	44	40.74%	86	79.63%	85	78.70%	68	62.96%	70	64.81%
tetrachloroethene (µg/kg)	61	42	68.63%	33	53.92%	16	26.14%	30	49.02%	37	60.46%	21	34.31%	33	53.92%
toluene (µg/kg)	89	69	77.44%	58	65.10%	37	41.53%	72	80.81%	72	80.81%	57	63.97%	57	63.97%
1,1,2-trichloroethane (µg/kg)	53	52	98.30%	41	77.50%	32	60.49%	51	96.41%	46	86.96%	38	71.83%	38	71.83%
trichloroethene (µg/kg)	129	88	68.22%	69	53.49%	33	25.58%	83	64.34%	90	69.77%	61	47.29%	73	56.59%
total xylenes (µg/kg)	328	260	79.27%	200	60.98%	140	42.68%	240	73.17%	250	76.22%	210	64.02%	210	64.02%
Aroclor 1254 (µg/kg)	181	150	82.87%	130	71.82%	160	88.40%	110	60.77%	130	71.82%	140	77.35%	170	93.92%
benzo(b)fluroanthene (µg/kg)	4,240	3600	84.91%	2700	63.68%	3500	82.55%	670	15.80%	2900	68.40%	5,000	117.92%	3100	73.11%
benzo(k)fluoranthene (µg/kg)	1,910	1600	83.77%	1,200	62.83%	1400	73.30%	350	18.32%	1,500	78.53%	2,100	109.95%	1,400	73.30%
benzo(a)pyrene (µg/kg)	4,170	2900	69.54%	2,200	52.76%	2300	55.16%	470	11.27%	2,500	59.95%	3,800	91.13%	2,500	59.95%
chrysene (µg/kg)	2,420	2300	95.04%	1,700	70.25%	1700	70.25%	490	20.25%	1700	70.25%	2,700	111.57%	1,800	74.38%
fluorene (µg/kg)	3,290	2800	85.11%	2,300	69.91%	3000	91.19%	740	22.49%	2,800	85.11%	3,300	100.30%	2,600	79.03%
naphthalene (µg/kg)	3,780	2,400	63.49%	2,100	55.56%	2,100	55.56%	1000	26.46%	2,100	55.56%	2,300	60.85%	2,300	60.85%
phenanthrene (µg/kg)	1,570	1400	89.17%	1,100	70.06%	1400	89.17%	380	24.20%	1,400	89.17%	1,600	101.91%	1,200	76.43%
pyrene (µg/kg)	4,940	3900	78.95%	2,700	54.66%	4100	83.00%	1400	28.34%	3,600	72.87%	5,500	111.34%	3,500	70.85%
antimony (mg/kg)	65	0.0		58.3	90.11%	12.2	18.86%	19.4	29.98%	24	37.09%	24.2	37.40%	27.7	42.81%
arsenic (mg/kg)	23.2	21	90.52%	23.8	102.59%	21.7	93.53%	21.1	90.95%	20.8	89.66%	21.8	93.97%	24.2	104.31%
barium (mg/kg)	385	330	85.71%	351	91.17%	331	85.97%	346	89.87%	255	66.23%	413	107.27%	336	87.27%
beryllium (mg/kg)	18.20	15	82.42%	17.3	95.05%	16.6	91.21%	16.8	92.31%	11.9	65.38%	19.0	104.40%	18.1	99.45%
cadmium (mg/kg)	19.4	16	82.47%	19.4	100.00%	16.7	86.08%	17.6	90.72%	5.8	29.90%	23.3	120.10%	18.4	94.85%
chromium (mg/kg)	191	160	83.77%	190	99.48%	169	88.48%	178	93.19%	190	99.48%	181	94.76%	197	103.14%
lead (mg/kg)	511	410	80.23%	494	96.67%	426	83.37%	448	87.67%	391	76.52%	519	101.57%	480	93.93%
mercury (mg/kg)	25.0	17.0	68.00%	15.7	62.80%	24.7	98.80%	21.8	87.20%	18.4	73.60%	27.5	110.00%	25.9	103.60%
nickel (mg/kg)	222	170	76.58%	206	92.79%	186	83.78%	198	89.19%	66.8	30.09%	272	122.52%	219	98.65%
silver (mg/kg)	391	130	33.25%	164	41.94%	326	83.38%	339	86.70%	208	53.20%	333	85.17%	361	92.33%

ROUND 2 (Cont.) Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	*Historical Average*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
benzene (µg/kg)	152	100	65.79%	84	55.26%	46	30.26%	110	72.37%	120	78.95%	76	50.00%	88	57.89%
chlorobenzene (µg/kg)	45	38	83.70%	31	68.28%	24	52.86%	36	79.30%	37	81.50%	28	61.67%	32	70.48%
1,2-dichloroethane (µg/kg)	80	68	85.53%	51	64.15%	34	42.77%	68	85.53%	74	93.08%	51	64.15%	54	67.92%
ethylbenzene (µg/kg)	112	87	77.68%	67	59.82%	44	39.29%	86	76.79%	85	75.89%	68	60.71%	70	62.50%
tetrachloroethene (µg/kg)	63	42	66.88%	33	52.55%	16	25.48%	30	47.77%	37	58.92%	21	33.44%	33	52.55%
toluene (µg/kg)	90	69	76.41%	58	64.23%	37	40.97%	72	79.73%	72	79.73%	57	63.12%	57	63.12%
1,1,2-trichloroethane (µg/kg)	55	52	94.89%	41	74.82%	32	58.39%	51	93.07%	46	83.94%	38	69.34%	38	69.34%
trichloroethene (µg/kg)	127	88	69.29%	69	54.33%	33	25.98%	83	65.35%	90	70.87%	61	48.03%	73	57.48%
total xylenes (µg/kg)	342	260	76.02%	200	58.48%	140	40.94%	240	70.18%	250	73.10%	210	61.40%	210	61.40%
Aroclor 1254 (µg/kg)	150	150	100.00%	130	86.67%	160	106.67%	110	73.33%	130	86.67%	140	93.33%	170	113.33%
benzo(b)fluroanthene (µg/kg)	2,780	3600	129.50%	2700	97.12%	3500	125.90%	670	24.10%	2900	104.32%	5,000	179.86%	3100	111.51%
benzo(k)fluoranthene (µg/kg)	1,470	1600	108.84%	1,200	81.63%	1400	95.24%	350	23.81%	1,500	102.04%	2,100	142.86%	1,400	95.24%
benzo(a)pyrene (µg/kg)	2,470	2900	117.41%	2,200	89.07%	2300	93.12%	470	19.03%	2,500	101.21%	3,800	153.85%	2,500	101.21%
chrysene (µg/kg)	1,840	2300	125.00%	1,700	92.39%	1700	92.39%	490	26.63%	1700	92.39%	2,700	146.74%	1,800	97.83%
fluorene (µg/kg)	2,240	2800	125.00%	2,300	102.68%	3000	133.93%	740	33.04%	2,800	125.00%	3,300	147.32%	2,600	116.07%
naphthalene (µg/kg)	2,150	2,400	111.63%	2,100	97.67%	2,100	97.67%	1000	46.51%	2,100	97.67%	2,300	106.98%	2,300	106.98%
phenanthrene (µg/kg)	1,140	1400	122.81%	1,100	96.49%	1400	122.81%	380	33.33%	1,400	122.81%	1,600	140.35%	1,200	105.26%
pyrene (µg/kg)	3,550	3900	109.86%	2,700	76.06%	4100	115.49%	1400	39.44%	3,600	101.41%	5,500	154.93%	3,500	98.59%
antimony (mg/kg)	21	0.0		58.3	276.30%	12.2	57.82%	19.4	91.94%	24	113.74%	24.2	114.69%	27.7	131.28%
arsenic (mg/kg)	19.3	21	108.81%	23.8	123.32%	21.7	112.44%	21.1	109.33%	20.8	107.77%	21.8	112.95%	24.2	125.39%
barium (mg/kg)	350	330	94.29%	351	100.29%	331	94.57%	346	98.86%	255	72.86%	413	118.00%	336	96.00%
beryllium (mg/kg)	15.00	15	100.00%	17.3	115.33%	16.6	110.67%	16.8	112.00%	11.9	79.33%	19.0	126.67%	18.1	120.67%
cadmium (mg/kg)	16.5	16	96.97%	19.4	117.58%	16.7	101.21%	17.6	106.67%	5.8	35.15%	23.3	141.21%	18.4	111.52%
chromium (mg/kg)	180	160	88.89%	190	105.56%	169	93.89%	178	98.89%	190	105.56%	181	100.56%	197	109.44%
lead (mg/kg)	451	410	90.91%	494	109.53%	426	94.46%	448	99.33%	391	86.70%	519	115.08%	480	106.43%
mercury (mg/kg)	19.2	17.0	88.54%	15.7	81.77%	24.7	128.65%	21.8	113.54%	18.4	95.83%	27.5	143.23%	25.9	134.90%
nickel (mg/kg)	190	170	89.47%	206	108.42%	186	97.89%	198	104.21%	66.8	35.16%	272	143.16%	219	115.26%
silver (mg/kg)	322	130	40.37%	164	50.93%	326	101.24%	339	105.28%	208	64.60%	333	103.42%	361	112.11%

ROUND 2 (Cont.) Summary of Laboratory Results and Recoveries

		Lab A		Lab B		Lab C		Lab D		Lab E		Lab F		Lab G	
Compound/Analyte (reporting units)[4]	*Referee Mean*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*	*Reported Value*	*Recovery*
benzene (µg/kg)	118	100	84.75%	84	71.19%	46	38.98%	110	93.22%	120	101.69%	76	64.41%	88	74.58%
chlorobenzene (µg/kg)	44	38	85.78%	31	69.98%	24	54.18%	36	81.26%	37	83.52%	28	63.21%	32	72.23%
1,2-dichloroethane (µg/kg)	80	68	85.53%	51	64.15%	34	42.77%	68	85.53%	74	93.08%	51	64.15%	54	67.92%
ethylbenzene (µg/kg)	97	87	89.69%	67	69.07%	44	45.36%	86	88.66%	85	87.63%	68	70.10%	70	72.16%
tetrachloroethene (µg/kg)	45	42	93.75%	33	73.66%	16	35.71%	30	66.96%	37	82.59%	21	46.88%	33	73.66%
toluene (µg/kg)	83	69	82.83%	58	69.63%	37	44.42%	72	86.43%	72	86.43%	57	68.43%	57	68.43%
1,1,2-trichloroethane (µg/kg)	54	52	96.65%	41	76.21%	32	59.48%	51	94.80%	46	85.50%	38	70.63%	38	70.63%
trichloroethene (µg/kg)	92	88	95.65%	69	75.00%	33	35.87%	83	90.22%	90	97.83%	61	66.30%	73	79.35%
total xylenes (µg/kg)	295	260	88.14%	200	67.80%	140	47.46%	240	81.36%	250	84.75%	210	71.19%	210	71.19%
Aroclor 1254 (µg/kg)	183	150	81.97%	130	71.04%	160	87.43%	110	60.11%	130	71.04%	140	76.50%	170	92.90%
benzo(b)fluroanthene (µg/kg)	2,880	3600	125.00%	2700	93.75%	3500	121.53%	670	23.26%	2900	100.69%	5,000	173.61%	3100	107.64%
benzo(k)fluoranthene (µg/kg)	1,200	1600	133.33%	1,200	100.00%	1400	116.67%	350	29.17%	1,500	125.00%	2,100	175.00%	1,400	116.67%
benzo(a)pyrene (µg/kg)	2,220	2900	130.63%	2,200	99.10%	2300	103.60%	470	21.17%	2,500	112.61%	3,800	171.17%	2,500	112.61%
chrysene (µg/kg)	1,780	2300	129.21%	1,700	95.51%	1700	95.51%	490	27.53%	1700	95.51%	2,700	151.69%	1,800	101.12%
fluorene (µg/kg)	2,700	2800	103.70%	2,300	85.19%	3000	111.11%	740	27.41%	2,800	103.70%	3,300	122.22%	2,600	96.30%
naphthalene (µg/kg)	2,400	2,400	100.00%	2,100	87.50%	2,100	87.50%	1000	41.67%	2,100	87.50%	2,300	95.83%	2,300	95.83%
phenanthrene (µg/kg)	1,240	1400	112.90%	1,100	88.71%	1400	112.90%	380	30.65%	1,400	112.90%	1,600	129.03%	1,200	96.77%
pyrene (µg/kg)	3,760	3900	103.72%	2,700	71.81%	4100	109.04%	1400	37.23%	3,600	95.74%	5,500	146.28%	3,500	93.09%
antimony (mg/kg)	25	0.0		58.3	236.99%	12.2	49.59%	19.4	78.86%	24	97.56%	24.2	98.37%	27.7	112.60%
arsenic (mg/kg)	21.8	21	96.33%	23.8	109.17%	21.7	99.54%	21.1	96.79%	20.8	95.41%	21.8	100.00%	24.2	111.01%
barium (mg/kg)	344	330	95.93%	351	102.03%	331	96.22%	346	100.58%	255	74.13%	413	120.06%	336	97.67%
beryllium (mg/kg)	15.80	15	94.94%	17.3	109.49%	16.6	105.06%	16.8	106.33%	11.9	75.32%	19.0	120.25%	18.1	114.56%
cadmium (mg/kg)	17.4	16	91.95%	19.4	111.49%	16.7	95.98%	17.6	101.15%	5.8	33.33%	23.3	133.91%	18.4	105.75%
chromium (mg/kg)	170	160	94.12%	190	111.76%	169	99.41%	178	104.71%	190	111.76%	181	106.47%	197	115.88%
lead (mg/kg)	424	410	96.70%	494	116.51%	426	100.47%	448	105.66%	391	92.22%	519	122.41%	480	113.21%
mercury (mg/kg)	23.8	17.0	71.43%	15.7	65.97%	24.7	103.78%	21.8	91.60%	18.4	77.31%	27.5	115.55%	25.9	108.82%
nickel (mg/kg)	193	170	88.08%	206	106.74%	186	96.37%	198	102.59%	66.8	34.61%	272	140.93%	219	113.47%
silver (mg/kg)	290	130	44.83%	164	56.55%	326	112.41%	339	116.90%	208	71.72%	333	114.83%	361	124.48%

In the first PE study, some general observations can be made. Lower recoveries were observed for the volatile fraction for laboratory C, D, and G. In addition, the project laboratories had higher recoveries in the volatiles fraction than the referee laboratories. Furthermore, the recoveries of the PAH fraction were somewhat on the low side across all laboratories, with laboratory D exhibiting very low PAH recoveries (<10%). In addition, laboratory A exhibited a low recovery for the PCB fraction. Finally, the recoveries for antimony were observed to be low for both the project laboratories and the referee laboratories.

At the conclusion of the first PE study, sanitized versions of the PE study results were provided to the project laboratories as a mechanism for feedback. The project laboratories were requested to investigate the origin of the problem areas that were identified in the study and take appropriate corrective action to identify and correct the problem. In the second PE study, some general observations can be made. Lower recoveries were observed for the volatile fraction for laboratory C, G, B, and F. The recoveries of the PAH fraction were greatly improved from the previous round, with exception of laboratory D. Laboratory D still exhibited very low recoveries for the PAH fraction. In addition, the recoveries of the PCB fraction were within acceptance limits (as previously defined) for all project laboratories. Furthermore, the recoveries for antimony were observed to be low for both the project laboratories and the referee laboratories.

DISCUSSION

There are several reasons why a PE result could be outside the defined acceptance limits. First, there could be a laboratory performance issue. This is usually observed when one laboratory performs very differently than all of the other project laboratories for a given fraction or analyte. This was observed to be the case for laboratory D for the PAH fraction. Second, there could be a method limitation for analyzing a sample for a given analyte. This was observed to be the case for antimony where both the project laboratories and the referee laboratories exhibited low recoveries for both rounds of PE samples. Furthermore, there could be a PE vendor preparation issue. This is usually observed when all laboratories exhibit recoveries that are not within the defined acceptance range for most of the analytes in a fraction. This was not observed to be the case for any of the PE samples issued to the project laboratories.

LESSONS LEARNED/CONCLUSIONS

There were some inherent issues regarding the addition of water to the soil PE samples. Typically, dried, pulverized sands are utilized for the solid matrix PE samples. Laboratories that perform well on the analysis of dried solid PE samples do not necessarily perform well on the analysis of the multi-phasic PE samples (the latter being samples that typically are submitted for analysis during environmental investigations), particularly for the PAH fraction. Laboratories that utilized a single-solvent extraction for the preparation of the pre-moistened PAH soil PE samples exhibited low recoveries. Laboratories that utilized a 1:1 mixture of methylene chloride/acetone for the preparation of the pre-moistened PAH soil PE samples exhibited recoveries within the project-defined acceptance limits. Another lesson learned is that often times laboratories pay close attention to the instrumentation and data review but may not carefully evaluate the chemistry inherently embedded in the prescribed method. As such, laboratory results can exceed the defined acceptance limits. For instance, between the first PE round and the second PE round, laboratory A identified that their volumetric glassware had not been calibrated in the manufacturer's recommended frequency and the tolerance of the glassware they were using for the preparation of the PCB fraction was outside the tolerance specifications.

Another observation is that the percent moisture that is added to each fraction of the PE sample should be as consistent as possible. Often the laboratory will analyze an aliquot of sample from one of the designated analytical fractions for percent moisture and cross-apply that one determination to all fractions from dry-weight calculations. If the percent moisture is different for each fraction in the PE sample, the laboratory may unknowingly cross-apply an incorrect percent moisture to the other fractions. Similarly, it was observed that the addition of water to the volatile fraction of the soil PE sample resulted in a matrix that was not homogeneous. To overcome this problem that was identified through the course of the PE studies, it was determined that a special coring tool was required to properly subsample the volatile fraction of the PE sample to obtain acceptable (as previously defined) PE results.

REFERENCES

1. Dupes, L.J., and G.R. Rose. 1995. "Conducting a Performance Evaluation Study - It's Not Just Analytical Results." Eleventh Annual *Waste Testing & Quality Assurance Symposium*, Washington, DC.
2. Vitale, R.J. and R.L. Forman. 1998. "A Comparison Of Single-Blind Versus Double-Blind Performance Evaluation Sample Results From Commercial Environmental Laboratories." The 75th Annual American Institute of Chemists National Meeting. Philadelphia, PA.

A CONTAMINATED MARINE SEDIMENT STANDARD REFERENCE MATERIAL: SRM 1944, NEW YORK/NEW JERSEY WATERWAY SEDIMENT

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ABSTRACT

A Standard Reference Material (SRM) of contaminated marine sediment, SRM 1944 New York/New Jersey Waterway Sediment, was recently issued by the National Institute of Standards and Technology (NIST) with certified and reference values for over 100 organic and inorganic trace level constituents, along with total organic carbon, total extractable material, and particle-size characteristics. The sediment material, which was collected from multiple sites within the New York/New Jersey coastal waterways, has levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides that are a factor of 5 to 10 higher than the previously issued SRM 1941a, Organics in Marine Sediment. SRM 1944 is the first NIST natural matrix SRM with values assigned for selected dibenzo-*p*-dioxin and dibenzofuran congeners.

INTRODUCTION

For nearly two decades the National Institute of Standards and Technology (NIST) has been involved in the development of Standard Reference Materials (SRMs) for the determination of organic contaminants such as polycychc aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides in natural matrix environmental samples such as fossil fuels, air and diesel particulate material, coal tar, sediment, and mussel tissue[1-4]. Recently NIST issued a contaminated marine sediment, SRM 1944 New York/New Jersey Waterway Sediment, to meet the needs of laboratories involved in the testing of dredging materials from waterways and harbors of contaminants to determine the appropriate disposal methods.

ANALYTICAL APPROACH

The general approach for the value assignment of the PAHs, PCB congeners, and chlorinated pesticides in natural matrix SRMs has been described previously[1-3]. Briefly, the analytical approach for SRM 1944 consisted of combining results from analyses using several combinations of different extraction techniques (Soxhlet and pressurized fluid extraction) and extraction solvents, cleanup/isolation procedures (solid phase extraction and normal-phase liquid chromatography), and chromatographic separation and detection techniques. For PAH measurements reversed-phase liquid chromatography with fluorescence detection and gas chromatography/mass spectrometry (GC/MS) using three different stationary phase columns were used. For the determination of PCBs and pesticides, GC with electron capture detection and GC/MS on two different stationary phase columns were used. In addition, for the PCB congeners and chlorinated pesticides, results from 19 laboratories that participated in the 1995 NIST Intercomparison Exercise Program for Organic Contanrinants in the Marine Environment were used as part of the value assignment[4]. The value assignment for the concentrations of selected trace elements was accomplished by combining results from NIST [isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) or instrumental neutron activation analysis (INAA)], the National Research Council of Canada (NRCC) (ID-ICPMS, graphite furnace atomic absorption spectrometry, and inductively coupled plasma atomic emission spectrometry), the International Atomic Energy Agency (IAEA) (INAA), and seven selected laboratories using several different analytical techniques that participated in an interlaboratory comparison exercise coordinated by the NRCC[5]. Analytical measurements for the polychlorinated dibenzo-p-dioxins and dibenzofurans were the results of an interlaboratory comparison study among 14 laboratories coordinated by NIST and Environment Canada, Environmental Technology Centre, Analysis and Air Quality Division.

RESULTS AND DISCUSSION

The typical mode used at NIST for value assignment of natural matrix SRMs for organic contaminants has been the analysis of the material using two or more "chemically independent" analytical techniques. The results of these multiple technique analyses, if in agreement, are used to determine the "certified" concentrations for the measured analytes. The requirement for using two or more analytical techniques is based on the assumption that the agreement of the results from the independent methods minimizes the possibility of biases within the analytical methods. When results are obtained from only one analytical technique (or multiple techniques that are not sufficiently independent), the concentrations are typically reported as reference values and are considered as a best estimate of the true value. The

uncertainties associated with the reference values may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient agreement among multiple methods.

For value assignment for the PAHs, PCBs, and pesticides, the results from the various techniques (up to seven sets of data for each group of compounds) were combined to provide the certified values listed in Tables 1-3. For the 24 PAHs with certified values, the uncertainties range from 2% to 27% with 14 less than 10%. For the PCBs and pesticides, the uncertainties for the certified values range from 2% to 14% with the majority in the 4% to 8% range. Reference values are included in Table 3 for additional chlorinated pesticides. Reference values were also determined for 32 additional PAHs including a number of methyl- and dimethyl-substituted PAHs (values not shown). For the inorganic constituents in Table 4, the certified values were determined by combining results from one NIST method with results from several outside laboratories. The reference values in Table 4 were determined from results using only results from outside laboratories. Reference values for the concentrations of the seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners and the total tetra- through hepta- substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans were assigned by combining results from the analysis of SRM 1944 by 14 laboratories that participated in an interlaboratory comparison study (see Table 5). These reference values represent the first natural matrix NIST SRM with values assigned for natural levels of polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners. Reference values are also provided for total organic carbon (4.4% ± 0.3%), extractable mass (1.15 % ± 0.04%), and particle size characteristics. With over 100 certified and reference values, SRM 1944 is one of the most characterized natural matrix SRMs available.

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REFERENCES

1 . Wise, S.A., Schantz, M.M., Benner, B.A. Jr., Hays, M.J., and Schiller, S.B. *Anal. Chem.* 67, **1995,** 1171-1178.
2. Schantz, M.M., Demiralp, R., Greenberg, R.R., Hays, M.J., Parris, R.M., Porter, B.J., Poster, D.L., Sander, L.C., Schiller, S.B., Sharpless, K.S., and Wise, S.A. *Fresenius J. Anal. Chem.* 358, **1997,** 431-440.
3. Schantz, M.M., Koster, B.J., Oakley, L.M., Schiller, S.B., and Wise, S.A. *Anal. Chem.* 67, **1995,** 901-910.
4. Parris, R.M., Schantz, M.M., and Wise, S.A. NIST/NOAA *NS&T/EPA EMAP Intercomparison Exercise Program for Organic Contaminants in the Marine Environment: Description and Results of 1995 Organic Intercomparison Exercises,* NOAA Technical Memorandum NOS ORCA 104, Silver Spring, MD, Nov. 1996.
5. Willie, S. and Berman, S. *NOAA National Status and Trends Program Tenth Round Intercomparison Exercise Resultsfor Trace Metals in Marine Sediments and Biological Tissues,* NOAA Technical Memorandum NOS ORCA 106, Silver Spring, MD, Nov. 1996.
6. Paule, R.C. and Mandel, J. *J. Research NBS,* 87, **1982**, 377-385.
7. *Guide to the Expression of Uncertainty in Measurement,* ISBN 92-67-10188-9, 1st Ed. ISO, Switzerland, 1993.
8. *International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds,* North Atlantic Treaty Organization Committee on Challenges in the Modern Society, Report No. 176, North Atlantic Treaty Organization (NATO), Brussels, Belgium (1988).

Table 1. Certified Concentrations for Selected PAHs in SRM 1944

	mg/kg (dry-mass basis)[a]
Naphthalene	1.65 ± 0.31
Phenanthrene	5.27 ± 0.22
Anthracene	1.77 ± 0.33
Fluoranthene	8.92 ± 0.32
Pyrene	9.70 ± 0.42
Benzo[*c*]phenathrene	0.76 ± 0.10
Benz[*a*]anthracene	4.72 ± 0.11
Chrysene	4.86 ± 0.10

Table 1. Certified Concentrations for Selected PAHs in SRM 1944(continued)

	mg/kg (dry-mass basis)[a]
Triphenylene	1.04 ± 0.27
Benzo[*b*]fluoranthene	3.87 ± 0.42
Benzo[*j*]fluoranthene	2.09 ± 0.44
Benzo[*k*]fluoranthene	2.30 ± 0.20
Benzo[*a*]fluoranthene	0.78 ± 0.12
Benzo[*e*]pyrene	3.28 ± 0.11
Benzo[*a*]pyrene	4.30 ± 0.13
Perylene	1.17 ± 0.24
Benzo[*ghi*]perylene	2.84 ± 0.10
Indeno[1,2,3-*cd*]pyrene	2.78 ± 0.10
Dibenz[*a*, *j*]anthracene	0.500 ± 0.044
Dibenz[*a*, *c*]anthracene	0.335 ± 0.013
Dibenz[*a*, *h*]anthracene	0.424 ± 0.069
Pentaphene	0.289 ± 0.026
Benzo[*b*]chrysene	0.63 ± 0.10
Picene	0.518 ± 0.093

[a]The results are expressed as the certified value ± the expanded uncertainty. Each certified value is a mean of the means from two or more analytical methods, weighted as described in Paule and Mandel[6]. Each uncertainty, computed according to the CIPM approach as described in the ISO Guide[7], is an expanded uncertainty at the 95% level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values within which the true value is believed to lie, at a level of confidence of approximately 95%.

Table 2. Certified Concentrations for Selected PCB Congeners in SRM 1944

			µg/kg (dry-mass basis)[a]
PCB	8	(2,4'-Dichlorobiphenyl)	22.3 ± 2.3
PCB	18	(2,2',5-Trichlorobiphenyl)	51.0 ± 2.6
PCB	28	(2,4,4'-Trichlorobiphenyl)	80.8 ± 2.7
PCB	31	(2,4',5-Trichlorobiphenyl)	78.7 ± 1.6
PCB	44	(2,2'3,5'-Tetrachlorobiphenyl)	60.2 ± 2.0
PCB	49	(2,2'4,5'-Tetrachlorobiphenyl)	53.0 ± 1.7
PCB	52	(2,2',5,5'-Tetrachlorobiphenyl)	79.4 ± 2.0
PCB	66	(2,3',4,4'-Tetrachlorobiphenyl)	71.9 ± 4.3
PCB	95	(2,2',3,5',6-Pentachlorobiphenyl)	65.0 ± 8.9
PCB	87	(2,2',3,4,5'-Pentachlorobiphenyl)	29.9 ± 4.3
PCB	99	(2,2',4,4',5-Pentachlorobiphenyl)	37.5 ± 2.4
PCB	101	(2,2',4,5,5'-Pentachlorobiphenyl)	73.4 ± 2.5
	90		
PCB	105	(2,3,3',4,4'-Pentachlorobiphenyl)	24.5 ± 1.1
PCB	110	(2,3,3',4',6-Pentachlorobiphenyl)	63.5 ± 4.7
PCB	118	(2,3',4,4',5-Pentachlorobiphenyl)	58.0 ± 4.3
PCB	128	(2,2',3,3',4,4'-Hexachlorobiphenyl)	8.47 ± 0.28
PCB	138	(2,2',3,4,4',5'-Hexachlorobiphenyl)	62.1 ± 3.0
	163	(2,3,3',4'5,6-Hexachlorobiphenyl)	
	164	(2,3,3',4',5',6-Hexachlorobiphenyl)	

Table 2. Certified Concentrations for Selected PCB Congeners in SRM 1944 (continued)

			µg/kg (dry-mass basis)[a]
PCB	149	(2,2',3,4',5',6-Hexachlorobiphenyl)	49.7 ± 1.2
PCB	151	(2,2',3,5,5',6-HexacWorobiphenyl)	16.93 ± 0.36
PCB	153	(2,2',4,4',5,5'-Hexachlorobiphenyl)	74.0 ± 2.9
PCB	156	(2,3,3',4,4',5-Hexachlorobiphenyl)	6.52 ± 0.66
PCB	170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)	22.6 ± 1.4
	190		
PCB	180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)	44.3 ± 1.2
PCB	183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)	12.19 ± 0.57
PCB	187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)	25.1 ± 1
	159	(2,3,3',4,5,5'-Hexachlorobiphenyl)	
	182	(2,2',3',4,4',5,6'-Heptachlorobiphenyl)	
PCB	194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl)	11.2 ± 1.4
PCB	195	(2,2',3,3',4,4',5,6-Octachlorbiphenyl)	3.75 ± 0.39
PCB	206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl)	9.21 ± 0.51
PCB	209	Decachlorobiphenyl	6.81 ± 0.33

[a]See uncertainty statement for Table 1.

Table 3. Certified and Reference Concentrations for Selected Chlorinated Pesticides in SRM 1944

Certified Values[a]	µg/kg (dry-mass basis)
Hexachlorobenzene	6.03 ± 0.35
cis-Chlordane (α-Chlordane)	16.51 ± 0.83
trans-Nonachlor	8.20 ± 0.51
4,4'-DDT	119 ± 11I
Reference Values[b]	
α-HCH	2.0 ± 0.3
trans-Chlordane (γ-Chlordane)	8 ± 2
cis-Nonachlor	3.7 ± 0.7
2,4'-DDE	19 ± 3
2,4'-DDD	38 ± 8
4,4'-DDE	86 ± 12
4,4'-DDD	108 ± 16

[a]The results are expressed as the certified value ± the expanded uncertainty. Each certified value is a mean of the means from two or more analytical methods, weighted as described in Paule and Mandel[6]. Each uncertainty, computed according to the CIPM approach as described in the ISO Guide[7], is an expanded uncertainty at the 95% level of confidence, which includes random sources of uncertainty within each analytical method as well as uncertainty due to the drying study. The expanded uncertainty defines a range of values within which the true value is believed to lie, at a level of confidence of approximately 95%.

[b]The reference value for each analyte is the equally-weighted mean of the means from two or more analytical methods or the mean from one analytical technique. The uncertainty in the reference value defines a range of values that is intended to function as an interval that contains the true value at a level of confidence of 95%. This uncertainty includes sources of uncertainty within each analytical method, among methods, and from the drying study.

Table 4. Certified and Reference Concentrations for Selected Inorganic Constituents in SRM 1944

Certified Values (mg/kg, unless noted)[a]

Aluminum	5.33 ± 0.49(%)	Lead	330 ± 48
Arsenic	18.9 ± 2.8	Manganese	505 ± 25
Cadmium	8.8 ± 1.4	Nickel	76.1 ± 5.6
Chromium	266 ± 24	Silver	6.4 ± 1.7
Iron	3.53 ± 0.16(%)	Zinc	656 ± 75

Reference Values (mg/kg, unless noted)[a]

Antimony	4.6 ± 0.9	Rubidium[b]	75 ± 2
Beryllium	1.6 ± 0.3	Scandium[b]	10.2 ± 0.2
Bromine	86 ± 10	Selenium	1.4 ± 0.2
Calcium[b]	1.0 ± 0.1 (%)	Silicon	31 ± 3 (%)
Cesium[b]	3.0 ± 0.3	Sodium[b]	1.9 ± 0.1 (%)
Chlorine[b]	1.4 ± 0.2(%)	Thallium	0.59 ± 0.1
Cobalt	14 ± 2	Tin	42 ± 6
Copper	380 ± 40	Titanium[b]	4300 ± 300
Mercury	3.4 ± 0.5	Vanadium[b]	100 ± 9
Potassium[b]	1.6 ± 0.2(%)		

[a]The results are expressed as the certified (or reference) value ± the expanded uncertainty. The certified (or reference) value is based on the mean of available results from: (1) the mean of NIST INAA or ID-ICPMS analyses, (2) the mean of two methods performed at NRC, and (3) the mean of results from seven selected laboratories participating in the NRC intercomparison exercise, and (4) the mean results from INAA analyses at IAEA. The expanded uncertainty in the certified value is equal to $U = k u_c$ where u_c is the combined standard uncertainty and k is the coverage factor, both calculated according to the ISO Guide[24]. The value of u_c is intended to represent at the level of one standard deviation the combined effect of all the uncertainties in the certified value. Here u_c accounts for both possible method biases, within-method variation, and material inhomogeneity. The coverage factor, *k,* is the Student's t-value for a 95 % confidence interval with the corresponding degrees of freedom. Because of the material inhomogeneity, the variability among the measurements of multiple samples can be expected to be greater than that due to measurement variability alone.

[b]This reference value is based only on NIST INAA measurements.

Table 5. Reference Concentrations for Selected Dibenzo-*p*-dioxin and Dibenzoluran Congeners in SRM 1944

	µg/kg (dry-mass basis)[a]
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	0.133 ± 0.009
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	0.019 ± 0.002
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	0.026 ± 0.003
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	0.056 ± 0.006
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	0.053 ± 0.007
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	0.80 ± 0.07
Octachlorodibenzo-*p*-dioxin	5.8 ± 0.7
2,3,7,8-Tetrachlorodibenzofuran	0.039 ± 0.015
1,2,3,7,8-Pentachlorodibenzofuran	0.045 ± 0.007
2,3,4,7,8-Pentachlorodibenzofuran	0.045 ± 0.004
1,2,3,4,7,8-Hexachlorodibenzofuran	0.22 ± 0.03
1,2,3,6,7,8-Hexachlorodibenzofuran	0.09 ±0.01
2,3,4,6,7,8-Hexachlorodibenzofuran	0.054 ± 0.006

Table 5. Reference Concentrations for Selected Dibenzo-*p*-dioxin and Dibenzoluran Congeners in SRM 1944 (continued)

	µg/kg (dry-mass basis)[a]
1,2,3,7,8,9-Hexachlorodibenzofuran	0.019 ± 0.018
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.0 ± 0.1
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.040 ± 0.006
Octachlorodibenzofuran	1.0 ± 0.1
Total Toxic Equivalents (TEQ)[b]	0.25 ± 0.01
Total Tetrachlorodibenzo-*p*-dioxins	0.25 ± 0.05
Total Pentachlorodibenzo-*p*-dioxins	0.19 ± 0.06
Total Hexachlorodibenzo-*p*-dioxins	0.63 ± 0.09
Total Heptachlorodibenzo-*p*-dioxins	1.8 ± 0.2
Total Tetrachlorodibenzofurans	0.7 ± 0.2
Total Pentachlorodibenzofurans	0.74 ± 0.07
Total Hexachlorodibenzofurans	1.0 ± 0.1
Total Heptachlorodibenzofurans	1.5 ± 0.1
Total Dibenzo-*p*-dioxins[c]	8.7 ± 0.9
Total Dibenzofurans[c]	5.0 ± 0.5

[a]Each reference value is the mean of the results from up to 14 laboratories participating in an interlaboratory exercise. The expanded uncertainty in the reference value is equal to $U = k u_c$ where u_c is the combined standard uncertainty calculated according to the ISO Guide[8] and *k is* the coverage factor. The value of u_c is intended to represent at the level of one standard deviation the combined effect of all the uncertainties in the reference value. Here u_c is the uncertainty in the mean arising from the variation among the laboratory results. The degrees of freedom is equal to the number of available results minus one. The coverage factor, *k, is* the value from a student's t-distribution for a 95 % confidence interval .

[b]TEQ is the sum of the products of each of the 2,3,7,8-substituted congeners multiplied by their individual toxic equivalency factors recommended by the North Atlantic Treaty Organization[9]

[c]Total of tetra- through octachlorinated congeners.

AN APPLICATION OF USEPA'S DATA QUALITY OBJECTIVE PROCESS

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ABSTRACT

The United States Environmental Protection Agency (USEPA) states that all collected data have error, no one can afford absolute certainty about the data, and uninformed decisions associated with data collection tend to be conservative and expensive.[1] The USEPA proposed that, before an environmental data collection project begins, criteria should be established for decision making that is defendable. To accomplish this, the USEPA developed the data quality objective, or DQO, process. This is a systematic planning tool used to establish criteria for data quality, to define tolerable error rates and to develop a data collection design. Gathering the information for the DQO process is time-consuming and may negatively impact the project budget and schedule. Therefore, a computerized worksheet that summarizes the DQO steps was developed and distributed for review by a team of consultant specialists.

Based on comments received from the consultant specialists, the limitations of the DQO process, from the consultant's aspect, were outlined. This paper presents a streamlined approach to the DQO process, involving use of a computerized worksheet to aid a project team through the DQO process. Comments pertaining to the worksheet and the DQO process, which were solicited from the consultant specialists, are described, including the limitations outlined by the consultant specialists.

INTRODUCTION

The Quality Assurance Management Staff (QAMS) of the USEPA developed the DQO process to improve effectiveness, efficiency, and defensibility of decisions related to environmental data collection, while minimizing expenditures by eliminating unnecessary duplication or overly precise data.[2] The DQO process is presented in the USEPA's *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, EPA/600/R-96/055, September 1994. The DQO process results in qualitative and quantitative statements that are developed through a multi-step process that includes the following:

- Step 1. State the problem to be resolved. Identify the team members, the general problem, the project budget, the time for the study, and the social/political issues that may impact the project.
- Step 2. Identify the decision to be made. Identify the main issue to be resolved, the alternative actions that would result from each resolution, and the specific decision statement that must be resolved to address the project problem.
- Step 3. Identify the inputs to the decision. Identify the variables to be measured and the basis for the action level.
- Step 4. Define the boundaries of the study. Define the geographical area, the media of concern, the homogeneous strata, the time frame, the start and ending time periods, the scale of the decision, and the practical constraints for the project.
- Step 5. Develop a decision rule. The decision rule involves the population parameter of interest, the scale of the decision making, the action level, and the alternative action. Develop the test of the hypothesis and decision error.
- Step 6. Specify the tolerable limits on decision errors. Determine the consequences of each decision error, the quantitation limits of the error, the range of the parameter of interest, the grey region, and the acceptable probability of committing decision errors, or how much error is acceptable before the data becomes unusable.
- Step 7. Optimize the design for obtaining the data. Choose a sampling design that meets the DQO requirements and the budget.

The statements from the DQO process are summarized and presented in the Project Management Section A5 of the Quality Assurance Project Plan (QAPP).

CONSULTANT SPECIALISTS FEEDBACK

Since each step of the DQO process is critical in choosing a sampling design, electronic worksheets that prompt team members for responses were developed, in order to efficiently and cost effectively gather the information for each step from busy and remotely located consultant specialists. Examples of appropriate responses to each request were included in the worksheets. The electronic worksheets were distributed to a team of consultant specialists in the environmental consulting firm. The consultant specialists consisted of project managers, risk assessors, quality control officers, project officers, hydrogeologists, field samplers, and data validators. Comments, which were based on practical experience in the environmental field, were obtained from each of the consultant specialists.

In general, the initial response from the team to the DQO process worksheets was positive. The team indicated that the process of gathering project information together in a form that can be shared with the project team early on is very critical, and is not always done properly or completely. This worksheet could be used to effectively accomplish this task. Several comments received from the team requested clarification of some of the steps or that additional information be requested in the steps. Based on these responses, the worksheets were modified. However, the team had significant concerns with the DQO process, as formulated, since this process anticipates having an idealized situation for an environmental project. The process appears to be relatively in-flexible with respect to application of the process to real-life situations involving consent order schedules, information gaps, large number of target constituents, and tight budgets. The team indicated that picture-perfect projects that neatly fit the requirements of this process rarely occur.

The following sections present some of the comments received from the various consultant specialists.

Comment: The consultant specialists were unsure about how the worksheets would be used if little background data, such as the target compounds to be measured, is known.
Resolution: The worksheets may not be applicable to projects where information is not known. A statement to this effect was added to the introduction.

Comment: Decision errors are typically not evaluated. Rather, if sample data is questionable, the data is validated, and samples are recollected and reanalyzed. In addition, sufficient number of samples is collected to support the project decision.
Resolution: The goal of the USEPA is to minimize costs related to data collection by decreasing unnecessary duplication samples, and overly precise data. Utilizing the DQO process may help to decrease the number of samples collected, thereby decreasing costs. A statement to this effect was added to the introduction.

Comment: The consultant specialists commented that following the worksheets alone to develop a sampling design for a project could potentially leave out important issues. The worksheets attempt to put the real world in an organized box. This structured approach typically does not work in environmental projects.
Resolution: Environmental professionals, who can use a broad breath of knowledge, experience, and complex data to solve DQO problems, are needed to evaluate the information in the worksheets. The worksheets are to only be used as a guide to gather the information and the DEFT software is only used to evaluate the feasibility of the chosen sampling design. The professionals must choose the sampling design that meets the DQO needs based on the information gathered. A statement to this effect was added to the introduction.

Comment: Some of the consultant specialists may not be able to provide information requested by the DQO Steps.
Resolution: The worksheets would be distributed to a core group of consultant specialists, consisting of the project manager, the risk assessor(s), and the Quality Assurance Officer, for completion. After the worksheets are completed, the remaining consultant specialists would receive a copy for information purposes. Asterisks indicated the consultant specialists identified as responsible for completing the worksheet.

Comment: Step 1 should include the regulatory agencies and the client name.
Resolution: These requests were added to Step 1.

Comment: Less time should be spent on the alternative actions requested in Step 2B since these actions are often not relevant until a basic understanding of the site has been developed.
Resolution: The assumption is that the background information is available to the project team. A statement to this effect was added to the introduction.

Comment: There may be several variables identified in Step 3.
Resolution: The worksheets are intended to be used for only one constituent. Separate worksheets must be used for each constituent for a project. A statement to this effect was added to the introduction.

Comment: The action levels may not be defined until the risk assessment has been performed.
Resolution: It is assumed that the action levels are fixed such as regulatory thresholds and standards. A statement to this effect was added to Step 3.

Comment: The information requested in Step 3B, the basis for the action levels require prior agreement between the consultant and the client before the action levels can be presented in a QAPP.
Resolution: The action levels that will be used to evaluate the sample data are critical to a project, and should always be included in the QAPP. If the action levels are not established, the methods that can provide method detection limits that are appropriate for the action levels may not be chosen. In addition, the data user may compare the sample results to incorrect action levels, resulting in incorrect decisions being made and the need for resampling. The importance of the action level was noted in Step 3B.

Comment: The information requested in Step 4 fails to consider the complexities of sampling soil, groundwater, sediment, and surface water, potential sources, and how contaminants reside in subsurface soil. Without considering these observations, the quality of the investigation may be low.
Resolution: The DQO software makes assumptions that there are no temporal issues associated with the project, and that the sample locations can be randomized. The DQO process and software is to be used only to evaluate the feasibility of a sample design. Statements to this effect were added to Step 7.

Comment: The significance of the y-axis in the decision performance goal diagram and how the limits of tolerable probability are established are unclear.
Resolution: The y-axis represents the probability that a decision error will be made; deciding that the parameter of

interest is on one side of the action level when the true value is on the other side of the action level. The grey area is where the consequences of a decision error are minimal. Below the action level, a decision error will result in unneeded actions and increased costs. Above the action level, error will result in human health and environmental hazard issues. The probability of decision error is set above and below the grey area to indicate the tolerable error limits. The limits of tolerable probability are established by the project team. Clarification of these issues was presented in Steps 6A and 6B.

Comment: The worksheets are not clear with respect to how the DQO outputs are incorporated into the sampling design.
Resolution: Step 7 was expanded to demonstrate how the DQO outputs were utilized to choose the sampling design.

Comment: The worksheets don't explain how information from the DQO process is added to the QAPP.
Resolution: The DQO process results in qualitative and quantitative statements summarizing the project objective, which are added to Section A5, Problem Definition and Background, of the QAPP. An example of the information added to the project QAPP was added to Section 7, and a statement to this effect was added to the introduction.

Based on the previously discussed comments, the worksheets were edited. The final version of the worksheets, with edits in bold print, is presented at the end of the paper. An example of the Decision Performance Goal Diagram from the DEFT program is presented at the end of the paper.

CONCLUSION

The DQO process, as presented in USEPA Guidance for the Data Quality Objectives Process, EPA QA/G-4, is a good planning tool for environmental projects. Electronic worksheets that summarize the various inputs required for the DQO steps help to decrease the time required from each team member for the information gathering process.

After review by the consultant specialist team, it was determined that there are limitations associated with the DQO process. All consultant specialists agreed that the process of gathering and clarifying important project information, including the action level, that is requested by the DQO process, and having this summarized for consultant specialists before the project begins, is advantageous. However, the remaining steps of the DQO process may not be applicable to all projects. In some cases, historical background is not available, and there is an abundance of target analytes. The application of the remaining steps of the DQO process under these circumstances would lead to increased time and budget demands which would not be beneficial to the overall project.

The team also concluded that only a core team of consultant specialists would be responsible for filling out the worksheets. Also, the DQO process makes assumptions, including that there are no temporal issues associated with the project and that the sample locations can be randomized. The team also noted that the DQO process is only to be used as a guide to determine the sampling design. Environmental professionals, who can use a broad breath of knowledge and experience, are needed to evaluate the information in the worksheets. The DEFT software is only used to evaluate the feasibility of the chosen sampling design. The professionals must choose the sampling design that meets the DQO needs based on the information gathered. These limitations must be considered when implementing the DQO process.

Data Quality Objective Worksheet 1999

This worksheet is a project-planning tool, based on the Data Quality Objective (DQO) process, presented in USEPA QA/G-4. This process is used to establish criteria for data quality and sampling designs **for each constituent at the site**, so that decisions made are reasonable, defendable, and represent a logical approach to solving the project problem**, while minimizing unnecessary duplication or overly precise data**. This worksheet should be used to organize project information and is intended to be **used in projects for which the basic site problem is known and background information is available to the project team. The DQO process results in qualitative and quantitative statements that are presented in the project QAPP. This worksheet, along with experience, should be used by professionals to establish the data quality and sampling design.**

The steps of the DQO process are presented as well as examples of appropriate responses to each request.

Please fill out appropriate steps and return to K. Storne within 5 working days.

Example provided: Investigation of possible soil contamination with trichloroethene (TCE). Early sampling activities indicate that there is a low concentration area (0-50 ppm) and a high concentration area (0-80 ppm); TCE is not detected off-site; Future land use is residential; Total budget is $100,000; Remediation must take place within one year.

Step 1. State the problem to be resolved:
A. Who are the team members? (* indicates member responsible for completing worksheet)
Project Manager*_____Risk Assessor*_____
Quality Control Officer*_____Data Validator_____
Data User_____Laboratory Project Manager_____
Field sampler_____**Client** _____
Regulatory agencies_____
B. What is the general problem? (Contamination of TCE in soil. Affects human health and the environment. Low activity area is 0-50 ppm and high activity area is 0-80 ppm) _____
C. What project budget is available? ($100,000) _____
D. What time is available? (One year for remediation) _____
E. What social/political issues have an impact? (Future land use is residential.) _____

Step 2. Identify the decision to be made:
A. What is the main issue to be resolved? (Does the TCE contamination pose unacceptable danger to human health or the environment?) _____
B. Specify alternative actions that would result from each resolution. (ActionA – Remediate soil; Action B – Do not remediate soil) _____
C. Combine main issue and the alternative actions into a specific decision statement that must be resolved to address the problem: (Determine whether or not TCE contamination in soil poses a danger that requires remediation) _____

Step 3. Identify inputs for the decision:
A. What are the variables/characteristics to be measured? (TCE) _____
B. What is the basis for the action **level (regulatory threshold or standard), that must be established and included in the QAPP before sample collection?** (Risk assessor/toxicologist set site-specific exposure assessment at 50 ppm) _____

Step 4. Define the boundaries of the investigation:
A. What are the spacial boundaries?
1. What is the geographical area? (property boundary; none detected off site) _____
2. What is the media of concern? (TCE in surface soil to depth of 15cm) _____
3. What are the homogeneous strata? (Area of high concentration to 80 ppm, area of low concentration to 50 ppm)
B. What are the temporal boundaries?
1. What is the time frame? (Results represent future conditions at sites) _____
2. When will the investigation start and end? (Starts in 1 month and ends in 1 year) _____
C. What is the scale of decision to be made? (For each residential lot-sized acre.) _____
D. What are the practical constraints on data collection? (Existing structures exist) _____

Step 5A. Develop a decision rule or if/then statement that includes:
1. The population parameter of interest (do not consider sample depth) (average mean)
2. The scale of the decision making (resident lot size)
3. The action level (50 ppm)
4. The alternative action (remediate / do not remediate) (If the true mean TCE concentration in the residential lot is greater than 50 ppm, the soil is remediated. If not, the soil will be left in place)

Step 5B. Develop a test of hypothesis and decision error:
1. If the assumption is that the site is clean:
Null Hypothesis: *Site is clean; true mean level <50 ppm*
Alternative Hypothesis: *Site is not clean; true mean level >50 ppm*

- False positive (F+) Type 1 Error: *Decide that the site is not clean when it is which results in action when none was required, which is an overreaction to a situation, wasted resources, unnecessary expenditure and cleanup.*
- False negative (F-), Type II Error: *Decide the site is clean when it is not which results in no action when some was required, which is a missed opportunity for correction, allows a hazard to public health or environment.*

Step 6A. Specify limits on decision error; how much error is acceptable:

1. Determine consequences of each decision error; how sensitive is each decision? (health/ecological/political/social/resource risk)
2. Set quantitation limits of false positive/negative error (0-20ppm, 20-35ppm, 35-50ppm, 50-60ppm, 60-100ppm, 100-200ppm, 200-250ppm)
3. Determine range of parameter of interest; should fall within range of possible concentration (0-250 ppm)
4. Specify grey region (see table - *), **where consequence of decision/error are minor**; grey area is bounded by:
   A. the action level (50 ppm)
   B. The value **where the consequences of making decision begins to be significant** (60 ppm)

Step 6B. Develop the "what/if " table:

1. Specify limits on probability of committing decision errors. **(For 0.3 tolerable probability, at 30% of the time a wrong decision will be tolerated)**; (50ppm- 30%, 35ppm – 20%, 20ppm– 10%, 60ppm – 30%, 100ppm– 20%, 200ppm– 10%)

What/If Table

Reported TCE Concentration	Decision Made	True Concentration#	Error Type	Aversion	**Tolerable Probability
>50ppm	Cleanup	0-20ppm	F(+)	Severe **(Cost high)**	10%
>50ppm	Cleanup	20-35ppm	F(+)	Moderate	20%
>50ppm	Cleanup	35-50ppm	F(+)	Minor	30%
<50ppm	No action	50-60ppm	F(-)	Minor	*Grey Region
<50ppm	No action	60-100ppm	F(-)	Moderate	30%
<50ppm	No action	100-200ppm	F(-)	Severe	20%
<50ppm	No action	200-250ppm	F(-)	Very Severe **(Risk to human health and environment)**	10%

Note: Null hypothesis - the site is clean

This completes the question section of the worksheet. The information gathered and professional experience is then used to generate the sampling design. This process is described below.

Step 7. Based on the DQO outputs and historical information develop a sampling design. The sampling design must be cost-effective and balance sample size with method performance and decision error tolerance. For example, it may be more cost effective to use less expensive and less precise methods in cases of high variability in samples exist, so that a large number of samples can be taken and so that the sample design error can be controlled. If less variability in samples exists, more expensive and precise methods can be used to collection fewer samples to control the measurement error.

The USEPA DEFT software is used only as a guide to develop the sampling design alternatives. DEFT does not account for the difference between media, spacial or temporal boundaries. Inputs for the DEFT program include:

A. Parameter of interest; assumption is that the population mean is used (mean)
B. Limits on probability of committing decision errors (50ppm- 30%, 35ppm – 20%, 20ppm – 10%, 60ppm – 30%, 100ppm – 20%, 200ppm – 10%)
C. Action level (50ppm)
D. Possible range of parameter (250ppm)
E. Unit cost of sample collection and analysis per sample ($30, $220)
F. Location and width of grey region; range of possible parameter values where consequences of F(-) error are minor; bounded by action level and parameter value where consequences of F(-) begin to become significant (50-60ppm)
G. Estimated standard deviation (default is used; max concentration – minimum concentration /6)
H. Null hypothesis; which error is F(+) and which is F(-) (Site is clean)

Three basic sampling designs available in the DEFT program include:

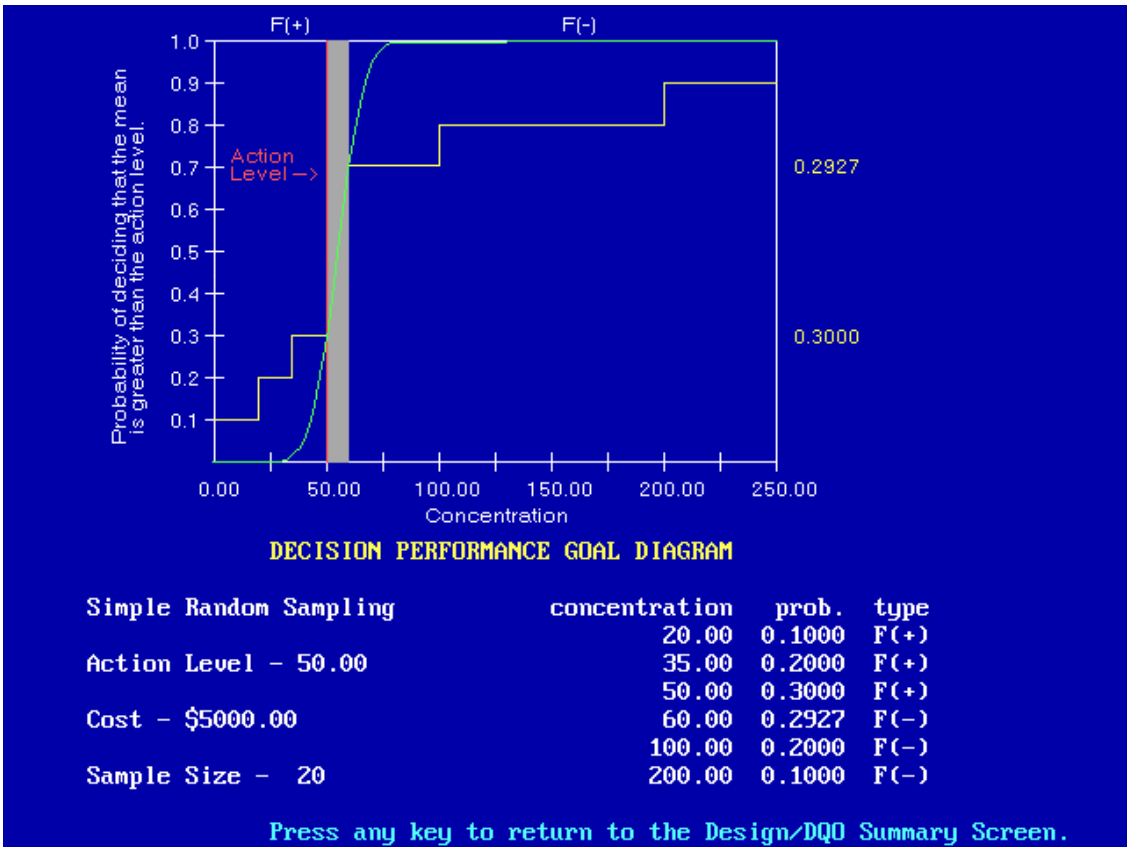
A. Simple random; Many samples are taken and total costs are high. Every possible point at the site has equal chance of being sampled. Simple random is used when variability is small and field and analytical costs are low to detect peak concentrations.
B. Composite; Multiple samples are collected and combined; subsamples are collected for additional analysis. Composite is used when the average concentration and sampling of a large number of sample sites at a reduced cost is desired.
C. Stratified random; The site is divided into two or more subsets. Each subset is sampled separately with one of the designs previously described. Stratified random is used to improve the precision of the design.

The previously listed inputs, the initial sample design, and the sample size are entered into the DEFT program, and a performance goal diagram is drawn. Altering the inputs, the design, or the sampling size may change the decision performance goal. The performance of the design is evaluated by the performance curve, which is based on the graph of the power function, and which is overlaid onto the performance goal diagram. The design that produces a very steep performance curve is preferred over one that is flatter. The power function is the probability that the null hypothesis is rejected when the null hypothesis is false. Ideally, the power function would be zero if the null hypothesis were true and one if the null hypothesis were false. Due to imperfect data, it is not possible to achieve the ideal power function. However, the power function will yield values that are small when the null hypothesis is true and large when the null hypothesis is false.

If the design fails to meet the DQOs, increase the budget, increase the width of the grey area, or increase the tolerable decision error rates.

The statements resulting from the DQO process are presented in the Project Management, Section A5, of the QAPP. (A simple random sample design should be used to compare concentrations of samples collected for TCE analysis from the site to the action level of 50 ppm. 20 samples shall be collected from each sample location. Each sample location will be generated randomly.)

The Decision Performance Goal Diagram for the example provided in the DQO worksheets



Footnotes

1. USEPA 1997. *Introduction to Data Quality Objectives,* Quality Assurance Division, Washington D.C., page 4.
2. USEPA 1994. *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, Washington D.C., page 1.

References

USEPA. 1994a. *Data Quality Objectives Decision Error Feasibility Trials (DQO/DEFT)*, Version 4.0, EPA QA/G-4D, Washington, D.C.

USEPA. 1994b. *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, EPA/600/R-96/055, Washington, D.C.

USEPA. 1997a. *Introduction to the Data Quality Objectives, Quality Assurance Division*, Washington, D.C.

USEPA. 1997b. *Overview of EPA Quality System Requirements for Environmental Programs*, Quality Assurance Division, Washington, D.C.

NEW SAMPLING DEVICE PROVIDES LABORATORY VERIFICATION -- PART 1 PRELIMINARY DATA PROVIDES SOME INTERESTING POSSIBILITIES

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ABSTRACT

Laboratory accuracy and efficacy with regards to groundwater testing has long been a concern for environmental investigators. Bench standards used in laboratory certification offer some degree of reliability, however, as many investigators have learned, laboratory equipment is prone to radical and sudden departures from expected results. These departures often go undetected by the laboratory chemist operating the analysis equipment until the report is issued and questioned by the investigator. Usually, by the time a question has been raised, the samples are out-of-date for viability and the question of validity falls to the QA/QC sheets and the calibration log for the instrument. Since recalibration, again under ideal conditions and with bench standards, almost always indicates a proper functioning of the instrument, erroneous data are accepted as valid and improper and false assumptions are made based on such data. A new groundwater-sampling instrument has been invented which may, however, provide immediate warning of aberrant analysis results. Preliminary data indicate a remarkable 98.75% reproducibility of sampling results is possible using the KABIS Sampler.

INORGANIC ANALYSIS

RECENT DEVELOPMENTS IN THE DETERMINATION OF TRACE LEVEL PERCHLORATE BY ION CHROMATOGRAPHY

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ABSTRACT

Ammonium perchlorate, a key ingredient in solid rocket propellants, has recently been found in ground and surface waters in a number of states in the U.S. Perchlorate poses a health risk and preliminary data from the U.S. EPA reports that exposure to less than 4 - 18 µg/L provides adequate human health protection. Ion chromatographic (IC) methods, based on either IonPac AS5 or AS11 columns, a large loop injection, and suppressed conductivity detection have been developed for the determination of low µg/L levels of perchlorate in drinking and ground waters. These methods provide similar freedom from common anion interferences, are linear in the range of 2 - 100 µg/L, and quantitative recoveries are obtained for low µg/L levels of perchlorate in spiked drinking and ground water samples. MDLs obtained using IC permit quantification of perchlorate below the levels which ensure adequate health protection.

INTRODUCTION

Ammonium perchlorate, a key ingredient in solid rocket propellants, has recently been found in drinking water wells in regions of the U.S. where aerospace material, munitions and fireworks were developed, tested, or manufactured. To date, perchlorate has been found in ground and surface waters in California, Nevada, Utah, Texas, New York, Maryland, Arkansas and West Virgina, although the total extent of the contamination problem is not known[1]. The presence of perchlorate in drinking water poses a considerable health risk, even at trace levels[2].

While perchlorate is listed on the EPA Contaminant Candidate List as a research priority, it is not currently regulated under the Federal Safe Drinking Water Act. The California Department of Health Services (CDHS) developed an ion chromatographic (IC) method for the analysis of trace perchlorate in 1997 to support the CDHS action level of 18 µg/L in drinking water[3]. The CDHS method uses a large loop injection with an IonPac AS5 column and a hydroxide eluent containing p-cyanophenol. Detection is by suppressed conductivity using a chemically regenerated AMMS suppressor.

An updated IC method employing an IonPac AS11 column, hydroxide eluent, and suppressed conductivity detection with a self regenerating ASRS suppressor, was developed in 1998[4]. Draft Update IVB Method 9058, titled "Determination of Perchlorate by Ion Chromatography" includes conditions for using either the IonPac AS5 or AS11 columns[5].

This paper will report on a recent developments for the determination of trace level perchlorate using ion chromatography. The performance of the AS5 and AS11 methods will be discussed and their application to the analysis of perchlorate in a variety of environmental samples, including drinking water, ground and surface waters, soils and contaminated wastes will be demonstrated. The application an EG40 automated eluent generator with a new polarizable anion analysis column, the IonPac AS16, for the determination of perchlorate in high ionic strength samples will be also presented.

EXPERIMENTAL

Instrumentation

Either 4500 or DX-500 ion chromatographs (Dionex Corporation, Sunnyvale, CA) were used for this work. Separations were carried using Dionex IonPac® AS5, AS11 and AS16 (250 x 4.0 mm) analytical columns and IonPac AG5, AG11 and AG16 (50 x 4.0 mm) guard columns. Anions were detected by suppressed conductivity detection using either an Anion Micro-Membrane Suppressor, AMMS® with a regenerant of 35 mN sulfuric acid at 10 mL/minute; or an Anion Self-Regenerating Suppressor, ASRS®-ULTRA operated at 300 mA in the external water mode.

Reagents

All water used was deionized water, Type I reagent grade, 18 MΩ-cm resistance or better. Sodium hydroxide, 50% w/w aqueous solution was obtained from Fisher Scientific (Pittsburgh, PA). Sodium perchlorate, 99% ACS reagent grade was obtained from Aldrich (Milwaukee, WI), as was 95% p-cyanophenol. ACS reagent grade chemicals were used for the preparation of the standards for the interference and recovery studies, with the exception of humic acid and selenate standards, which were prepared from technical grade reagents.

RESULTS AND DISCUSSION

In order to quantify perchlorate at low µg/L levels, it is essential to optimize chromatographic conditions in terms of retention time, peak shape and baseline noise. The perchlorate ion is a "polarizable" anion, consequently it should be chromatographed on a hydrophilic anion exchanger to minimize peak tailing. In addition, perchlorate is highly retained on anion exchange resins and requires a strong mobile phase to elute it within a reasonable timeframe, which is desirable for lower detection limits. Initial investigations on an IonPac AS5 column showed that an eluent of 120 mM hydroxide containing an organic modifier, such as p-cyanophenol, was required to elute perchlorate from the AS5 column. The effect of p-cyanophenol over the range of 0 - 3 mM on perchlorate retention was investigated, with an eluent of 120 mM NaOH containing 2.0 mM p-cyanophenol providing optimal peak shape and a retention time for perchlorate of approximately 7 minutes[3]. The perchlorate anion is well resolved from common inorganic anions, which essentially elute at the void volume under these conditions.

A large loop injection (740 µL) is required for this application in order to achieve sub-ppb detection limits for perchlorate. The method detection limit (MDL) using the IonPac AS5 column was determined by spiking perchlorate at concentrations of 1.0, 2.5, and 4.0 µg/L into reagent water, as shown below in Table I.

TABLE I. Method Detection Limit in Reagent Water.

Perchlorate Spike Conc. (µg/L)	No of Spiked Replicates	Mean Recovery (µg/L)	Standard Deviation (µg/L)	Calculated MDL (µg/L)
1.0	14	0.87	0.11	0.6
2.5	16	2.3	0.12	0.8
4.0	16	3.9	0.11	0.7
			Pooled MDL (*df* = 43)	**0.7 µg/L**
			MRL (5 x MDL)	**4 µg/L**

A linearity study was performed to ensure accurate quantification of perchlorate in the low µg/L range. A correlation coefficient of 0.9998 was obtained for a plot of peak area *versus* concentration in the 2 - 100 µg/L range, demonstrating that calibration is linear at the levels required for the quantification of perchlorate in drinking and ground waters.

In addition to the AS5 column, it has also been shown that perchlorate can be successfully chromatographed on an IonPac AS11 column[4]. The major advantage of using this more hydrophilic column is that p-cyanophenol is not required in the eluent in order to achieve good peak shape for perchlorate. This enables the use of electrolytic self regererating suppressors (e.g. ASRS-ULTRA), which add considerable convenience to the operation of the ion chromatograph, as SRS devices are not recommended for use with eluents containing electroactive modifiers, such as p-cyanophenol.

The IonPac AS11 column with an eluent of 100 mM sodium hydroxide permits the elution of perchlorate in less than 10 minutes. Figure 1 shows a typical chromatogram of a 20 µg/L perchlorate standard obtained using the AS11 column.

The method detection limit was determined for the AS11 column using seven replicates of 2.5 mg/L perchlorate spiked into reagent water according to the procedure outlined in U.S. EPA Method 300.0[6]. The single operator MDL was was calculated to be 0.3 µg/L using the conditions shown in Figure 1.

Both the IonPac AS5 and AS11 columns were tested for interferences by injecting low µg/L levels of perchlorate in the presence of 100 µg/L solutions of 22 common anions. Of the anions investigated, only cyanide, iodide, and thiocyanate display any significant retention on either column using the elution conditions described above. Perchlorate is resolved by at least 2 minutes from the nearest eluting anion, thiocyanate, which would not be typically found at high levels in drinking or ground waters.

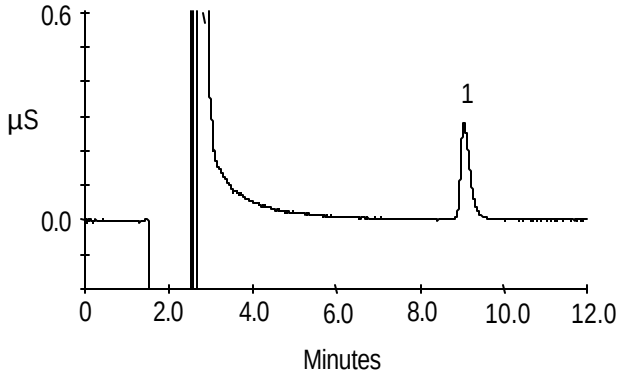

Figure 1. Perchlorate standard at 20 µg/L. Conditions: guard column, Dionex IonPac AG11; analytical column, Dionex IonPac AS11; eluent, 100 mM sodium hydroxide; flow-rate, 1.0 mL/min; detection, suppressed conductivity; injection volume, 1000 µL; peak 1 - perchlorate.

The effect of mg/L levels of common anions on perchlorate recovery was investigated by injecting solutions of low µg/L levels of perchlorate in the presence of 50, 200, 600 and 1000 mg/L chloride, carbonate and sulfate, respectively. Quantitative recoveries were obtained for perchlorate in all cases, demonstrating that mg/L levels of common anions have no significant effect on the recovery of low µg/L levels of perchlorate.

Essentially, the AS5 and AS11 columns give similar method performance, in terms of linearity, MDLs, freedom from interferences, and spiked recoveries, as was demonstrated in the recent IPSC collaborative study[7]. The IPSC study, which involved 19 laboratories, was organized to quantitatively evaluate the performance of ion chromatographic methods for the measurement of perchlorate in drinking and ground water. The study samples consisted of well water at three total dissolved solids levels of 72, 144, and 288 mg/L, which were spiked with perchlorate at concentrations of 6, 18 ppb and 36 µg/L. Both the AS5 and AS11 columns were found satisfactory for perchlorate analysis in typical ground and surface water samples.

Tables II and III show examples of single operator accuracy and precision obtained using the AS5 column for perchlorate standard solutions and matrix spikes into ground water.

TABLE II. Single Operator Accuracy and Precision for Perchlorate Standard Solutions.

Sample Type	Sample Matrix	Known Conc. (µg/L)	Number of Replicates	Mean Recovery		SD (µg/L)	RSD(%)
				(µg/L)	(%)		
IPC Standard	RW	5.0	48	4.9	98	0.35	7.1
		100	47	100	100	4.2	4.2
QCS	RW	4.0	16	4.0	100	0.31	7.8
		100	4	100	100	2.8	2.8
LFB	RW	4.0	22	3.9	98	0.33	8.5

RW = reagent water

TABLE III. Single Operator Accuracy and Precision for Perchlorate Matrix Spikes.

Sample Type	Sample Matrix	Spike Conc. (µg/L)	Number of Spiked Pairs	Duplicate Spike Mean Recovery		SD of Mean RPD (%)	Mean RPD (%)
				(µg/L)	(%)		
Matrix Spike/Matrix Spike Duplicate	GW	4.0	20	3.8	95	0.02	2.1

GW = ground water

Dionex has recently developed a new column for the analysis of polarizable anions, such as perchlorate. The IonPac AS16 column is more hydrophilic and has a significantly higher ion exchange capacity than either the AS5 or AS11 columns. This column will allow the injection of higher ionic strength samples and is also compatible with the EG40 automated KOH eluent generator. Current work on perchlorate analysis by IC involves extending the range of applications to more complex samples, such as wastewaters containing solvents, and to high ionic strength samples (> 2000 µS/cm) using either direct injection or with appropriate sample pretreatment.

CONCLUSION

The use of ion chromatography with the IonPac AS5 or AS11 columns, large loop injection and suppressed conductivity detection provides a simple, interference free method for the determination of perchlorate at low µg/L levels in drinking and ground waters. The method is linear over the range of 2 - 100 µg/L and quantitative recoveries were obtained for perchlorate in spiked drinking and ground water samples. The MDLs permit quantification of perchlorate below the levels which ensure adequate health protection (4 - 18 µg/L), as recommended by the U.S. EPA. The new AS16 column provides similar performance to the AS5 and AS11 columns for drinking water samples, although its higher capacity makes it more suitable for the analysis of trace perchlorate in high ionic strength matrices.

REFERENCES

1. California Department of Health Services (1998), Perchlorate in California Drinking Water, October Update.
2. Jarabek, A. (1999), Toxicology and Health Effects, paper presented at the Perchlorate Conference, Ontario, CA.
3. California Department of Health Services (1997), Determination of Perchlorate by Ion Chromatography.
4. Wirt, K., Laikhtman, M., Rohrer, J. and Jackson, P.E. (1998), *Am. Env. Lab.*, **10(4)**, 1.
5. Proposed Method 9058 in U.S. EPA "SW-846 Test Methods for Evaluating Solid Waste Physical/Chemical Methods", Draft Update IVB, U.S. EPA, Washington, DC.
6. U.S. EPA. Method 300.0 (1993), The Determination of Inorganic Anions in Water by Ion Chromatography.
7. Chaudhuri, S., Okamoto, H., Pia, S. and Tsui, D. (1999), Inter-Agency Perchlorate Steering Committee Analytical Subcommittee Report.

A GENERIC LEACHING PROCEDURE TO PREDICT ENVIRONMENTAL IMPACT OF REACTIVE MATERIALS SUCH AS COAL COMBUSTION BY-PRODUCTS

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ABSTRACT

Leaching characterization of many materials can give misleading data if materials are reactive or undergo chemical, physical, or mineralogical transformations upon contact with water. Additionally, if a reactive material can undergo mineralogical transformations that take up to 30 days or more, short-term leaching tests with equilibration times of 18 hours may not provide data relevant to what is likely to occur under field conditions. Many coal combustion by-products (CCBs) fall into this category, and for this reason, leaching must take into account site-specific conditions and must be based on a thorough and fundamental understanding of the nature of the materials being characterized. This paper describes a generic leaching test developed for the characterization of CCBs that is site-specific and also takes into account the reactivity and unique characteristics of many CCBs. The test is also appropriate for numerous other waste materials likely to be disposed in monofills or under conditions other than codisposal in sanitary landfills. The test incorporates a long-term leaching component. The original leaching test, the synthetic groundwater leaching procedure (SGLP), was developed in 1982 at the University of North Dakota. Since that time, the test has been used in numerous research projects and environmental assessments. In many cases, the test provides significantly different data from that generated through the use of the toxicity characteristic leach procedure (TCLP). In addition to leaching tests of real process and CCB streams, pilot plant studies have been used in conjunction with this test to predict potential for environmental impact from materials to be generated in units either in the planning or permitting stages. Studies of leached materials using x-ray diffraction have provided insights into mechanisms responsible for unexpected leaching behavior. In the case of some alkaline CCBs, initial leachate solution concentration increases of select trace elements have been followed by dramatic concentration decreases of more than 1 or 2 orders of magnitude. Elements for which this type of behavior have been noted are oxyanionic

species of environmentally sensitive elements such as boron, chromium, selenium, and vanadium. The phenomenon is referred to as anomalous leaching. Supporting data as well as examples of mineralogical characterizations of leached residues to support hypotheses and conclusions are provided.

INTRODUCTION

The determination of potential for environmental impact of disposed materials is a topic important enough to warrant the application of only the best in characterization methods. Decisions based on waste characterization prior to disposal are by necessity long-term decisions and must be based on data generated using scientific protocols that are the most predictive of what can be expected to occur under actual disposal conditions. The nature of laboratory leaching imposes certain limitations on the information that it is possible to generate. Current protocols allow the measurement of total mass of analyte in any given waste form (bulk chemical analysis), and leaching techniques allow the determination of mass of easily leached analyte as well as an assessment of leachate concentration trends with respect to time. Normal leaching trends would predict the concentration of many trace analytes to increase rapidly during the first few hours of leaching, with a subsequent gradual increase to an equilibrium concentration. As this discussion will demonstrate, concentration in certain reactive solids may actually decrease during the course of long-term leaching with equilibration times of up to 60, or even 90, days. The reactive solid wastes under consideration here are coal combustion solid residues, primarily fly ash. Currently over 40 million tons of fly ash are disposed yearly in the United States[1], making the topic of ash disposal an important and timely one. Ash disposal is a focus of U.S. Environmental Protection Agency (EPA) efforts to determine the Resource Conservation and Recovery Act (RCRA) status of wastes from the combustion of fossil fuels, including ash from combustion fuels (coal and other fuels), oil ash, and small-volume wastes[2], as well as being a hot topic for several state and environmental groups.

The accepted practice of using the toxicity characteristic leaching procedure (TCLP) for determination of hazardousness of disposed wastes employs a technique that has been shown to be effective in determining leaching trends from materials disposed of in sanitary landfills. The procedure utilizes acidic leaching conditions with acetic acid and simulates what occurs in a landfill where decomposition of cellulosic materials and other garbage produces acidic conditions, with acetic acid as a major component.

The TCLP is sometimes used to predict the nature of leachate generation in disposed coal combustion by-products (CCBs). Although this test is adequate for its intended purpose, the simulation of leaching under codisposal conditions in a sanitary landfill, its use for evaluation of CCBs disposed in monofills is clearly inappropriate. Many CCBs, especially those from low-rank coals, are highly alkaline, and even those that are not alkaline are unlikely to contact acetic acid with monofill disposal. Under most monofill disposal scenarios, it is the ash itself that will likely determine the major composition of leaching solution regardless of the initial chemistry of the water contacting the material. This is due to the relatively high mobility of calcium, sodium, and sulfate in many ash types, which is enhanced in a monofill because of the tendency for there to be a condition where a relatively large mass of ash would be mixed with a relatively small volume of pore water, either through infiltration of rainwater prior to capping the facility or through infiltration of groundwater if the monofill is situated below the water table. In the event that the monofill is wetted, the normally low permeability of liners or geologic materials in well-situated monofills would produce conditions where the contact time of ash and water would be relatively long prior to the generation of substantial volumes of leachate outside of the facility. Thus it is envisioned that most scenarios of leachate generation in ash monofills would entail a long contact/equilibration period where ash and water would have an opportunity to react together, should reactions be possible. In the case of CCBs from low- rank coal or CCBs from advanced coal combustion techniques, it is likely that secondary hydrated phases will form upon contact of the ash with water.

EXPERIMENTAL

Recognizing the inadequacy of TCLP to simulate leaching in ash monofills, researchers began an effort to fill this gap and provide a protocol for estimating trace element mobility in this unique but important situation. A long-term leaching project begun in 1987 provided data that indicated that not only was there a problem from the standpoint of leaching solution chemistry, but a problem in the short-term nature of currently available protocols such as the American Society for Testing and Materials (ASTM) water leach procedure was also uncovered[3]. It was observed that certain important leachate components from ash–water leaching systems increased in concentration initially, as would be expected, then decreased suddenly. At the same time, x-ray diffraction characterization of the waste materials indicated the formation of a mineral called ettringite. It was also observed that the formation of this mineral paralleled the decrease in concentration of several key trace components of the ash– water systems. These elements were arsenic, boron, and selenium, and it was later determined that these and several other important

elements can substitute into the ettringite structure and thus be incorporated into a highly insoluble phase formed from the hydration of ash. This was true in many low-rank CCBs and in all CCBs from advanced coal combustion processes such as fluidized-bed combustion (FBC), duct injection acid gas control processes, and lime injection multiburner (LIMB) processes. The following is a summary of the research that led to the development of a synthetic groundwater leaching procedure (SGLP) and long-term leaching (LTL) procedure.

An investigation of the leachability of trace elements from CCBs was conducted at the University of North Dakota Energy & Environmental Research Center (EERC). The primary objectives of the investigation were to develop protocols for the estimation of trace element mobility and to begin to understand the processes in ash hydration responsible for the anomalous leaching behavior observed in numerous cases. For purposes of discussion, it is assumed here that "normal" leaching behavior is a rapid rise in concentration followed by a more gradual rise leading to a stable but increased concentration of analyte. "Anomalous" leaching is defined as the situation where analyte concentration initially rises, as would be expected, but then decreases with time, often to extremely low levels. In most cases where anomalous leaching behavior was observed, ettringite was detected or conditions for ettringite formation were met, although in some cases ettringite was not detected by x-ray diffraction.

Ettringite is a mineral with the nominal composition $Ca_6Al_2(SO_4)_3(OH)_{12}•26H_2O$. Ettringite is also the family name for a series of related compounds, as is the case for many mineral families. Included in this family are the following minerals[4]:

Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}•26H_2O$
Charlesite	$Ca_6(Si,Al)_2(SO_4)_2[B(OH)_4](OH,O)_{12}•26H_2O$
Sturmanite	$Ca_6Fe_2(SO_4)_2[B(OH)_4](OH)_{12}•26H_2O$
Thaumasite	$Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}•24H_2O$
Jouravskite	$Ca_6Mn_2(SO_4)_2(CO_3)_2(OH)_{12}•24H_2O$
Bentorite	$Ca_6(Cr,Al)_2(SO_4)_3(OH)_{12}•26H_2O$

Ettringite has fairly unique characteristic structural features. The structure comprises calcium aluminate columns $\{Ca_6Al_2(OH)_{12}24H_2O\}^{6+}$, with the channels between these columns containing the other components, which include an oxyanion such as sulfate with hydroxide and water $\{(SO_4)_{2-4}\ (OH)_{0-4}\ (H_2O)_{0-6}\}^{6-}$. The structure of ettringite is shown in Figure 1[5-7].

Although ettringite was reported in the scientific literature in the early 1930s, it has only been recently recognized just how great a potential impact this mineral could have on human activities. Ettringite is relatively easy to synthesize in the laboratory. All that is necessary is an aqueous solution containing calcium, aluminum, and sulfate at a pH between 11.5 and 12.5. If the proper concentrations of components are provided along with high alkalinity, ettringite forms readily. These conditions are often met when low-rank CCBs contact water. The ash in most cases has all of the potential ingredients for ettringite formation, and it has been found that many low-rank CCBs do form ettringite as a primary hydration product. The availability of alkaline constituents to provide the required high pH conditions are often the limiting factor with CCBs. Extensive research into ettringite formation has been carried out at the EERC in conjunction with North Dakota State University. In this study, numerous substituted ettringites were synthesized in the laboratory. The substituents were elements that tend to exist as oxyanions in aqueous solution, and they enter into the ettringite structure by substituting for sulfate. Ettringites substituted with arsenic, boron, chromium, molybdenum, vanadium, and selenium have been

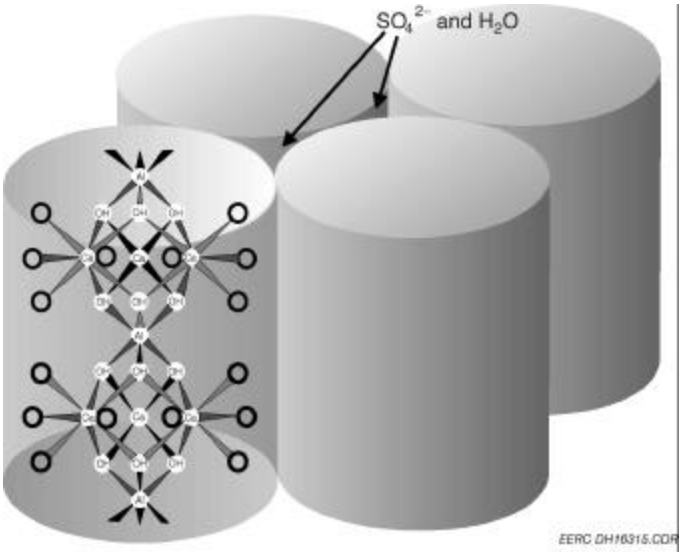

Figure 1. Ettringite Structure

prepared in the laboratory[8]. Thus ettringite formation has the potential to influence the solution concentrations of these and probably numerous other elements, including aluminum, calcium, and sulfate, major constituents of the ettringite structure. It is also important to note that the rate of formation of ettringite in CCBs is dependent on the availability of the key ingredients in the structure. Since many of these are leached from the ash from various crystalline and amorphous phases, the formation of ettringite can take from hours to months, depending on the characteristics of the individual ash. Each ash, due to the variability of the phases making up these materials, is unique in this manner.

A short-term leaching test of 18-hour duration such as the TCLP or ASTM water shake test may be concluded before ettringite has even begun to form in some CCBs. This could resultin highly misleading information regarding leachability of several very important and potentially problematic trace elements.

The following protocols were developed to fill the gap in leaching procedures for the characterization of materials for which the TCLP was clearly inappropriate and for materials for which short-term leaching was not predictive of field phenomena. The protocol for the TCLP is given for reference.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The TCLP9 is the EPA regulatory leaching procedure. The TCLP has also been adopted by many state regulatory agencies to provide leaching information on solid wastes (not hazardous) which are not federally regulated. This test uses end-over-end agitation and a 20- to-1 liquid-to-solid ratio with an 18-hour equilibration time. Two leaching solutions are specified for use with this test. Leaching Solution No. 1 is an acetate buffer prepared with 5.7 mL of glacial acetic acid per liter of distilled deionized water which is adjusted to pH 4.93 with 1 N sodium hydroxide solution. Leaching Solution No. 2 is an acetic acid solution prepared by diluting 5.7 mL of glacial acetic acid to one liter with distilled deionized water. This solution will have a pH of 2.88. The TCLP specifies a test to determine the alkalinity of the waste to be leached which, in turn, determines which leaching solution should be used. More alkaline materials utilize Solution No. 2, while less alkaline materials are leached with Solution No. 1.

SYNTHETIC GROUNDWATER LEACHING PROCEDURE

The SGLP[10] was developed as a generic leaching test to be applied to materials to simulate actual field leaching conditions. Since the TCLP was designed to simulate leaching in a sanitary landfill under codisposal conditions, it is not appropriate to evaluate leaching of CCBs in typical disposal or utilization scenarios. To provide more appropriate and predictive information for CCBs and other unique materials, a leaching test was developed using the same basic protocol as the TCLP, but allowing for the appropriate leaching solution chemistry. Test conditions are end-over-end agitation, a 20-to-1 liquid-to-solid ratio, and an 18-hour equilibration time. The leachate often used is distilled deionized water.

For certain predictive applications, this may not be totally appropriate, since mercury, for example, would likely be influenced by the presence of chloride, leading to the formation of an extremely stable mercury chloride complex. Local, site-specific factors, such as the presence of significant halide concentrations or other geochemical factors likely to influence trace element mobility, would have to be considered in any real disposal setting. Additionally, because of the extremely alkaline nature of most low-rank coal combustion ash and their high acid neutralization capacity beyond the simple high pH, acidity from the impact of varying acid precipitation concentrations is generally not considered to be an important factor, although, as with every imaginable factor, it would, no doubt, influence results to some small degree. The purpose of this test is to provide data that are not influenced by the presence of acetate ion or the initial acid impact when sample and leaching solution are mixed. The composition of leaching solution is site-specific. In the original test applied to disposal in sites in central and western North Dakota, a composition of leaching solution designed to simulate sodium sulfate bicarbonate-buffered water was used. The solution used for leaching was prepared by dissolving 0.50 grams of sodium sulfate and 1.00 gram of sodium bicarbonate in 1 liter of distilled deionized water.

The analysis of this synthetic groundwater leaching solution is as follows:

Na	436 mg/L
SO_4	338 mg/L
HCO_3	726 mg/L
pH	8.3–8.7

This composition is typical of groundwater in central and western North Dakota where the water is slightly alkaline as a result of bicarbonate buffering, and primary mineralization is from sodium sulfate.

In another research project designed to simulate leaching of coal conversion solid residues in Indiana[11], a solution was prepared with the following nominal composition:

Na	120 mg/L
Mg	310 mg/L
Ca	500 mg/L
CO_3	300 mg/L
SO_4	2810 mg/L
pH	7

Although the alkalinity is expressed as carbonate, at this pH it would be present primarily as bicarbonate.

In practice, with many CCBs it is not necessary to add calcium, since the solubility of calcium in the leaching system is determined by the ash contributions from leaching solution, which are negligible compared to the mass of calcium available from the ash at a 20-to-1 liquid-to-solid ratio.

LONG-TERM LEACHING

A LTL procedure, also using distilled deionized water or a synthetic groundwater, can be used to identify effects associated with any mineralogical changes that may occur in the waste forms upon long-term contact with water. It was found in a previous research project[3] that on long-term contact with water, certain coal conversion solid waste materials form secondary hydrated phases with mineralogical and chemical compositions different from any of the material in the original ash. It was also demonstrated that the formation of these hydrated phases was often accompanied by dramatic decreases in solution concentrations of oxyanionic species such as borate, chromate, selenate, and vanadate. The decrease in concentration of these elements would not be predicted from the results of short-term leaching tests.

In the context of the SGLP, the LTL procedure is simply a continuation of the SGLP. In practice, several SGLP leaching containers are prepared and rotated. One is sampled at 18 hours, thus fulfilling the SGLP requirement; another is sampled at 30 days; and a final container is sampled at 60 days. In practice, additional containers can be started and continued for 90 days, 120 days, or any time duration that is desired. The containers are placed on the rotator in stages so that all of the containers are equilibrated at the same time. Thus one container is started; 30 days later, a second container is started; and 18 hours before the test is to end, a final container is started. This simplifies the analytical process and results in considerable time savings.

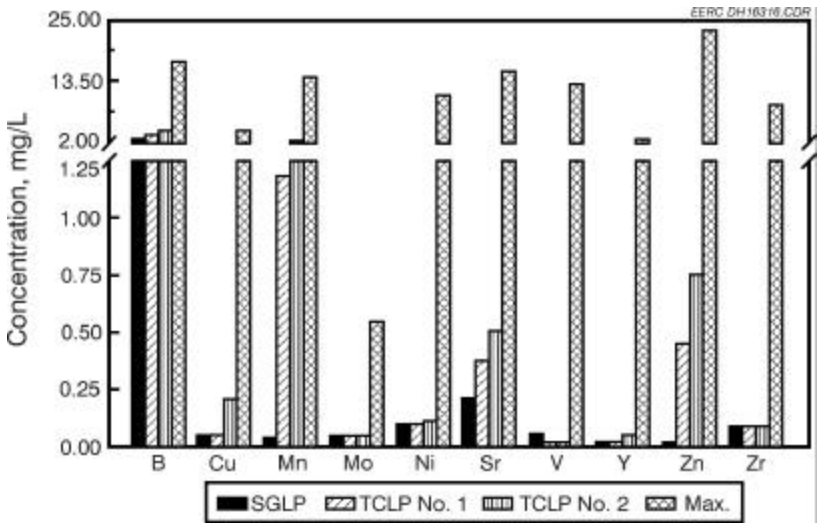

Figure 2. Comparative Leaching of Bituminous Fly Ash

RESULTS AND DISCUSSION

The results of short-term and long-term leaching of several CCBs are shown in Figures 2 and 3.

Results for these two ash types are included to illustrate several important leaching trends. Figure 2 illustrates two of them. First, it can be seen in the results for vanadium that the acidic solutions used in the TCLP produced solutions with concentrations of vanadium lower than those of the alkaline SGLP. This is not an isolated case and indicates that acid is not a worst-case scenario; rather, it is the phase location of trace elements that determine acid or base solubility of the analytes of interest. Second, it can be seen that although analyte was mobilized for most of the trace elements measured at above detection limits, concentrations were still well below the maximum calculated

concentrations indicated by the designation "Max." in the figure. Maximum calculated concentrations in these figures are theoretical maximum concentrations, assuming total dissolution of the ash at a 20:1 liquid-to-solid ratio. Total dissolution of most ash samples is highly unlikely, even within geological time intervals.

Figure 3 shows long-term leaching trends of a lignite fly ash. This highly alkaline ash sample with measured pH values of over 11.5 is what would be considered an ettringite-forming ash. This is suggested by the trends of decreasing concentration for boron and selenium. These are two of the trace elements that exist as oxyanions in aqueous solution that are known to substitute into the ettringite structure. Although vanadium, chromium, and to a lesser extent, arsenic, are also known to be removed by ettringite, it appears that this was not significant in this example. It is not known, however, what the concentrations of these three elements would have been in the absence of ettringite formation, so this is merely an assumption.

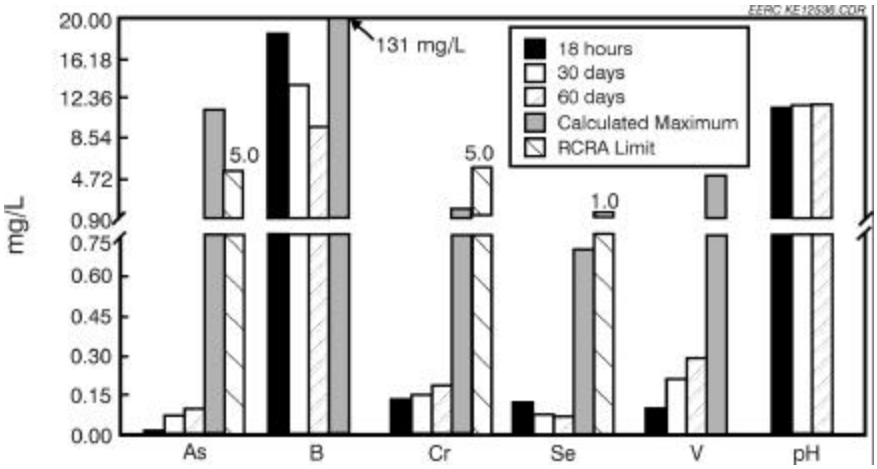

Figure 3. Long-Term Leaching of Lignite Fly Ash

SUMMARY

One of the more important conclusions that can be drawn from leaching to predict environmental impact is that there are currently no laboratory leaching tests available that will reliably and consistently predict the concentration of analytes in field leachates at coal ash monofill sites. This does not reduce the value of laboratory leaching; rather, it should influence the way in which laboratory leaching is interpreted and perhaps used in future studies. Laboratory leaching is a means of generating input data for models to predict field leachate concentrations. Laboratory leaching will provide information regarding the mass of easily mobilized analyte as well as leachate concentration trends. Concentrations of analytes in field leachate at the source could be calculated using information on water infiltration and the permeability of the disposed material. Leachate concentrations at the source of generation are of limited value, considering the effects of sediment attenuation, dispersion, diffusion, and dilution as leachates travel through the subsurface environment. Leaching information combined with batch sediment attenuation experiments to determine numerical values for chemical and physical attenuation, along with factors for other phenomena leading to decreases in solution concentration of analytes, suggest a means to predict field leaching without the complication of thermodynamic models that often omit important information such as secondary hydrated phase formation and sorption of iron and aluminum oxide– hydroxides, as is the case with coal ash leaching models. Considering the complications involved with predicting sorption and chemical incorporation of analytes in these important concentration-reducing mechanisms, thermodynamic models may not always be the best approach for predicting field effects. This is not to say that thermodynamic models can not be developed for reliable prediction.

The implication for leaching characterization is straightforward. In ash characterization where secondary hydrated phase formation reactions and release of iron and aluminum that can form highly sorptive materials may ultimately control the concentrations of numerous environmentally important trace elements, short-term leaching is clearly insufficient for predicting leachate concentrations and, thus, trace element mobility. Because of the importance of decisions made on the leachability of potentially problematic trace elements such as those with the potential to substitute into the ettringite phase, decisions made on the basis of short-term leaching are likely flawed. Considering the importance of the potential impact of these trace elements on the environment, the overestimation or underestimation of their mobility could be an invitation to disaster—either environmental, in the case of overestimation where a problem is missed, or financial, where a nonexistent problem is projected, leading to costly and unnecessary efforts to protect the environment from a nonexistent problem.

REFERENCES

1. *1997 Coal Combustion Product (CCP) Production and Use*; American Coal Ash Association, 2760 Eisenhower Avenue, Suite 304, Alexandria, VA 22314-4569.

2. *Waste from the Combustion of Fossil Fuels – Volume 1, Executive Summary*; U.S. EPA Report to Congress EPA 530-5-99-010; March 1999.
3. Stevenson, R.J.; Hassett, D.J.; McCarthy, G.J.; Manz, O.E. *Solid Waste Codisposal Screening Study*; Topical report to the Gas Research Institute and Radian Corporation, North Dakota Mining and Mineral Resources Research Institute: Grand Forks, ND, 1986.
4. Dunn, P.J.; Peacor, D.R; Leavens, P.B.; Baum, J.L. *Am. Mineralog*. **1983** *68* 1033–1037.
5. Moore, A.E.; Taylor, H.F.W. *Nature* **1968**, *218*, 1085.
6. Moore, A.E.; Taylor, H.F.W. *Acta Cryst.* **1970**, *B26*, 383–393.
7. Moore, A.E.; Taylor, H.F.W. *Min. Mag.* **1973**, *39*, 377–389.
8. Hassett, D.J.; Thompson, J.S.; McCarthy G.J. *Ettringite Formation as a Fixation Technology for Immobilizing Trace Elements;* Internal Report 5089-253-1829 for the Gas Research Institute; EERC publication, June 1992.
9. U.S. Environmental Protection Agency. *Federal Register* **1986**, *51* (9), 1750–1758.
10. Hassett, D.J. A Generic Test of Leachability: The Synthetic Groundwater Leaching Procedure. In *Proceedings of the Waste Management for the Energy Industries Conference*, University of North Dakota, April 29–May 1, 1987.
11. Hassett, D.J. *Evaluation of Leaching Potential of Solid Coal Combustion Wastes;* final report to the Indiana Coal Council, Dec. 4, 1991; 40 p.

EFFECT OF ZERO VALENT IRON ON EXTRACTION OF LEAD, ZINC AND COPPER IN THE TCLP

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Abstract
The presence of metallic iron in a TCLP extraction can dramatically change the concentration of lead and other metals in the extract. Wastes, which exhibit the characteristic of toxicity due to the presence of extractable lead, can pass the test if iron is added to the waste before TCLP testing. The reason for this is the reduction by iron of lead (II) ions. Using results from TCLP tests of waste casting sand from a brass foundry and related experiments, this paper will discuss this redox reaction. The possibility of hydroxide precipitation, and adsorption by hydrous ferric oxide, will also be addressed. pH is important to each of these three possibilities. Lead, copper, and zinc behave differently with respect to oxidation/reduction, adsorption, and hydroxide precipitation, and their measurement allows deductions as to which mechanism is operating. Iron treatment does not result in long term stabilization of a waste placed in the ground, and this will be illustrated by results from actual landfill samples. Wastes which are treated to pass the TCLP test, but are not permanently stabilized, are an area of concern.

Introduction
The TCLP test is used to determine if wastes exhibit the characteristic of toxicity. If an extract of the waste contains a regulated element or compound in a concentration greater than the limits in the regulation, then the waste exhibits the characteristic of toxicity. As the principal test for toxicity, it is obvious that many waste streams have been subjected to the TCLP test, and that the results of this testing have a large economic impact. Since the test can be so important, it is not surprising that many waste treatments, and additions to industrial processes, have been designed to affect the outcome of the TCLP test.

As a technical support center for EPA enforcement, the laboratory of the National Enforcement Investigations Center (NEIC) has examined a number of additions to wastes designed to "beat" or pass the TCLP test. Not all these additions can be considered treatments in the sense of conferring long term stability. This account will describe one such treatment, the addition of iron to brass foundry waste.

Brass Casting Using Sand Molds
Brass can be formed into many useful items by casting the molten metal into sand molds. Numerous foundries make a wide variety of metal parts this way. Information and data from one foundry is presented in this report, but the results are applicable to many foundries using the same process and generating the same wastes. This information was generated in support of an enforcement investigation, but only the technical aspects will be discussed.

The brass foundry under study prepared brass valves for use in applications such as drinking water systems. The brass used at the foundry had a composition as follows:

copper	80% to 88%
zinc	5% to 9%
tin	3% to 6%
lead	1.5% to 7.0%

The source of the lead and some of the rest of the brass was recycled automobile radiators. The lead is a desirable component since it aids in machinability of the brass. It is surprising that lead is still allowed in the brass used for drinking water valves. Lead is not allowed in the solder used for drinking water systems. It is possible to make brass valves without lead, but the foundry indicated that it would increase their costs.

Waste Sand

The molding sand used in brass casting is used many times, but eventually it must be replaced. Thus waste sand is continually being generated. Since the sand has been in contact with molten brass, and exposed to metallic vapors, it becomes contaminated with the components of the brass. In particular it contains significant amounts of the principal components as follows:

lead	1500 to 6000 mg/kg
copper	1% to 3%
zinc	1% to 6%

TCLP extractions performed in our laboratory showed that the extract typically contained about 50 mg/L lead. Copper and zinc were even more concentrated in the extract.

Iron Addition

As many foundries have discovered, the addition of iron metal, of zero valent iron, can profoundly affect the outcome of a TCLP extraction involving lead[1]. The recipe used in this particular case was 10% iron by weight. The iron was added to the waste sand in the form of filings or shavings procured as waste from a machining operation. The TCLP extracts of the waste after the iron addition contain less than the regulatory limit of 5 mg/L of lead. Copper was similarly diminished in the extract. Zinc was not significantly diminished by the presence of iron.

The explanation for the observed effects of iron addition are straightforward. A partial listing of the electromotive series follows:

Na
Al
Zn
Fe
Cd
Pb
Cu

The higher an element is on the list, the easier it is to oxidize, and the harder to reduce. The nearer an element is to the bottom of the list, the harder it is to oxidize, and the easier to reduce. The electromotive series is a way of summarizing electrode potentials, and predicting oxidation reduction reactions. From the list, or from electrode potentials, it is clear that metallic iron will reduce lead (II) or copper (II) ions to the zero valent states, which are essentially insoluble. Iron will not reduce zinc (II) ions. The iron itself will be oxidized. As long as metallic iron is present, either in the TCLP bottle or in a landfill, any lead ions appearing in solution will be reduced by the iron. The concentration of lead ions will not reach the regulatory limit of 5 mg/L.

Why is iron treatment not a long term solution? Simply because iron metal cannot be expected to remain in a landfill without oxidizing. The time required to completely oxidize all the iron present will depend upon the climate. Oxidation will be faster in a wetter and warmer location than in a drier and colder one.

This theoretical prediction that oxidation will occur, and that lead will eventually become extractable, is confirmed by actual samples and testing. Waste sand from the foundry, which is being described in this report, was placed in a municipal landfill. It was placed in separate cells, so that it was not mixed with municipal waste. A drill rig was used to collect samples of the waste sand after it had been in the ground for several years. The cores were divided into

sections, and TCLP tests and total elemental measurements were made. The TCLP results for one core follow, listed in order from top to bottom.

Location	Lead in TCLP extract (mg/L)
Top of Core	5.9
	0.22
	0.75
	2.4
	5.7
Bottom of Core	65.

Three of the samples exceeded the limit for extractable lead. All of them would have passed the TCLP test easily when they were first placed in the landfill - total iron measurements showed that they had been treated with iron. It is thus clear that, as expected, the iron treatment was by no means a permanent means of stabilizing lead. Also, iron treatment has little effect on zinc, whose leachability should be of concern.

Adsorption by Iron Oxides

It is well known and well studied that iron oxides and hydroxides can adsorb lead, copper, and zinc ions under certain conditions[2]. If ferric ions are in solution, and the pH is raised, then hydrous ferric oxide will precipitate. This is an amorphous phase which incorporates considerable amounts of water. As it ages, hydrous ferric oxide (HFO) converts to crystalline iron oxides, but not in the time period of a TCLP test. If lead, zinc, or copper ions are present, they can compete with hydrogen ions for sites on the surface of the HFO. Thus as pH is increased the fraction of the metal ions adsorbed increases. When the fraction of a particular ion which is adsorbed is plotted as a function of pH, there is a sharp transition, a pH edge, from no adsorption to complete adsorption. Studies cited in the reference show that HFO adsorbs lead more strongly than zinc, and zinc more strongly than copper. In other words, lead is adsorbed at a lower pH than zinc or copper. Tests in our laboratory confirmed this under TCLP conditions. A distinction can thus be made as to which mechanism is operating. A redox reaction reduces copper to lower levels than lead, while the opposite is true for adsorption on HFO.

Will HFO be formed from iron filings during a TCLP test? This is unlikely, for the following reasons. Iron metal added to a waste in a TCLP test will surely oxidize. However, in the absence of oxygen, ferrous iron is the most stable state of iron. And in a well sealed TCLP bottle, all the oxygen will soon be used up by the iron oxidation. Dissolved iron will be in the ferrous state. There will be no ferric iron to form HFO. This has been observed in experiments at NEIC. TCLP extracts to which iron has been added typically show several hundred ppm of dissolved iron. This must have been in the form of iron (II) during the extraction, since at the observed pH's ferric iron would have been much less soluble. As the extracts are filtered, exposing them to air, visual observation shows that the ferrous ions are rapidly oxidized, and HFO forms.

Perhaps the more important question is what happens to the iron treated waste as it sits in a landfill. If the water which percolates through the waste is oxygenated, the iron filings could very well form HFO, and the HFO could adsorb lead, zinc, and copper ions. There are several problems with this scenario of permanent treatment. If the pH gets much below five the ions will desorb. If the local environment becomes anaerobic, the iron will be reduced to the ferrous state, and the dissolved iron and other ions will be carried away by the groundwater flow. There may be a place for iron oxide adsorption, but certainly not as a permanent treatment of lead-containing wastes.

Hydroxide Precipitation

The hydroxides of many metals, including copper, lead, and zinc, will precipitate if the pH is raised higher than about 7 [3]. Hydroxide precipitation can lower the concentration of lead to below the TCLP regulatory limit. The exact pH at which hydroxides will precipitate depends on the metal and other factors. Complexing agents can raise the pH

at which hydroxides will precipitate. The acetate buffer present in the TCLP test does tend to solubilize metals at higher pHs than otherwise would be possible.

Hydroxide precipitation does not explain the observed effects of iron treatment of lead-contaminated wastes. While the presence and oxidation of iron metal does raise the pH of TCLP extraction fluid number one above 5, it does not raise it nearly high enough to precipitate lead, copper or zinc as the hydroxides, especially with acetate present. Of course, with TCLP extraction fluid number two the pH would be even lower than with fluid one, and hydroxide precipitation would be even less of a factor.

Other Treatments

Other treatments used on wastes have as their main effects an influence on the outcome of the TCLP test. Lime treatment is a common example. If enough lime is added to the waste, then any lead, zinc, copper, and a number of other elements will precipitate as hydroxides. Whether this lime treatment will also serve as a permanent treatment for the landfilled waste is far from certain. The length of time which the waste remains stabilized surely depends on many factors, such as the amount and acidity of water which percolates through the waste. A large burden is placed on the TCLP test, requiring its use as the principal determinant of the suitability of waste treatment. Whether materials containing well over 1000 mg/kg of lead should be considered nontoxic just because they pass the TCLP test is an open question. Perhaps it is time to consider additional tests to determine toxicity. An obvious and simple method is to consider total amounts. In addition to leachable amounts determined in the TCLP test, total concentrations in a waste should be used to determine the characteristic of toxicity.

Summary

The reason iron addition to lead-contaminated waste reduces the lead level in the TCLP extract to below the regulatory limit (copper is also diminished) has been shown to be an oxidation reduction reaction. Two other mechanisms which can reduce solution levels of lead, copper, and zinc in some situations are adsorption by hydrous ferric oxide (HFO) and hydroxide precipitation. The relative concentrations of lead, copper and zinc, as well as the pH, can be used to distinguish between these mechanisms.

The TCLP test certainly has a role in characterizing hazardous wastes. The question is whether it should be the sole test. Experience has shown that the TCLP test by itself is not sufficient to establish long term stability of treated hazardous waste placed in a landfill. Additional tests, and perhaps additional regulations, may be necessary to compel the regulated community to concentrate on permanent, long-term treatment of hazardous wastes, rather than focusing on passing the TCLP test.

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References

1. T.R. Ostrom and P.K. Trojan, "Lead Compound Formation in Alloy CDA 84400 and the Effect of Iron on Leachable Lead," *AFS Transactions*, 94, pp. 725-734, 1986.
2. D.A. Dzombak and F.M. Morel, *Surface Complexation Modeling, Hydrous Ferric Oxide*, John Wiley, 1990.
3. J.F. Pankow, *Aquatic Chemistry Concepts*, Lewis Publishers, 1991, pp.219-242.

NEW DEVELOPMENTS OF METHOD 7473 FOR MERCURY ANALYSIS

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ABSTRACT

EPA draft Method 7473 is a new technique based on traditional methodologies operating on the basis of thermal decomposition, amalgamation, and atomic absorption spectrometry. With Method 7473, sample preparation and analysis are essentially integrated into a single analytical instrument, allowing for direct analysis of both solid and liquid samples. Direct analysis gives Method 7473 the capability to be applied in either laboratory or field settings. This method has been previously validated for use with traditional environmental matrices in both the lab and field[1]. There is a need, however, to extend this method to include the analysis of unique sample types and mercury species. This paper will discuss the determination of total mercury in coal and other fossil fuels, fish tissue, and additional significant matrices. Extraction techniques to be coupled with Method 7473 for the analysis of operationally-defined mercury species will also be detailed.

INTRODUCTION

As a RCRA-regulated element, mercury is routinely analyzed in soil, water, and other environmental matrices. The most common method for mercury analysis used today is the cold vapor technique, which originated in the late 1960s[2]. The cold vapor technique is problematic, as it is a very time-consuming and labor-intensive process and also requires a significant amount of reagents for sample preparation. Method 7473 is able to minimize these problems associated with the traditional technique and is very adept at routine environmental mercury monitoring. The next phase of method development is expansion of Method 7473 to include other matrices and mercury speciation.

Regulations are typically a main driving force behind advancements in method development. Recent EPA initiatives have sparked an interest in analyzing coal and its by-products for mercury content. Information Collection Request no. 1858.01 requires coal-powered electric utilities to report the mercury content in coal, fly ash, and stack gases on a monthly basis. Some states are proposing mercury emission regulations in other fossil fuels, such as oil and gasoline. A simple and rapid method for mercury analysis in a broad range of fuel sources is therefore desired.

Since the Minamata Bay tragedy of the 1950s where hundreds of people were poisoned as a result of consumption of mercury-contaminated seafood, mercury has been regulated in food products. An action level of 1 ppm mercury in fish has been set by the FDA. With the ability to perform 'dockside' analysis, Method 7473 has tremendous potential in the fishery industry.

Because the toxicity and mobility of an element is dependent on its chemical form, the trend in environmental monitoring is shifting from total to species-based measurements. The EPA has recognized the need for a reliable measurement technique for mercury speciation. Use of selective extraction for separation of operationally-defined mercury species has been reported[3]. Coupling such an extraction procedure to analysis by Method 7473 will allow for rapid (and potentially on-site) characterziation of mercury speciation.

SUMMARY

The analysis of coal and other combustible materials containing a high organic content by Method 7473 is not as straightforward as that of standard environmental samples. An exothermic oxidation occurs during decomposition due to the presence of oxygen as a carrier gas. Modifications to the analytical parameters have been evaluated, including the use of nitrogen and air as a carrier gas. These less oxidizing gases eliminated the pyrotechnics, but also changed the chemistry of both the catalyst and the amalgamation processes of the instrument. A discussion of the chemical parameters that control these processes will be presented to evaluate the use of alternative carrier gases. The optimization of Method 7473 for the analysis of such difficult matrices will be discussed. Data collected on a variety of coal samples, fish tissue, and other matrices will be presented.

Selective extraction coupled to Method 7473 will be evaluated for the characterization of mercury species. The species will be operationally-defined based on their respective solubilities. Examples of operational definitions are provided in Table 1.

Table 1. Operationally-Defined Mercury Species

Operational Definition	*Individual Species Example*	*Relative Toxicity*	*Relative Mobility*
Soluble in Organics	Methylmercury	High	Low
Water-Soluble	Mercuric nitrate	Low	High
Acid-Soluble	Mercuric sulfide	Low	Low

While selective extraction will not provide results based on individual species, it can provide information on groups of species, allowing for a relatively quick risk assesment based on mercury speciation. Refinement of the extraction procedure for the matrices and species of interest will be discussed.

REFERENCES

1. Boylan, H.M., H.M. Kingston, and R.C. Richter. *Direct Mercury Analysis: Field and Laboratory Applications*. in *Waste Testing and Quality Assurance Symposium*. 1998. Arlington, VA.
2. Hatch, W.R. and W.L. Ott, *Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry.* Anal. Chem., 1968. **40**(14): p. 2085-2087.
3. Miller, E.L., *Draft Method: Determination of Organic, Inorganic, and Total Mercury in Soils.* SW-846, 1993.

SPECIATION OF MERCURY IN SOIL

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Introduction

The species of a metal contaminant will often determine its fate and transport. Species can mean the oxidation state, crystal structure, or mineral form of the metal. In the environment, organic mercury species can both bio-accumulate and bio-magnify through the ecosystem. Methylmercury is the most prevalent form and can be found at concentrations more than 10^6 times as concentrated in a fish as it is in the water in which it lives. Mercury species associated with natural organic agents such as humic acids seem to be difficult to extract even under vigorous conditions.

The contaminant species can also play a role in its fate and transport within the organism. Chromium in the dichromate species can be taken up by the body at a much faster rate than the Cr^{3+} form which is thought to be a micronutrient for humans. The hexavalent form is a known carcinogen. The procedure for determining the concentration and nature of mercury species in soils is to expose the soil to a series of solvents, with the intent of having each solvent selectively remove a different mercury form. The literature reports more than 10 different combinations of extracting media, each applied to a different soil type. Results are “operationally defined”; e.g., the part of the extraction procedure intended to remove organic mercury is not stated to remove all of the organic species; rather, the amount removed is defined as the organic fraction. Several studies report the re-distribution of mercury species during extraction, further complicating data interpretation. A reliable, predictable method for identifying the in situ amounts of various forms of mercury in soil is highly desirable from both a scientific and a regulatory perspective. The objectives of this study are to:

- compare existing methods for the sequential extraction of mercury in soil using various aqueous and mixed liquid phases to speciate mercury in contaminated soil, and
- develop a method for the sequential extraction of mercury in contaminated soil with defined values for the precision and accuracy for the elemental, inorganic and mercury species.

An evaluation of various solvent mixtures and chromatographic elution schemes was conducted to explore the capability of extracting various mercury species. Ion chromatography (IC) was employed to separate the various mercury species. Analysis of the eluent was performed by direct coupling to an Inductively Coupled Plasma Mass Spectrometer (ICPMS), which allowed the concurrent measurement of various mercury forms. The procedure can correct for extraction and pre-concentration efficiencies as low as 30% using stable enriched isotopes, and adding two isotopes simultaneously can be used to monitor specie interconversion.

Experimental

The chromatographic system consisted an ion chromatograph fitted with a 400 µl sample loop. An 0.45 µm inline filter is placed between the injection loop and the column to prevent column clogging. The mobile phase consists of a methanol/HCl (1M) mixture in a ratio of 55:45 (v/v). A flow rate of 1 ml/min was used for all determinations. After

the analyses were completed the column was stored in a 10 % solution of the mobile phase diluted with 18 Mohm water.

The output of the IC was connected directly to the Meinhard nebulizer. The detection unit was an ICPMS. Argon was used as the plasma support gas. The ICPMS sensitivity was optimized with a solution of 10 ppb $Hg(NO_3)_2$ with the mobile phase used as the solvent. The ICP was optimal operated at 1.3 kW forward power and the coolant, auxiliary and nebulizer argon flow rates were 14, 0.8 and 0.8 l/min, respectively. The data were collected unless otherwise indicated by single ion monitoring of mass 202 (the most abundant isotope for mercury) and the signals were calculated using a peak integration time of 21 sec.

Methanol, hydrochloric acid and nitric acid were of analytical grade and were used without further purification. Water was of HPLC grade and was delivered by a Millipore water purification system. Standard solutions of mercury (100 ppm $Hg(NO_3)_2$ in 5 % hydrochloric acid) and methylmercury (100 ppm in 55 % methanol and 2 % hydrochloric acid) were used. The analytical solutions with different concentrations were made from these stock solutions by diluting with the mobile phase. Isotopically-labeled mercury standards were prepared from enriched mercury oxide. The $^{200}Hg^{2+}$ standard solution was made by reacting the mercury oxide powder with concentrated HCl and diluted with 5% HCl. Methylmercury was formed from ^{202}Hg using a methylcobalamine reaction.

The microwave extractions of soil samples were carried out using a microwave digestion system. 500 mg of a soil sample, known to ± 0.01 g, was weighed in a polypropylene volumetric flask and subsequently 5 ml of methanol and 100 µl of 6 M hydrochloric acid were added. A microwave digestion program consisting of 30 W for 20 min was applied. After cooling to room temperature (25 ºC), the sample was diluted to 10 ml using 18-M water. This solution was then injected through a 0.45 µm syringe filter into the IC-ICPMS analytical system. Recoveries were determined by adding known amounts of the mercury species to the soil.

Results and Discussion

Methanol fractions between 50 and 70% and HCl concentrations ranging from 0.4 to 1.2 M were used to minimize analysis time while achieving complete separation. The acid concentration effected the Hg^{2+} to a much greater extent than the methylmercury. Going from 0.4 M to 1.2 M HCl eluent decreased the Hg^{2+} ion retention time 4 times and increased the signal 5 times, whereas the retention time and the sensitivity of the organomercury signal were only slightly changed. This was expected, because the inorganic mercury ion is doubly charged. All further studies used a 1 M HCl eluent concentration. While the inorganic ion retention time remained unchanged, the methylmercury retention time decreased with increasing methanol fractions. Increasing of the organic content also resulted in a decrease in analyte sensitivity. Nebulization of volatile solvents such as methanol extinguishes the plasma or causes it to be unstable. A mobile phase composition of 1 M HCl and 55% methanol enabled the species to be fully resolved with complete separation in less than 7 minutes.

The linear range and the limits of detection of the ICPMS response for inorganic and methylmercury were determined by using a mobile phase composition of 1 M HCl and 55% methanol and a integration time of 21 sec. The calibration graph is linear from the detection limit to the low parts per million level by using single ion monitoring of mass 202. The linear range could be extended further by switching to a less abundant isotope of mercury, but wasn't done because of contamination concerns. The limit of detection, defined as three times the standard deviation of 6 repeated scans of 500 ppt of inorganic and 500 ppt of methylmercury was 15 and 50 ppt, respectively.

The determination of inorganic and methylmercury in soil samples was performed using the techniques described above. Mercury-free soil was spiked with 1 ppm of each isotopically labeled mercury species ($^{200}Hg^{2+}$ and $Me^{202}Hg^{+}$) and left untouched for at least 3 days. The influence of various parameters such as amount and composition of the extraction solvent as well as the power and time program of the extraction procedure was investigated to obtain the best recovery rates of the mercury species. Preliminary studies found that using either hydrochloric or nitric acid for the methanolic extraction eluent, the same results were obtained. For further experiments, a methanol/HCl mixture was used. With increasing methanolic content the recovery for the organic mercury is increasing constantly whereas the rates for the inorganic species decreased similarly. Using 2 ml of HCl as the extraction solvent, the calculated recoveries for inorganic mercury were 200%, whereas the methylmercury couldn't be recovered at all. The reason for this result is that all the methylmercury got converted into the inorganic form as the separate monitoring of mass 200 and 202 showed. Experiments performed using 100% of methanol for the extraction recovered 75% of the organic species and 25% of the inorganic mercury. The recovery rate for the organic species increase from 60 to 85% with

increasing amounts of methanol up to 5 ml; the recovery of the inorganic mercury increases even more, from 10 to 50% before it leveling off. Decreased recoveries for the organic species using more than 5 ml of methanol is due the saturation of the methylmercury in the solvent. For subsequent experiments, 5 ml of methanol was used as extraction solvent. The chromatogram is shown in ***Figure 1***.

In order to improve the efficiency of the method for the inorganic species, different amounts of 6 M HCl were added to 5 ml of methanol, the soils extracted and the recovery rates calculated. Going from up to 100 µl HCl the recovery rates for the inorganic and organic mercury increase from 50% to 107% and from 80% to 93%, respectively. Adding more acid (1 ml of 6 M HCl) converts more organic mercury to the inorganic form, leading to elevated recoveries for inorganic mercury (140 %) and decreased methylmercury recoveries (75%). Using a mixture of 5 ml of methanol and 100 µl of 6 M HCl as extraction solvent, only 5% of methylmercury was converted to inorganic mercury, and recovery rates were found for the both species of 93 and 107 %, respectively. The power of the microwave was varied between 10 and 80 W and each level was run for periods of time between 5 and 30 minutes. The obtained recovery rates under the different microwave conditions are summarized in ***Figure 2***. The best results were achieved by running the microwave for 20 min. at 30 W power. Under these conditions the inorganic and the organic mercury could be recovered with 98 and 99% efficiency and only 1% of the organic mercury was converted to the inorganic form. It was found that the conversion process increases drastically by running the microwave with more than 40% power and especially longer than 20 min.

The linear range and the limits of detection for the determination of the two mercury species are determined by spiking soil samples with different concentrations (between 50 ppb and 50 ppm) of the mercury species and extract the samples under the conditions described in the experimental section. For each concentration, at least 3 soil samples were spiked and their extracts were injected into the analytical system 3 times. Under these conditions the inorganic and organic mercury could be recovered with 97% and 96% efficiency respectively over a concentration range of 50 ppb to 50 ppm. Using higher volumes of the extraction solvent could extend the linear range. The deviation of the retention time was less than 5%. Calibration graphs based on peak areas were linear (correlation coefficients better than 0.999) for each compound in the range tested. The detection limit, defined as three times the standard deviation of 9 repeated scans (3 injections per soil extract) of 50 ppb each of inorganic and organic mercury was 3 and 15 ppb, respectively.

The method described above was applied to three different soils. The accuracy of the method was tested by analysis of three different certified soil samples (obtained from the National Institute of Standards and Technology, NIST). All three soils contained certified concentrations of inorganic mercury in a range between 1.4 and 32 ppm (there is no certified soil that contains methylmercury). The soils were extracted and the mercury species determined using the optimized microwave technique in combination with the IC-ICPMS method. The found concentrations (n=6) for inorganic mercury compared very well with the certified values, as shown in ***Figure 3***.

Conclusion

A rapid and efficient procedure is described for the quantification of inorganic and methylmercury in soil samples by employing microwave extraction and subsequent IC-ICPMS detection. Under the optimal microwave conditions the inorganic and organic mercury could be recovered with 97% and 96% efficiency over a concentration range of 50 ppb to 50 ppm. The limits of detection for the inorganic and organic species using a methanol/HCl (1M) eluent (55:45, v/v) were found to be 3 and 10 ppb, respectively. The method was successfully employed for the determination of inorganic mercury in 3 certified soil samples.

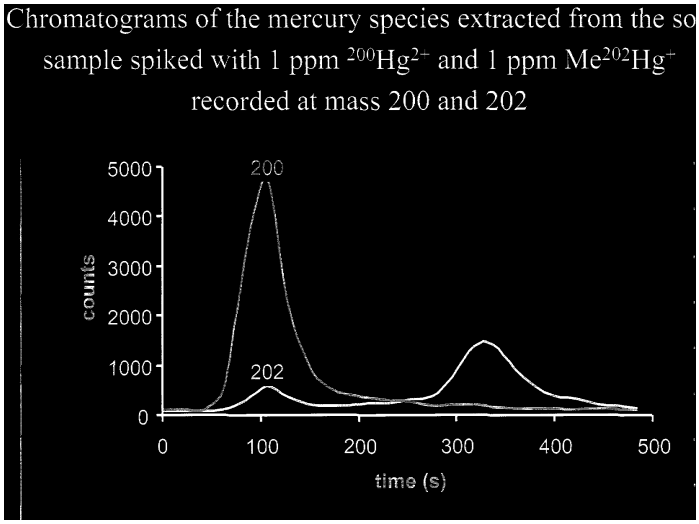

Figure 1.

Effect of the applied power and time program of the microwave for the recovery rates (Rec) of Hg^{2+} and $MeHg^{+}$

time (min) →	5		10		20		30	
power (W) ↓	Hg^{2+} Rec (%)	$MeHg^{+}$ Rec (%)	Hg^{2+} Rec (%)	$MeHg^{+}$ Rec (%)	Hg^{2+} Rec (%)	$MeHg^{+}$ Rec (%)	Hg^{2+} Rec (%)	$MeHg^{+}$ Rec (%)
10	45	63	66	69	78	74	87	75
20	75	85	85	90	87	92	91	93
30	81	93	89	98	98	99	107	93
40	90	95	102	96	113	87	120	75
60	95	54	124	60	130	61	135	56
80	116	54	130	45	138	40	150	33

Figure 2.

Figure 3. Comparison of the found concentrations of inorganic mercury in 3 different soil samples with the certified NIST values. (For chromatogaphic, ICPMS and extraction conditions see Experimental)

NIST#	Soil type	CERTIFIED Hg^{2+} conc. (ppm)	FOUND Hg^{2+} conc. (ppm)
2710	Montana Soil High Traces	32.6 ppm	32.1 ± 0.5
2704	Buffalo River Sediment	1.47 ppm	1.32 ± 0.1
2709	San Joaquin Soil Baseline	1.40 ppm	1.30 ± 0.1

METHOD DEVELOPMENT FOR SPECIATION ANALYSIS OF MERCURY AND TIN COMPOUNDS IN STANDARD REFERENCE MATERIALS USING GC-AED AND GC-MS

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Speciation analysis of mercury and tin organic compounds has been a topic of concern among analytical chemists for several years. Tin compounds, used in anti-fouling coatings and as stabilizing agents in polymers, show a very high toxicity and are subject to restriction on their use in a number of countries. One of the concerns with respect to mercury pollution is the investigation of the pathways for its conversion in the environment.

To understand the pathways of these elements in the environment and to avoid the health hazards associated with them, it is necessary to develop methods for the determination of these compounds at very low concentrations in different matrices. The hyphenation of high resolution separations, available with modern chromatographic techniques, coupled with the high sensitivity and selectivity of atomic spectroscopic detection, provides a powerful tool for speciation analysis. For the monitoring and investigating of those compounds in a wide field of samples routinely, it is necessary to provide Standard Reference Materials (SRMs).

Analytical methods for the determination of methylmercury, mercury(II) and buty-tin-compounds in different SRMs like mussels, sediments, fish and blood samples have been developed. For the separation and detection of the analytes, gas chromatography (GC) with atomic emission detection (AED) and GC with mas spectrometric detection (MSD) were used. After optimization of the instrumental parameters, determination of mercury and tin compounds in the low mg/L-level is possible.

However, the biggest problem for the analysis of environmental samples is sample preparation. In most cases, sample preparation is time consuming and extraction recoveries are low. In biological and sediment samples, the analytes are strongly bound to the matrix, and they have to be released prior to their determination. At the same time, losses or changes in the composition can occur. Different methods of leaching were used and derivatization of the species of interest with Sodium tetraethylborate and Sodium tetraphenylborate were investigated. Also conventional liquid-liquid extraction, Solid-Phase-Micro-Extraction (SPME) - a new sample extraction and enrichment technique - was used and optimized. Analytical variables of the extraction such as fiber coatings, sorption time and desorption time have been investigated. The methods developed provide rapid and sensitive determination of mercury and tin organic compounds in sediments and marine organisms.

A UNIVERSAL ICP-OES METHOD FOR ENVIRONMENTAL ANALYSES

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Abstract
Environmental analyses are performed on a variety of matrices such as drinking water, wastewater, and solid and hazardous waste materials. The metals of interest can vary and the concentrations can range from trace levels to higher. The methods developed by the various environmental programs have differed in the quality control required and only slightly in the analyte list. With the move toward method streamlining and performance-based measurements, it now is possible to consider a universal method that will include a superset of the analytes most often determined.

The concentration range requirements will vary by element and is very different among matrices. For the method to be truly universal it must cover the full concentration range requirements covered by several methods or by different sets of conditions used today. The dual-view capability of an ICP-OES spectrometer can be used to extend the dynamic range for elements expected to exceed the range offered by analyses using either a radial or axial view exclusively.

This paper will explore the utility of a universal method for ICP-OES environmental analysis. The analyte list will be developed and compared with environmental requirements in other countries and US. The linear dynamic range will be evaluated for a dual-view spectrometer and the precision, time for analysis, and interference correction will be demonstrated.

Reference materials and real samples will be used to test the capabilities of the developed method. Low level concentrations in drinking water and wastewater will challenge the method for detection capabilities. Soils and digested waste samples will challenge the spectral overlap correction abilities.

Once the method is fully developed and characterized, the parameters necessary for speeding up the analysis will be evaluated. The sample introduction system, washing parameters, and autosampler set up will be optimized and the general procedures described.

Introduction
The trend in recent years has been for laboratories to push the limits of efficiency and productivity. With the move towards a performance-based measurement system (PBMS), laboratories will have additional opportunities to optimize methodology for analytical performance and range of application. This work describes work performed to develop a universal inductively coupled plasma optical emission (ICP-OES) method for the analysis of a wide range of environmental matrices.

ICP-OES has been used for environmental measurements for many years, and the applicability expanded with the use of accessories and new instrumental capabilities. The speed and flexibility of systems have increased, while at the same time the systems have become more widely available. Methods such as US EPA 200.7, USEPA 6010, and EN ISO 11885 have been developed by different programs to take advantage of ICP technology. The methods are similar, but differ in quality control requirements and the European method differs in the list of analytes. Table 1 compares the methods in general terms.

Ideally, in the environmental laboratory, one ICP-OES method would handle all elements and most of the matrices encountered. The quality control requirements would be uniform and the reporting requirements would be the same for all samples. The method developed for the instrument should be as fast as possible for two replicate measurements while meeting the data quality objectives for precision and detection limits. The method should provide accurate results and the QC should be built-in. Data transfer to third party software or LIMS should be easily accomplished.

The goals for this study were to develop an ICP-OES method that incorporates the USEPA elements (European elements will be added later) that covers the full concentration range expected. The performance of the method was demonstrated on a variety of matrices containing a range of concentrations.

Table 1. ICP-OES Method Comparison

	US EPA 200.7	US EPA 6010B	EN ISO 11885
Elements	32	Same 31, no Ce	Same 29, no Tl, Ce, Hg; Bi, W, Zr, S included
QC	Initial and Continuing	Initial and Continuing	Varies by state in Germany
Concentration Range	Water, typically low	Solid and Hazardous Waste, low and high concentrations	Water and sludge, used for other matrices, low and high concentrations

Experimental

The Perkin-Elmer Optima 3300™ DV ICP-OES equipped with a low flow GemConeä nebulizer and cyclonic spray chamber was used for all determinations. The Optima 3000 DV ICP-OES is a simultaneous ICP with an echelle polychromator and Segmented-Array Charge-Coupled Detector (SCD). Simultaneous measurement of the background and analyte emission allows for accurate correction of transient background fluctuations. The instrument can collect data from either the radial viewing configuration or axial configuration or a combination of the two during a single analysis, this study was performed using the full dual view capability.

The instrumental conditions used for all determinations are shown in Table 2. The nebulizer flow was optimized for the best detection limits. Calibration standards were prepared from PE Pure multielement and single element standards. Table 3 lists the wavelengths chosen for the method, background correction points used, and the standard concentration used for calibration. The background correction points are typical and provide a starting point for method development. It is likely that individual instruments will require minor adjustment to the points to optimize the correction. In several cases, two wavelengths are included for evaluation. In method development this is a common procedure, when the evaluation is complete the more appropriate wavelength or view can be chosen and the extra wavelength eliminated. Alternatively, since the analysis time is not increased by the addition of wavelengths, a second wavelength may be retained for confirmation, if desired.

Table 2. Instrumental Conditions

Parameter	Optima 3300 DV
RF Power	1450 watts
Nebulizer Flow	0.55 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.8 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto Integration	5 sec min –20 sec max
Read delay	45 sec
Rinse	10 sec
Replicates	2
Background correction	Manual selection of one or two points

Yttrium was used as the internal standard and added on-line to the blanks, standards, and samples. The rinse solution contained 2% HNO_3 + 0.1% Triton-X 100™.

EPA method 200.7, revised in 1994, and EPA method 6010B, revised in 1996, were used for guidance in developing the method.[1,2]

Table 3. Elements, Wavelengths, Correction Intervals, and Calibrations Standards

Element and Wavelength (nm)	Lower Correction Interval (nm)	Upper Correction Interval (nm)	Standard Concentration (mg/L)
Ag 338.289	-0.052	0.031	5.0
Al 308.215R		0.045	250
As 188.979	-0.024	0.011	1.0
B 182.527	-0.026	0.020	5.0
Ba 233.527R	-0.055		5.0
Be 313.107		0.034	5.0
Ca 227.546	-0.048		250
Ca 315.887R	-0.042	0.045	250
Cd 226.502		0.038	5.0
Ce 413.765	-0.054		5.0
Co 228.616	0.024		5.0
Cr 205.560R	-0.019	0.019	5.0
Cr 267.716	-0.038	0.031	5.0
Cu 324.754		0.030	5.0
Fe 238.204R	-0.022	0.025	1.0, 100
Fe 273.955R	-0.031	0.033	100
Hg 194.168	-0.016	0.012	0.5
K 766.490R	-0.136		1.0, 100
Li 670.784R	-0.124		5.0
Mg 279.079R	-0.031	0.032	250
Mn 257.610	0.036		5.0
Mo 202.030	-0.019		5.0
Na 589.592R	-0.074	0.074	100
Na 330.237	-0.030		100
Ni 231.604	-0.021	0.021	5.0
P 178.221	-0.021		5.0
Pb 220.353	-0.020	0.013	1.0
Sb 206.833	-0.012		5.0
Se 196.026	-0.015		1.0
Si 251.611R	-0.023	0.023	5.0
Sn 189.933	0.017		5.0
Sr 460.733R	0.046		5.0
Ti 334.441		0.044	5.0
Tl 190.800		0.041	1.0
V 292.402	-0.027	0.027	5.0
Zn 206.200		0.027	5.0

Samples consisted of soil and sediment digests and wastewater reference materials from High-Purity Standards, Inc. (Charleston, SC). NIST Drinking Water reference material 1643D, Trace Elements in Water was used for validation at low levels.

Results and Discussion

The choice of axial or radial viewing was chosen based on the range of concentrations expected and the detection limit needed to meet the quality objectives. The detection limits and linear range are shown in Table 4 for a variety of elements.

Table 4. Detection Limits and Linear Ranges Dual View Method

Element	IDL(mg/L)	Linear Range (mg/L)	Observation
Fe	2.2	1000	Radial
Al	36	1000	Radial
Ca	6.4	1000	Radial
Mg	14	1000	Radial
Na	19	1000	Radial
Pb	1.6	100	Axial
Tl	4.2	100	Axial
Se	5.0	100	Axial
As	6.3	100	Axial

Freedom from interferences is also a consideration and the easily-ionizable element effect (EIE) was considered for Na and K. Easily ionizable elements such as the alkalis can vary in signal intensity depending upon the concentration of other easily ionizable elements present in the sample. This can cause inaccurate measurements of Na and K in samples that contain varying amounts of these elements or are calibrated with single element standards. This type of interference is enhanced in axial-viewing and can be resolved in several ways. An ionization buffer can be used to minimize the differences between samples (matrix matching). The element chosen for the buffer must not be required as an analyte element, ruling out the most commonly used element, Li. In addition, high concentrations of one alkali often contain trace contamination of other alkalis, which may cause unacceptable inaccuracies in analytical measurements at low concentrations. Another solution is to use an element as an internal standard that shows a similar effect. Radial viewing of the plasma does not show the same effect and can be used as an alternative for these elements. Rubidium was evaluated as an internal standard element for K and compared with yttrium as an internal standard, matrix matching and radial viewing. Table 5 summarizes the results and shows that, although Rb is a better internal standard than Y for K, if radial viewing is an option it will require less method development to implement.

Table 5. EIE Compensation Recoveries and (standard deviation)

	Axial View			*Radial View*	
Sample	No IS, No matrix matching	Matrix matching (250 Na added)	Rb IS	Y IS	No IS, No matrix matching
2 K, 250 Na	4.46 (0.035)	1.98 (0.031)	2.29 (0.011)	4.87 (0.009)	2.08 (0.012)
2 K, 250 Na, 250 Ca	4.72 (0.042)	2.08 (0.006)	2.33(0.003)	5.23 (0.081)	2.12 (0.026)
River Sediment B (Certified 200 K)	230(1.0)	212 (1.6)	165 (0.1)	266 (0.1)	184 (0)

Once the method was developed and characterized reference materials were used for validation. Drinking water and wastewater reference materials were used to test the method at low concentrations. Table 6 shows the results, including the certified values and recoveries of the certified values. Recovery values of 80-120% of the certified value are generally acceptable and the values are well within this range.

Table 6. Drinking Water and Wastewater Results (standard deviation)

Element	1643D Certified (mg/L)	1643D Measured (mg/L)	**1643D Recovery**	HPS WW Certified (mg/L)	HPS WW Measured (mg/L)	**HPS WW % Recovery**
As 188.979	0.05602 (0.00073)	0.0581 (0.0001)	**104**	0.15 (0.00075)	0.150 (0.001)	**99.9**
Be 313.107	0.01253 (0.00028)	0.0122 (0.00006)	**97.7**	0.15 (0.00075)	0.147 (0.0001)	**97.7**
Cd 226.502	0.00647 (0.00037)	0.0060 (0.00004)	**92.4**	0.15 (0.00075)	0.147 (0.0002)	**97.8**
K 766.490R	2.356 (0.035)	2.21 (0.033)	**93.8**	-	-	**-**
Mn 257.610	0.03766 (0.00083)	0.038 (0.0003)	**101**	0.5 (0.0025)	0.497 (0.0005)	**99.4**
Pb 220.353	0.01815 (0.00064)	0.0184 (0.0007)	**102**	0.5 (0.0025)	0.504 (0.003)	**101**
Sb 206.833	0.0541 (0.0011)	0.0521 (0.002)	**96.3**	0.15 (0.00075)	0.152 (0.003)	**101**
Sr 460.733R	0.2948 (0.0034)	0.288 (0.001)	**97.7**	-	-	**-**

High level and mixed concentrations were tested with soil and sediment digests. The results are shown in Tables 7, 8, and 9.

Table 7. Soil Results (standard deviation)

Element	HPS Soil A Certified (mg/L)	HPS Soil A Measured (mg/L)	HPS Soil A % Recovery
Al 308.215R	500 (2.5)	492 (11)	98.5
Cu 324.754	0.3 (0.002)	0.318 (0.0005)	106
Fe 238.204R	200 (1)	195 (4)	97.5
K 766.490R	200 (1)	196 (4)	97.8
P 178.221	10 (0.05)	11.2 (0.09)	112
Pb 220.353	0.4 (0.002)	0.371 (0.003)	92.8
V 292.402	0.1 (0.0005)	0.10 (0.0002)	100

Table 8. Sediment Results (standard deviation)

Element	HPS Sediment B Certified (mg/L)	HPS Sediment B Measured (mg/L)	HPS Sediment B % Recovery
Al 308.215R	600 (3)	605 (8)	101
Cd 226.502	0.03 (0.0002)	0.025 (0.0002)	83.3
Fe 238.204R	400 (2)	396 (6)	99
K 766.490R	200 (1)	203 (3)	102
P 178.221	10 (0.05)	11.1 (0.03)	111
Pb 220.353	2 (0.01)	1.94 (0.0002)	97.0
V 292.402	1 (0.005)	1.00 (0.0003)	101

Table 9. Estuarian Sediment Results (standard deviation)

Element	HPS Est. Sed. Certified (mg/L)	HPS Est. Sed. Measured (mg/L)	HPS Est. Sed. % Recovery
Al 308.215R	700 (3.5)	711 (0.77)	102
As 188.979	0.1 (0.0005)	0.093 (0.0026)	93.0
Fe 238.204R	350 (2)	355 (0.31)	101
K 766.490R	150 (0.75)	160 (0.08)	106
P 178.221	5 (0.03)	5.81 (0.03)	116
Pb 220.353	0.3 (0.0015)	0.276 (0.001)	92.0
V 292.402	1 (0.005)	1.02 (0.0009)	102

The results show that the method is operating properly for a variety of matrices and concentrations. The standard deviation for two replicates is excellent. A more thorough study of interferences is required to ensure that adequate compensation is built into the method. For the low-level samples, no interferences were observed. For the higher concentration samples, interferences were observed, but could be compensated with algorithms such as interfering element corrections (IEC) or multicomponent spectral fitting (MSF).

The method was evaluated for productivity. The rinse between each sample was maintained, but shortened from the usual 45-60 seconds to 10 seconds. This provides a wash of the probe, but more rinsing of the tubing is accomplished with the rinse-in of the next sample. The fast pumping speed option was not used for the washing since the 1.6-1.8 mL/min provides an adequate wash in a reasonable time. The exact time for wash-in was evaluated with a study of different read delays and monitoring of the precision to see when stability was achieved. A rinse station was added to the system to allow longer unattended runs. The internal standard was added on-line with a mixing block, reducing the need to pipet the solution into individual samples.

The overall measurement was documented based on an average run of samples with varying elemental compositions. The average time required for each sample, including wash, rinse-in, and two replicates was 3 minutes and 23 seconds.

Conclusions

In this work we have explored the possibility of a universal ICP-OES method fort he measurement of 32 elements in a variety of matrices at low and high concentration levels. Preliminary assessment of the method indicates that this is a viable approach, incorporating both views of the plasma for the optimal detection limit and linear range combinations. The time of analysis for 32 elements including trace and part-per-million concentrations was less than 3.5 minutes and provided excellent precision. Further work will include the evaluation of additional matrices. Interference algorithms will be more completely evaluated and compared.

References

1. Method 200.7, Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA/600/R-94/111 (1994).
2. Method 6010B, Methods for Chemical and Physical Testing (SW-846), Revision 2, December 1996, US EPA.

NEW TECHNOLOGIES FOR METALS DIGESTIONS FOR ENVIRONMENTAL SAMPLES

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For the last 40 years hot plate acid digestion methodology has provided an adequate digestion of samples for low level metals analysis. As detection limits of modern elemental analysis instrumentation have decreased, however, sample contamination resulting from hot plate digestion has become a serious issue. Glass beakers used for digestion, naturally carry many of the elements that are currently analyzed, and digesting on hotplates made of metal parts such as Aluminum, Iron, Chromium, Lead, Copper, etc only add to the contamination problem. Hot

spots on the hotplates creates problems including uneven evaporation, incomplete digestion, accidental boiling and sample dryness. Microwave digestion addresses some of these contamination issues; however, microwave is only EPA approved for up to 13 elements, which have restricted limits and still requires multiple transfer steps. With the development of the Environmental HotBlock digestion system, clean disposable cups are used for digestion, volume addition, filtration and sample storage without transfering the sample. Construction components of the HotBlock are non-corrosive, and the system delivers uniform temperature heating. Experiments show that this technology has solved most of the negative issues involving hotplate digestion while still allowing for the digestion of all elements at all levels. Experiments include digestion recoveries, heating uniformity, contamination and cross contamination, followed independent user findings of this technology.

MAGNESIUM CHLORIDE IN THE CYANIDE DISTILLATION

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Introduction

In the EPA wastewater and solid waste methods (EPA Method 335.2 and 9010B) and *Standard Methods* (SM 4500-CN^- C) for distillation of total cyanide, the addition of magnesium chloride solution to the distillation pot is mandated. In attempting to chemically describe the actual function of the magnesium chloride, one is normally at a loss to present a mechanism where it helps the isolation procedure. This paper presents the history of the magnesium chloride requirement and then evaluates the requirement based on the results of laboratory experiments designed to delineate its utility in current laboratory practice.

There are a number of chemical additives that are used in the distillation pot to reduce interferences in the cyanide isolation process, including ethylene diamine and sulfamic acid. Ethylene diamine is used to eliminate interferences from aldehydes by preventing cyanohydrin formation. Sulfamic acid is present to give an alternate substrate for nitrites to chew upon[1]. Magnesium chloride is specifically required in the table of approved methods in 40 CFR 136.3 as a distillation additive[2]. A literature search has revealed that the specification for use of magnesium chloride is due to an evolutionary process over several editions of *Standard Methods,* that culminated in the Fifteenth Edition with the present requirement. The appearance of this reagent dates back to a paper by Serfass[3] in the 1950's where it was reported that addition of magnesium chloride **and** mercuric chloride moderated the evolution of hydrogen cyanide from the acidified solution allowing for better recovery.

The moderating effect was ascribed to a slower release of the cyanide through formation and then degradation of tetracyanomercurate. Mercury forms a more stable cyanide complex than most metals, except iron and cobalt. If hydrogen cyanide is released by a metal, the cyanide is grabbed by the mercury. The magnesium chloride was added as a convenient source of chloride which effectively competes with cyanide for complexation to the mercury, resulting in a slow movement of hydrogen cyanide to the absorbing flask over the course of the one hour distillation. The combination of the two reagents was published in the 12th Edition of *Standard Methods* (1965).

In a paper in 1968[4], it was demonstrated that use of cuprous chloride, Cu_2Cl_2, with sulfuric acid (the Williams distillation procedure), was as effective as the mercury chloride/magnesium chloride mixture. The 13th Edition (1971) of *Standard Methods* repeated the use of the $HgCl_2$-$MgCl_2$ reagent. The 14th Edition of *Standard Methods* (1975) described use of cuprous chloride/magnesium chloride as a suitable catalyst. There seems to be no experimental justification for this combination of reagents. Rather it appears as though that the replacement of mercury by copper was a response to a growing awareness (or panic) of the hazards of mercury, and the revealing of the horrors of the Minamata Bay massive mercury poisoning incident. The 15th Edition of *Standard Methods* (1980) dropped the cuprous chloride and dictated use of only magnesium chloride catalyst[5]. Editions of *Standard Methods* since the 15th Edition have repeated the same information about magnesium chloride.

The EPA wastewater monitoring methods were developed for the 1983 publication of *Methods for the Chemical Analysis of Water and Wastes* (MCAWW), largely from the methods presented in *Standard Methods.* The use of magnesium chloride was not questioned, simply repeated. The EPA has for the most part simply copied the cyanide distillation from the Fifteenth Edition and MCAWW in other methods such as 9010B for SW-846. Of note is that methods for cyanide isolation developed independently of the *Standard Methods* Committee lack magnesium chloride as a reagent. In the automated continuous flow distillation-colorimeteric procedure (EPA Method 335.3), a mixture of hypophosphorus and phosphoric acids are used for the acidification and no magnesium chloride is required.

Materials and Methods

The cyanide distillations were performed in a 10-place midi-distillation unit (Kimble-Kontes, Vineland, NJ). The sulfate salts of silver, copper, nickel, manganese (II), cadmium, and mercury and the nitrates of cobalt, gold, silver, and mercury were purchased as ACS Reagent grade solids from Fisher Scientific, Pittsburgh PA, Aldrich Chemical Company, Milwaukee, WI, or J.T. Baker. Mixed metals standards was purchased from High-Purity Standards, Charleston, SC, as solutions of the nitrate salts. Magnesium chloride and sodium chloride were Fisher Scientific ACS Reagent Grade. Reagents were prepared with doubly-deionized water in Class A volumetric glassware.

The test metal solution and the cyanide spike were mixed in the reaction tube. Sulfamic acid was added to each tube. Sulfuric acid was added through the vent tube, followed by magnesium chloride or sodium chloride solution. The vacuum pump was turned on to generate an air flow through the system and mix the sample, then heating was begun. Samples were distilled with a reflux rate of at least 60 drops/min for a period of one hour. Evolved hydrogen cyanide was swept into a sodium hydroxide trap. The contents of the trap were assayed using the pyridine-babituric acid colorimetric reaction (EPA Method 9034, EPA Method 335.2, *Standard Methods* 18th Edition 4500-CN^- C). Calibration checks were run daily to verify the calibration curve. Blanks and laboratory control samples were run daily to assess laboratory contamination and method performance.

Results and Discussion

The results are presented in the Table and list the concentration of the cyanide spike, the metal ion, the presence or absence of magnesium chloride and the percent recovery of the cyanide spike. The data are assessed as relative percent recovery[6] and presented as a bar graph in the Figure. Bars above the centerline indicate decreased recovery on the addition of magnesium chloride. Bars below the centerline indicate increased recovery of cyanide on the addition of magnesium chloride.

Although the Figure might suggest that there is a small but persistent positive effect due to the magnesium chloride addition, the normal lab performance on cyanide distillation of duplicates exhibits 0-13 RPD. Any bars falling between plus or minus 13 of the centerline should be attributed to normal variation, and thus are not significant.

The first observations to make is that there are very few of the tested metals that exhibit any effect from magnesium chloride addition to the distillation. Cobalt gives poor recovery, 25 and 27%, regardless of any addition of magnesium chloride. Other metals give good recoveries.

The second observation is that any silver present in the sample is going to adversely react with magnesium chloride and cyanide recovery is significantly reduced. This was seen with both the sulfate and nitrate counterions. The effect also persists if chloride is added to the sample as sodium chloride. The conclusion is that it is the chloride ion that is the cause of the effect. Silver is well known to complex quite tightly with chloride, the $[Ag(Cl)_2]^-$ complex being important for solubilization of silver in acid digestions for total metals analysis[7]. Possibly what is being seen is a tightly bound mixed complex of chloride and cyanide associated with the silver.

A third observation is that addition of magnesium chloride to samples containing mercury gives marginally improved recoveries when sulfate is the counterion. Based on the paper by Serfass, one would expect dramatically increased recoveries, but this is not seen. This same observation was duplicated when the mercury, as the sulfate, concentration was increased five-fold. However significantly decreased recoveries are observed if nitrate is present with the mercury. Addition of sodium chloride, instead of magnesium chloride, in the presence of mercury nitrate, produces no effect, comparable to the results obtained from simple acidification and distillation. These observations are not easy to rationalize.

On the other hand, if gold and or palladium are present in the sample, the addition of magnesium chloride is beneficial. As is the case with silver, the effect is due to the presence of the added chloride, with addition of sodium

chloride almost doubling the recovery of cyanide from gold solutions. The increased efficacy of sodium chloride over magnesium chloride may be attributable to the amount of free ionic chloride in the solution. Magnesium chloride exhibits considerable covalent character even in solution, while sodium chloride is completely ionized.

Table. Results of cyanide experiments

Cyanide spike mg/L	Metal mg/L	$MgCl_2$	%R
1.0	-	N	94
1.0	-	Y	96
0.21	$AgSO_4$ 2.00	N	84, 72
0.21	$AgSO_4$ 2.00	Y	61, 50
0.42	$AgNO_3$ 2.00	N	73, 81
0.42	$AgNO_3$ 2.00	Y	55, 48
0.42	$AgNO_3$ 2.00	NaCl	51
0.21	Cu 2.00	N	82
0.21	Cu 2.00	Y	95
0.21	Ni 2.00	N	88
0.21	Ni 2.00	Y	92
0.21	Mn 2.00	N	89
0.21	Mn 2.00	Y	90
2.00	Ferrocyanide	N	90
2.00	Ferrocyanide	Y	95
2.00	Ferricyanide	N	88
2.00	Ferricyanide	Y	90
0.42	Cd 2.00	N	68, 74
0.42	Cd 2.00	Y	71, 75, 74
0.21	$HgSO_4$ 2.00	N	71
0.21	$HgSO_4$ 2.00	Y	81
0.21	$HgSO_4$ 10	N	83
0.21	$HgSO_4$ 10	Y	94
0.42	$Hg(NO_3)_2$ 2.00	N	76
0.42	$Hg(NO_3)_2$ 2.00	Y	50
0.42	$Hg(NO_3)_2$ 2.00	NaCl	71
0.21	Pd 2.00	N	46
0.21	Pd 2.00	Y	55, 58
0.42	Metals 1	N	81
0.42	Metals 1	Y	83
0.42	Metals 3	N	88
0.42	Metals 3	Y	92
0.42	Metals 4	N	83
0.42	Metals 4	Y	92
0.21	Co 2.00	N	25
0.21	Co 2.00	Y	27
0.42	Au 2.00	N	42, 38, 31
0.42	Au 2.00	Y	61, 59
0.42	Au 2.00	NaCl	8,176

Metals 1 = Al (4 ppm), Sb (1 ppm), As (4 ppm), Ba (4 ppm), Be (0.5 ppm), Cd (0.4 ppm), Cr (0.8 ppm), Co (1 ppm), Cu (0.5 ppm), Fe (2 ppm), Pb (2 ppm), Mn (1 ppm), Ni (1 ppm), Se (4 ppm), Tl (4 ppm), V (1 ppm), Zn (1 pm), Y (8 ppm)
Metals 3 = Sn (2 ppm), Ti (0.8 ppm), Mo (0.4 ppm), Si (2 ppm)
Metals 4 = Sr (0.2 ppm), Ca (4 ppm), Mg (4 ppm), Li (0.04 ppm), K (4 ppm), Na (4 ppm), B 0.4 ppm), P (4 ppm)

Conclusion

Considering the universe of samples received by a commercial laboratory for cyanide analysis, an analyst is probably going to encounter silver in samples much more frequently that gold or palladium. Addition of chloride ion is shown to be detrimental to cyanide recovery when silver is present in the sample. For samples with gold or palladium, chloride addition improves recovery. Analysts should add chloride to samples containing either of these metals.

For most analyses, however, the recommendation is to eliminate the addition of any chloride, magnesium or sodium, to samples for distillation of cyanide.

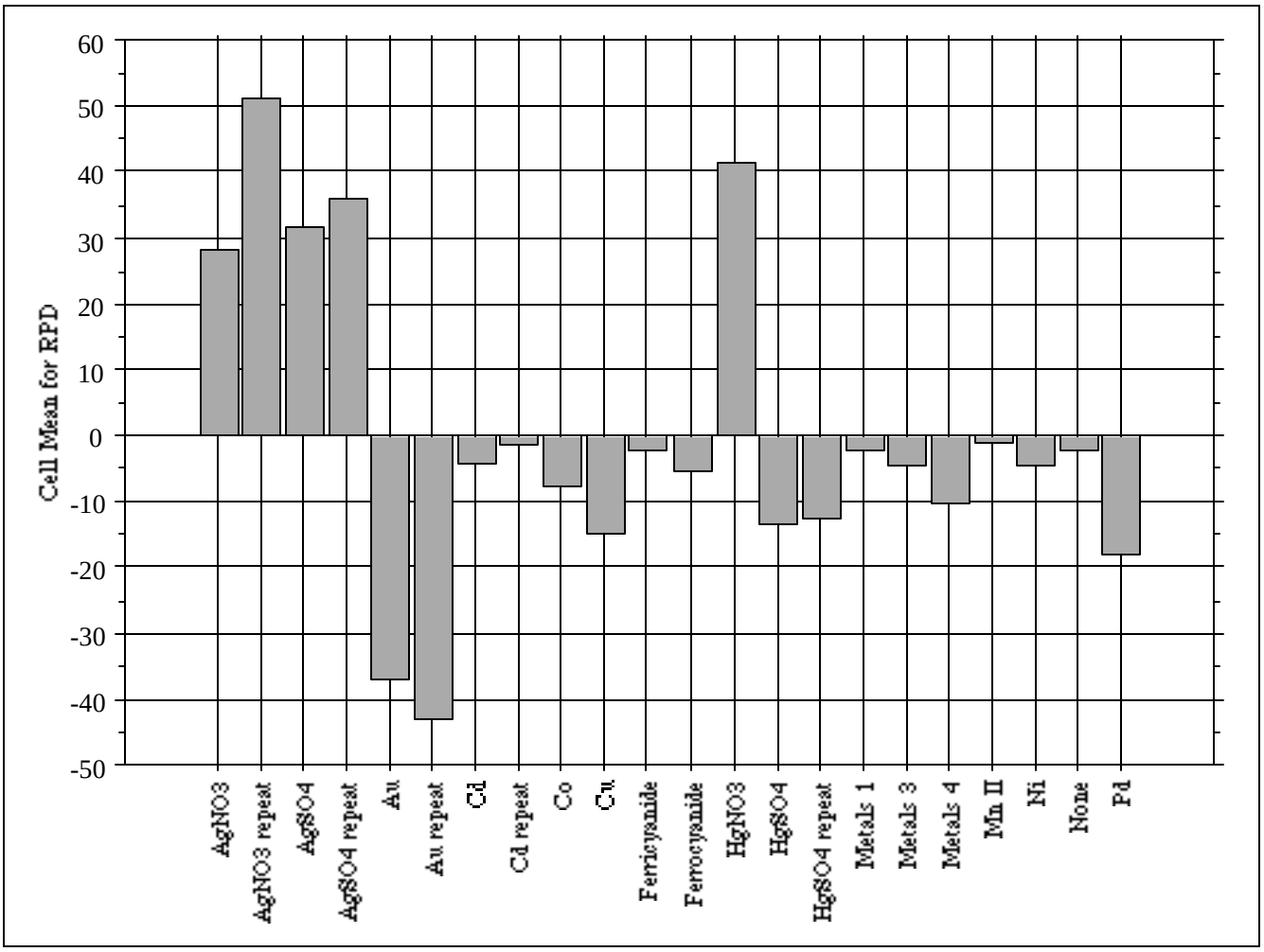

Figure. Bar chart of RPD of cyanide distillation recoveries from experiments without and with added magnesium chloride.

References

1. Smith, R.-K., 1999. *Lectures on Wastewater Analysis and Interpretation*, Genium Publishing, Schenectady, NY 1-800-243-6486.
2. *Guidelines establishing test procedures for the analysis of pollutants*, 40 CFR 136, 1 July 1998, USEPA.
3. Serfass, E.J. et al, 1952. Analytical Method for the determination of cyanides in plating wastes and in effluents from treatment processes. *Plating* 39:267.
4. Elly, C.T., 1968. Recovery of cyanides by modified Serfass distillation. *WPCF Journal*, Vol. 40. No. 5, pg 848-856.
5. In the balloting of the 15th Edition, there was a least one negative vote that strenuously objected to the used of magnesium chloride. The ballot was ignored.
6. Smith, R.-K., 1999. *Handbook of Environmental Analysis, Fourth Edition*, Genium Publishing, Schenectady, NY 1-800-243-6486.
7. Kimbrough, D.E., and J. Wakakuwa, 1992. "A study of the linear dynamic ranges of several acid digestion procedures", *Environ. Sci. Technol.* 26(1):173-178; Cohen, R.J., A.J. Meyer, E. O'Bryan, J. Kunze, and S. Kunze, 1996. "An improved digestion method for silver analysis in solid samples", *Am. Environ. Lab.*, 6/96: 28-29; EPA Methods 3010 and 3050, SW-846.

DECREASING HYDRAULIC CONDUCTIVITY BEHAVIOR AND REGULATORY COMPLIANCE OF ALTERNATIVE HYDRAULIC BARRIERS: AN EXERCISE IN PATIENCE

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Paper mill sludge used as landfill cover barrier material offers a viable alternative to compacted clay. Paper mill sludge is the residual material from the paper making process and is characterized by high water contents, high organic contents, high compressibilities and low shear strengths. Geotechnical research on this material has led to the successful construction of a number of paper mill sludge landfill covers in the Northeastern United States. A major challenge when dealing with paper sludge landfill capping projects is the process of educating regulatory officials about paper sludge properties and behavior. The purpose of this paper is to present typical geotechnical properties and discuss the hydraulic conductivity behavior of paper sludge landfill covers. Special emphasis will be placed on how the hydraulic conductivity of paper sludge decreases with time after placement. The typical hydraulic conductivity requirement of 1 x 10^{-7} cm/s is often accomplished by paper sludge hydraulic barriers, however, there are instances where the hydraulic conductivity is slightly above the maximum. The amount of barrier layer settlement typical of paper sludge landfill covers can range from 20% to 35% as compared to the 2% to 3% for compacted clays. During this period of consolidation, large reductions in void ratio occur which affect density, water content, shear strength and hydraulic conductivity. Hydraulic conductivity will be expected to decrease during consolidation. In general, the hydraulic conductivity of a paper sludge landfill cover can decrease about one order of magnitude over a period of one year. This is a reasonable time period when compared to the design life of the landfill. There has been a considerable amount of data accumulated over the years to show general trends of decreasing hydraulic conductivity to values lower than 1 x 10^{-7} cm/s. Field data from three paper sludge landfills in New York and Massachusetts will be presented. For instance, hydraulic conductivity tests from the Corinth (NY) Landfill decreased from 1 x 10^{-7} cm/s to 2 x 10^{-8} cm/s, a decrease of about one order of magnitude, during the post construction period. Other paper sludge landfill covers show similar trends. Due to the changing properties of the paper sludge barrier layer, a long-term monitoring plan is essential to completely evaluate the performance of paper sludge landfill cover. Also, the measurement of several geotechnical properties (such as organic content, specific gravity, density, hydraulic conductivity and shear strength) often not required for compacted clay C vers will be discussed.

Therefore, the hydraulic conductivity behavior of paper mill sludge landfill covers shows improvement over time. Compliance of hydraulic conductivity can be achieved in about one year after placement for initially marginal values of hydraulic conductivity. The paper sludge will behave accordingly, however - Will regulatory agencies permit the use of paper mill sludge and exercise patience allowing the paper sludge barrier layer to consolidate and decrease its hydraulic conductivity?

PBMS: HOW WILL IMPLEMENTATION CHANGE THE ANALYSIS OF ENVIRONMENTAL SAMPLES BY ICP-MS?

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Abstract
The results from the analysis of a variety of environmental samples by ICP-MS utilizing traditional methodologies, such as US EPA Methods 6020 and 6020A and under Performance Based Measurement System (PBMS) principles

will be discussed. Data will be presented illustrating the performance of ICP-MS for elements recently added to Method 6020A. In addition, the requirements regarding Interference Check Standards A and AB in Methods 6020 and 6020A will be discussed in relation to their relevance on data quality. Data showing the performance of Internal Standards will also be discussed in terms of what kind of drift is realistic for performing cost effective analyses, while maintaining acceptable data quality. Recommendations will be given for laboratories developing PBMS based methods for ICP-MS as well as for individuals auditing these laboratories on key issues affecting data quality in ICP-MS.

Introduction

Currently, laboratories are required to use strict prescriptive methodologies for the analysis of environmental samples. Although the methods contained in SW-846 are intended to be guidance methods and attempts have been made by the EPA to clarify this intent, many regulators see these methods not as a guide, but as a rule. Many samples being analyzed by environmental laboratories do not fit into the traditional water, soil, waste categories and the original SW-846 method may not give good results for a particular sample type without some modifications. Depending on the regulator, agency, or client the laboratory is reporting the data to, the laboratory's ability to make needed method modifications may be restricted or even forbidden. The movement of the EPA to a performance based measurement system will allow laboratories to use methodologies that will give reliable, accurate, and meaningful results for specific sample matrices, not just follow the rules.

Review of Limitations of Method 6020

Approved Elements. The version of Method 6020 that was originally promulgated in SW-846 Update II (January 1994) only contained a partial list of the elements normally analyzed under most regulatory programs. Noticeably missing from the method were the following elements: Se, Mo, V, Na, Ca, Mg, K, and Fe. The non-inclusion of these elements in Method 6020 limited the usefulness of ICP-MS in certain environmental applications. Laboratories wishing to use ICP-MS for these additional elements were either hesitant to do so, because the elements in question were not originally included in the method or regulators and/or state agencies would not allow modification of the method to include them, even with submission of relevant performance data. Application data published (see Table 1) by Perkin Elmer includes method performance data for these and several other additional elements. The data included in Table 1 show the detection limits and linear ranges attainable on modern ICP-MS instruments, such as the ELAN 6000/6100. New advances in detector technology and operation, including the use of the dual-range discreet dynode detectors, allow much higher concentrations, as much as 200 ppm Na, to be determined by ICP-MS. A recent revision of the method, Method 6020A, to be published in Update IVA, finally includes the alkali metals, Se, and Hg as analytes for which the EPA has demonstrated the acceptability of Method 6020. The inclusion of these elements in the updated Method 6020A will extend the applicability of the method until PBMS is fully approved and implemented.

Interference Check Standards. Although the number of interferences in ICP-MS is limited, there are some well known interferences that if not properly corrected for can lead to significant errors in the resulting data. The composition of the Interference Check Standards A and AB in both Methods 6020 and Method 6020A are designed to test the more common interferences encountered in environmental samples. These interferences include the argon-chloride and argon-carbide interferences that interfere with the determination of As, Se, and Cr, respectively. It should be recognized that the interference check standards required by Methods 6020 and 6020A have the same intent although the exact concentration of the elements in the matrix may vary slightly between the two different versions of the method as is illustrated by Table 2. For best results, the concentration of the matrix elements should be indicative of those in the types of samples analyzed by the laboratory. Both the analyst and the auditor should recognize that some of the interferences may be concentration dependent. This is particularly true of molecular interferences. It is more important that the limitations of the interference corrections be tested and documented by the laboratory than assuming that if the exact concentrations listed in the reference method are used, no interference problems will exist. The laboratory should determine to what concentration a correction is valid and establish a policy for samples exceeding that limit. Under the current two EPA methods, there are no requirements set for the pass/fail conditions of these standards. The only requirement is that the solutions are run at the beginning and end or every 12 hours, whichever is more frequent. Most laboratories have tried to follow the QC Limits for the ICSA and ICSAB solutions from the ICP-OES Method 6010 for Method 6020. However, the detection capabilities of ICP-MS are so low that it is very difficult, if not impossible, to find a source for ICSA where the measured concentrations of the analytes are below the MDLs of the analytes determined by Method 6020.

Table 1. ELAN 6000/6100 IDLs, MDLs, and Linear Ranges for Method 6020

Analyte	Mass	IDL (µg/L)	MDL (µg/L)	Linear Range (mg/L)
Be	9	0.02	0.02	10
Al	27	0.04	0.12	10
Cr	52	0.1	0.5	10
Mn	55	0.004	0.009	10
Co	59	0.002	0.002	10
Ni	60	0.007	0.04	10
Cu	65	0.005	0.02	10
Zn	66	0.015	0.03	5
As	75	0.06	0.2	5
Ag	107	0.03	0.03	5
Cd	114	0.002	0.004	5
Sb	123	0.003	0.03	10
Ba	135	0.01	0.01	10
Tl	205	0.0003	0.0003	10
Pb	208	0.001	0.009	10
Hg*	201	0.020	0.020	20**
Se*	82	0.09	0.09	5
Mo	98	0.004	0.004	5
Th	232	0.002	0.002	10
U	238	0.0009	0.0009	10
V*	51	0.03	1.2	10
Na*	23	0.6	4	100
Ca*	44	15	20	200**
Mg*	24	0.02	0.04	100
K*	39	9	9	100
Fe*	54	4	4	200**

* included in Method 6020A – SW-846 Update IVA.
** highest level standard ran for linearity test.

Table 2. Composition of Method 6020 ICSA and ICSAB solutions.

Analytes	Method 6020 Concentration in ICSA	Method 6020 Concentration in ICSAB	Method 6020A Concentration in ICSA	Method 6020A Concentration in ICSAB
Al Mg, P, K, S	100 mg/L	100 mg/L	100 mg/L	100 mg/L
Ca	100 mg/L	100 mg/L	300 mg/L	300 mg/L
Fe Na	100 mg/L	100 mg/L	250 mg/L	250 mg/L
C (carbon)	200 mg/L	200 mg/L	200 mg/L	200 mg/L
Cl (chloride)	1000 mg/L	1000 mg/L	2000 mg/L	20000 mg/L
Mo Ti	2 mg/L	2 mg/L	2 mg/L	2 mg/L
As Cd, Zn	0 mg/L	0.020 mg/L	0 mg/L	0.100 mg/L
Cr Co, Cu, Mn, Ni,	0 mg/L	0.020 mg/L	0 mg/L	0.200 mg/L
Ag	0 mg/L	0.020 mg/L	0 mg/L	0.050 mg/L
Hg	0 mg/L	0 mg/L	0 mg/L	0.020 mg/L
Se	0 mg/L	0 mg/L	0 mg/L	0.100 mg/L
V	0 mg/L	0 mg/L	0 mg/L	0.200 mg/L

Analysts either following Methods 6020 or 6020A or developing his/her own methods under the PBMS system should consider the use of such a solution to test the interference equations used in the method. It should also be realized by both analysts and auditors that the prescribed ICSA and ICSAB solutions listed in Methods 6020 and 6020A do not test for a common interference found in some environmental samples from wastewater treatment procedures and brackish or saline waters or sediments – bromide. Bromide is commonly used for disinfecting wastewaters and drinking waters. In addition, brackish and ground waters can have significant concentrations of bromide present. Bromine has naturally occurring isotopes at mass 79 and mass 81. The presence of part per million levels of bromide in a sample can form the molecular species ^{1}H-$^{81}Br^{+}$ in the plasma and interfere with the determination of Se at mass 8. Figure 1 shows a scan of 10 ppb Se superimposed over that of 10 ppm Bromide (from an ion chromatography standard). The signal at mass 82 in the bromide solution is equivalent to 27 ppb Se and can lead to an elevated result for selenium if this interference is not recognized and corrected for. The analyst must also be cognizant of the fact that the correction that can be done for the formation of H-Br^{+} in the plasma is not a dynamic correction and the concentration may only be valid over a limited concentration range. A dynamic correction is one where the actual interfering molecular species can be measured at a different mass (e.g. ^{1}H-$^{79}Br^{+}$ at mass 80) and the intensity due to the interfering species subtracted from that of the analyte at the desired mass. In the case of bromide interference, the amount of ^{1}H-$^{79}Br^{+}$ formed at mass 80 cannot be distinguished from the high background at mass 80 due to the ^{40}Ar-^{40}Ar dimer. The only way to correct for this interference is to measure the amount of formation of ^{1}H-$^{81}Br^{+}$ at mass 82 using a clean (selenium free) bromide standard and perform a correction very similar to an interelement correction in ICP-OES.

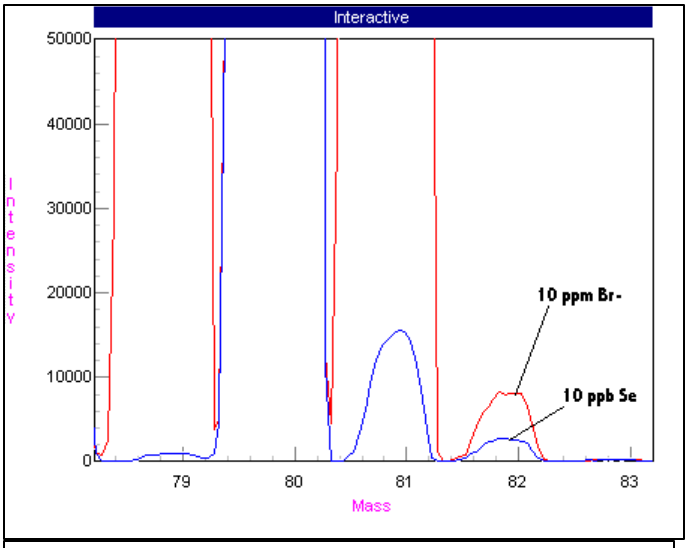

Figure 1. Interference of 10 ppm Br- on Se.

Quality Control Limits on Internal Standards. The use of internal standards in ICP-MS is a well documented and generally accepted practice used to compensate for signal drift caused by the gradual build-up of material on the interface cones. Both methods 6020 and 6020A require that the internal standard intensities in all samples and quality control standards be monitored throughout the course of the run and suitable actions carried out if either of the established control limits are exceeded. Method 6020 requires that the intensity of the internal standards in the subsequent continuing calibration check standards and blanks not vary more than ± 20% from the intensities originally monitored in the calibration blank, while the intensities in the actual samples are allowed to vary between 30-120%. It is common during the course of the analysis of real samples for the interface cones to become slightly clogged while performing analyses over several hours. The degree to which this happens is entirely dependent on the amount of dissolved material present in the samples. For digested soil samples, for example, it is not uncommon to observe drift between 10-40% over the course of several hours due to deposition of calcium, aluminum, and silicon oxides on the interface cones. To limit this deposition and the drift of the internal standards, samples are routinely diluted to reduce the amount of dissolved solids to less than 0.1 – 0.2% TDS. However, this amount of dilution may lead to unacceptably high detection limits for some determinations. The data shown in Table 3 shows that even with the internal standard recoveries less than the Method 6020 limit of 80%, acceptable results were obtained for a 1 ppb instrument check standard. This data indicates that the internal standards are correctly functioning and compensating for the signal drift.

Table 3. Accuracy of low level calibration check standard.

Analyte	True Concentration (µg/L)	Measured Concentration (µg/L)	Internal Standard Recovery %
Be	1.00	1.01	84
Cr	1.00	0.995	71
Ni	1.00	1.039	71
Cu	1.00	1.065	71
As	1.00	0.995	67
Se	1.00	0.958	67
Mo	1.00	0.982	71
Ag	1.00	0.983	71
Cd	1.00	1.024	71
Sb	1.00	1.035	71
Ba	1.00	0.991	71
Hg	1.00	0.981	69
Tl	1.00	1.062	69
Pb	1.00	1.058	69

Fortunately, in Method 6020A, this dual level requirement on the Internal Standard responses has been removed. The new requirement allows the internal standard response in the samples to drop to 30% of that in the original sample at which time, if similar recoveries are found in a calibration blank, corrective action must take place. Low internal standard recoveries at this point in a standard with no matrix (a blank) indicates the interface cones are becoming clogged. Either cleaning the cones or re-calibration is indicated. If, however, the calibration blank internal standards are not suppressed, the poor recoveries in the sample matrix indicates that the matrix is causing some interference and the sample should be diluted and re-analyzed. The new single limit in Method 6020A gives the analyst some flexibility in deciding what should be done and at what level. It should be stressed, however, that caution should be used when reporting concentration values obtained from readings where the internal standard response is very low (e.g. < 30-40%), as significant error could occur. The laboratory should decide upon the most prudent policy for the particular types of samples being analyzed and the data quality needed.

Sample Results for Method 6020

The data presented in Table 4 demonstrates the results obtained for NIST SRM 2711- Montana Soil using Method 6020, including the additional analytes for which method performance data was generated. Perkin-Elmer obtained SRM 2711 and processed it using U.S. EPA Method 3050 using the hydrochloric acid finish and analyzed this digested sample in order to assess performance of Method 6020 using the ELAN 6000/6100 ICP-MS. Because of the relatively high levels of many of the constituents in the SRM 2711 digestate and the relatively high acid content (15% total with 5% HCl), the digestate was diluted tenfold before analysis by Method 6020. The average values obtained by seventeen laboratories participating in a NIST round-robin study and the reported ranges are also given in Table 4. The SRM 2711 digestate was analyzed in duplicate and the Relative Percent Difference (RPD) between the duplicate measurements is well within the Method 6020 requirement of 20% RPD. The largest RPD observed was 5.3%. As Table 4 shows many of the elements analyzed using Method 6020 on the ELAN 6000/6100 are very close to the average values obtained for this SRM in the NIST study. Furthermore, all values (except for sodium) are also within the reported range from the NIST study. The sodium level obtained on the ELAN 6000/6100 is slightly higher than the high end of the NIST range; however, this difference is small and is probably due to contamination considering the ubiquitous nature of sodium. An analytical spike of 100 ppb in the diluted digestate was also analyzed and the spike recoveries calculated. The spike recoveries for all elements, except lead, were between 96-110% recovery. Lead was recovered at 132%; however, the spike value of the lead in solution was ten times less than the actual level of lead present in the digestate. As a result, acceptable spike recovery of between 75-125% was not expected.

Table 4. Results for NIST SRM 2711 - Moderately Contaminated Montana Soil

Analyte	Measured Conc mg/kg	RPD	NIST Leach Value mg/kg	Range low	Range high	Spike Amount (ppb)	Spike Recovery (%)
Be	**1.1**	3.59				100.0	104
Al	**20066.5**	4.38	**18000.0**	12000.0	23000.0	100.0	---
V	**48.2**	4.79	**42.0**	34.0	50.0	100.0	98
Cr	**23.7**	1.35	**20.0**	15.0	25.0	100.0	97
Mn	**493.0**	4.25	**490.0**	400.0	620.0	100.0	110
Co	**8.1**	2.03	**8.2**	7.0	12.0	100.0	98
Ni	**17.1**	0.11	**16.0**	14.0	20.0	100.0	96
Cu	**104.1**	4.92	**100.0**	91.0	110.0	100.0	99
Zn	**315.8**	3.94	**310.0**	290.0	340.0	100.0	111
As	**94.0**	2.91	**90.0**	88.0	110.0	100.0	103
Se	**2.2**	6.96	**NR**			100.0	109
Mo	**1.2**	2.09	**<2**			100.0	105
Ag	**4.3**	0.94	**4.0**	2.5	5.5	100.0	102
Cd	**40.0**	3.20	**40.0**	32.0	46.0	100.0	102
Sb	**3.9**	5.25	**<10**			100.0	98
Ba	**192.2**	4.88	**200.0**	170.0	260.0	100.0	98
Tl	**1.8**	5.07				100.0	105
Pb	**1087.3**	4.58	**1100.0**	930.0	1500.0	100.0	132
Na	**320.3**	2.57	**260.0**	200.0	290.0		---
Mg	**7726.8**	3.69	**8100.0**	7200.0	8900.0		---
K	**5064.4**	3.59	**3800.0**	2600.0	5300.0		---
Ca	**20742.0**	1.14	**21000.0**	20000.0	25000.0		---
Fe	**21662.2**	3.44	**22000.0**	17000.0	26000.0		---

Analysis of Samples by ICP-MS Using PBMS Principles – A Case Study

The following case study is presented to illustrate how sample analyses may be carried out by ICP-MS using PBMS principles. The client is a manufacturer of calcium supplements, antacid tablets, and vitamin supplements. Under California Proposition 65 (a.k.a. the Safe Drinking Water & Toxic Enforcement Act of 1985), lead is one of the elements identified by the State of California as both a cancer causing agent and reproductive toxin[1]. Under California Proposition 65 requirements, manufacturers of supplements and the raw materials used in their manufacture are now required to test these materials for lead content. A "no significant risk level" or NSRL established by the California Office of Environmental Health Hazard Assessment for lead exposure has been established at 0.5 µg /day[2]. Since the actual dose may vary due to intake rate, the level of lead present in a material is generally reported in units of mg lead per gram material (µg/g). The client in question has several raw materials that need to be routinely tested for lead content and would also like to obtain concentrations of 11 other elements of interest in the raw materials.

Since the NSRL level established for lead is given as a total exposure of 0.5 µg/day, it is necessary to determine what detection levels would be suitable to meet monitoring for this requirement. For example, the US RDA (Recommended Daily Allowance) for calcium in the adult diet is 1000 mg or 1g. If the entire RDA were to be obtained from a single calcium-containing supplement, the lead concentration in that supplement must be less than 0.5µg/g of supplement material. In order to state a material has a Pb concentration less than 0.5µg/g, the detection limit of Pb by the selected analytical technique must be significantly below 0.5µg/g to ensure reliable and accurate results. The client has requested that the method used have a practical quantitation limit (PQL) for Pb of 0.05µg/g or lower. The client has defined the PQL as the level equal to ten times the standard deviation of the blank. If these samples were to be run according to the strict Quality Control requirements in Method 6020, the samples would need to be diluted after preparation by 50-fold in order to keep the internal standard responses within the limits. This 50-fold dilution

would lead to a PQL of 0.055 µg/g, which is above the stated requirements of the client. Under the PBMS scheme, the method and quality control requirements would be developed to meet the stated data quality objectives of the client.

Analytical Objectives: To determine Pb in the samples at a PQL of 0.05µg/g or better. The results must be accurate to within 5% and have a minimum occurrence of false positives. The results are required to be reported under California's Safe Drinking Water & Toxic Enforcement Act of 1985. It is also desirable to determine the concentrations of As, Sb, Cd, Cr, Cu, Hg, Se, Tl, Sn, and Zn in all sample matrices. If possible, the client would like all elements to be determined in a single analytical run.

Sample matrices and preparation: The clients sample include antacid tablets, calcium carbonate, tri calcium phosphate, and magnesium oxide. NIST SRM 1400 – Bone Ash will be used to validate the method as the matrix is similar to the samples. Since the samples were relatively simple chemical compounds, a rigorous digestion method was not necessary. The samples were simply dissolved using nitric acid in the following manner: A 0.5 g portion of sample was accurately weighed into precleaned 50 mL polypropylene autosampler tube. Approximately 20 mL of de-ionized water was added to each tube wash down the sides of the tube and form a slurry. Five mL of concentrated Ultrex grade Nitric acid was added. The tubes were capped and shaken gently to mix. After dissolution, the samples were diluted to a final volume of 50mL using the graduated markings on the tubes.

Instrumental Method. The ICP-MS was set-up according to the manufacturers daily performance procedures. Due to the low level concentrations expected for the elements of interest, the instrument was calibrated for Pb, As, Sb, Cd, Cr, Cu, Se, Tl, Sn, and Zn at 0.1, 1.0, and 10.0 ppb. Mercury was calibrated at 0.2, 1.0, and 2.0 ppb. The isotopes used for the determination of the elements of interest were selected based on the analysts knowledge of the sample matrix and the possible interferences that could occur.

Determination of Practical Quantitation Limits (PQLs). In order to determine the practical quantitation limit, the standard deviation of 7 readings from the continuing check blank that was run every 10 samples throughout the course of the run was multiplied by 10 to determine the practical quantitation limit. The PQL in the solid was then determined by converting back to the units of ug/g using the sample preparation weight (0.5g), sample preparation volume (50mL), and dilution factor (10). The results are given below:

Element	Standard Deviation of Blank	PQL = 10 * STD DEV (µg/L)	PQL in Solid (µg/g)
Pb	0.0011	0.011	0.011
As	0.0119	0.119	0.119
Sb	0.0222	0.222	0.222
Cd	0.0007	0.007	0.007
Cr	0.0777	0.777	0.777
Cu	0.0082	0.082	0.082
Se	0.0313	0.313	0.313
Tl	0.0011	0.011	0.011
Sn	0.0600	0.600	0.600
Zn	0.0102	0.102	0.102
Hg	0.0283	0.283	0.283

Method Validation. NIST SRM 1400 – Bone Ash was selected as a reference material which could be used to validate this method because the calcium and phosphate matrix in this SRM is similar to the calcium matrices submitted for analysis by the client. Of particular importance is the accuracy of the Pb determination in SRM 1400, as the client wants an accurate determination for Pb. The other elements determined in SRM 1400 will be compared to both certified and reference values where applicable to evaluate the accuracy of the method for the other analytes. Matrix spikes will also be used to evaluate the effect of interferences and matrix effects on the results. The element of priority, Pb, is shown to be accurately determined (within 3%) as compared to the certified NIST value for this

element using the simple dissolution and analytical method described above. The results obtained for arsenic, cadmium copper, selenium, and zinc also agree with the values reported by NIST to within 25% in the worst case. The pre-digestion spikes and post digest spikes also show recoveries within 10% of the spike value in all cases where a spike was performed, indicating no severe matrix effects are present.

Results for NIST SRM 1400 – Bone Ash

Analyte	Measured Concentration (µg/g)	NIST Value * Certified Value (µg/g)	1 ppb Post Digest Spike Recovery (%)	10 ug/g Pre-Digestion Spike Recovery (%)
Pb	8.89	9.07 (*)	109	106
As	0.50	0.4	105	103
Sb	0.65		94	99
Cd	0.03	0.03 (*)	100	100
Cr	1.48		107	107
Cu	2.3	2	93	97
Se	< 0.3	0.08	96	94
Tl	<0.01		107	107
Sn	< 0.6			
Zn	181	181 (*)		
Hg	< 0.3		100	

Sample Results. The samples are then analyzed according to the developed method. Matrix spikes are performed in order to assess data quality. The results for the calcium phosphate matrix are given below:

Calcium Phosphate Analyte	Measured Concentration (µg/g)	1 ppb Post Digest Spike Recovery (%)	10 µg/g Pre-Digestion Spike Recovery (%)
Pb	0.097	107	106
As	2.84	112	107
Sb	0.4	100	105
Cd	0.134	108	106
Cr	33.8	123	96
Cu	0.725	95	93
Se	0.5	109	114
Tl	0.01	110	110
Sn	<0.6	99	
Zn	16.83		
Hg	<0.3	102	

Summary

The differences between US EPA Method 6020 and 6020A have been discussed. Data illustrating why changes were made in Method 6020A to make it more flexible were presented. The limitations of the Interference Check Standards as presented in Methods 6020 and 6020A were described and recommendations made regarding the limitations and possible modification of the content of these solutions. The example of the bromide interference on selenium was presented as a situation where the interference check solution in Methods 6020 and 6020A are not adequate. The use of internal standards in ICP-MS was discussed in regards to the accuracy of the analysis when the internal standard recoveries are low. Data for a certified reference material was presented showing the applicability ICP-MS for the determination of many elements, including those that are traditionally run by ICP-OES. Finally, an example of method development was briefly discussed under PBMS principles and data presented that validated the method developed to satisfy the clients stated data quality needs.

References
1. List of Chemicals Known to the State to Cause Cancer or Reproductive Toxicity, California Code of Regulations, Title 22, Section 12000, August 26, 1997.
2. "Method of Detection Argument in the Crystal Glassware Case", Prop 65 News, July 1994, Vol. 8, No. 7.

DETERMINATION OF MERCURY IN THE RANGE OF 1 – 100 ng/L USING CV-AAS

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Abstract
Mercury continues to be an environmentally relevant element. It must be determined in the low nanogram per liter range to measure background levels in ambient waters or groundwaters. The deposition of mercury is a global issue and trace contamination must be distinguished from background levels. Bioaccumulation in the food chain from even trace contamination can provide significant health hazards. The determination of extremely low mercury levels (below a few ppt) can be achieved by collecting the analyte on an adsorption agent. Usually gold/platinium or iridium is used to trap the mercury. The detection limits are mainly restricted by the level of the blank rather than by the photometric noise of the instrument at these low levels. Extreme care has to be taken not to contaminate the samples during sample handling, stabilization and measurement.

The automated measurements shown in this paper where performed under standard laboratory conditions. The detection limits can be further improved if the samples and standards are handled using more rigorous clean sampling and handling techniques. This paper shows how mercury in water can be analyzed in a range between 1 and 100 ng/L. An automated cold vapor technique atomic absorption technique and amalgamation on a gold/platinium gauze have been used to obtain these data. Ambient water and soil samples have been measured using this technique.

Introduction
Mercury pollution has decreased in the United States as sources of mercury have been controlled. Mercury is a global pollutant and can be spread through the air to even the most remote areas. This confounds the determination of the source of pollution and can bias the evaluation of local control effects. The measurement of mercury continues to be of interest; however, at lower levels. As the interest in speciated forms of mercury and the analysis of potential endocrine disrupting effects increases, measurement at lower concentrations will continue to grow in importance. Table 1 shows the current regulatory levels for mercury in a variety of matrices, in the U.S. and in Europe. The values are all listed in parts-per-trillion, unless otherwise noted, to allow for easy comparison. The solution concentrations from solid values were obtained by assuming a typical digestion using 1 gram of solid material and dilution to 100mL of final solution.

Ambient water is the single category currently requiring measurements at ultratrace levels.

Table 2 summarizes the methods for determination of mercury with AA and cold vapor generation. Flow injection can be used to automatically prepare small samples or can be used in the continuous flow mode for larger samples. Preconcentration of the vapor can be accomplished with amalgamation techniques or by collection in graphite tube. Detection can be performed with an atomic absorption spectrometer or a dedicated system.

The detection limits achieved with most of the listed techniques is more than sufficient to give a confident result at the decision-making concentration listed in Table 1. For ambient water concentrations, preconcentration using amalgamation or collection on a graphite tube coupled with a sensitive detector are necessary to achieve the desired results.

The scope of this work is to explore the factors involved in implementing the determination of mercury using flow injection-continuous flow with amalgamation and a dedicated mercury detection system.

Table 1. Summary of Mercury Regulatory Levels

Medium	US Maximum Contaminant Level (ng/L)	EU Regulatory Limit (ng/L)
Drinking Water	2000	1000
Wastewater (Chlor-Alkali-Mercury Cells) (new)	110,000 max for one day 48,000 avg. over 30 days	50,000 ng/L before it is mixed with other wastewater
Universal Treatment Stds	150,000 (wastewater) or 25,000-200,000 (nonwastewater)	
TCLP Extracts	200,000	
Soils	1-21 mg/kg cleanup goal (10,000-210,000 ng/L in solution, based on 1g sample)	0.5 - 10 mg/kg (1mg/kg for Agricultural soil) (5,000 –10,000 ng/L in solution, based on 1g sample)
Sludges		16-25 mg/kg (160,000-250,000 ng/L in solution, based on a 1g sample)
Ambient water	12 (freshwater cont. criteria) 1.8 (Quality Guidance for the Great Lakes)	Natural waters such as Lake Constance, Germany carry around 0.8 ng/L Hg

Table 2. Methods for the Determination of Mercury with CVAAS

Technique	Preconcentration	Detector	Detection Limit (ng/L)
Flow Injection	None	AAS	100
Flow Injection-Continuous	Au/Pt Gauze	AAS	10
Flow Injection	None	FIMS	4
Flow Injection-Continuous	Au/Pt Gauze	FIMS	0.5
Flow Injection	Graphite Tube	AAS	0.5

Experimental

All work was performed using the Perkin-Elmer FIMS™ 400, with an automated amalgamation accessory. Figure 1 shows a schematic of the system.

When the amalgamation accessory is used, the FI valve provides a reproducible and defined preconcentration time, preventing sample to sample carry-over in the continuous flow mode. Ultrapure chemicals were used to minimize contamination. Sample preparation and analysis was done in a clean hood. The concentrations used are documented in the Perkin-Elmer implementation of EPA method 245.1, approved through the alternate testing procedure.[1] The conditions for bromate digestion and cleaning of reagents were taken from draft EPA method 1631.[2]

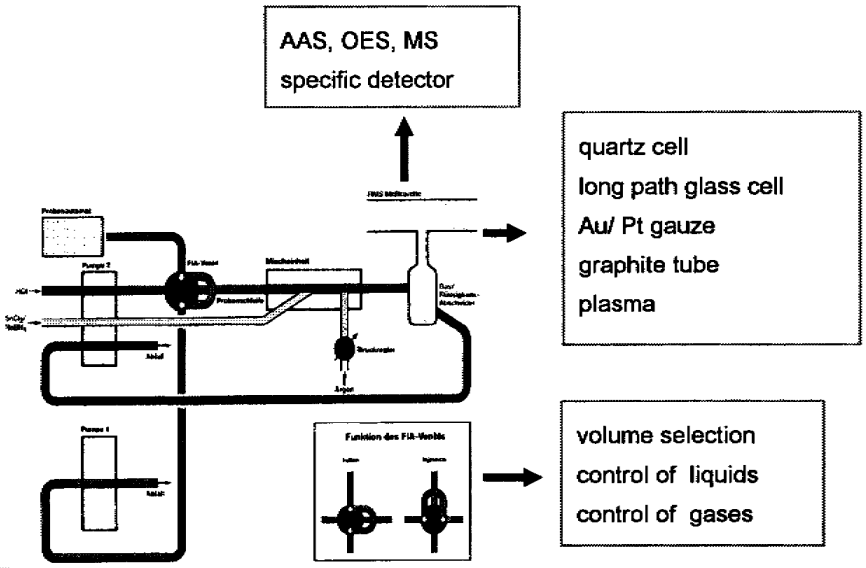


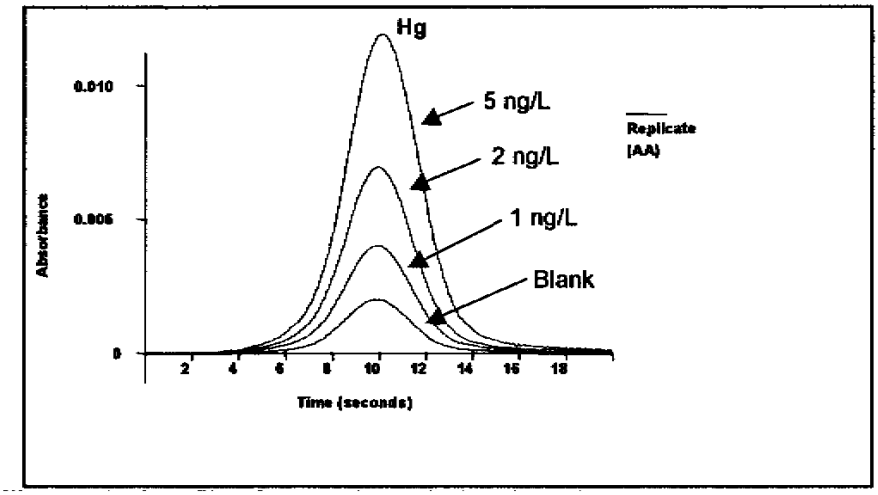
Figure 1. Schematic of Flow Injection System

Results and Discussion

Analysis at ultratrace levels requires careful sample collection and handling. The evaluation of the blank values from different conditions using amalgamation are summarized in Table 3. A 60-second amalgamation using 10 mL of sample is used in each case.

Table 3. Blank Values

	Peak Height	Concentration (ng/L)	%RSD
$SnCl_2$, not purified	0.0075	15.6	3.4
$SnCl_2$, Purified 1 hour with Argon	0.0004	0.8	9.8
ASTM Type 1 water with 0.5% HNO_3	0.0005	1.0	3.7
ASTM Type 1 water with 0.5% HNO_3 and $KMnO_4$	0.0008	1.6	8.2



Amalgamation typically improves detection limits by a factor of ten. Bromate reagent acts more quickly than $KMnO_4$ and may be cleaner. This also can contribute to lower detection limits. The time of amalga- mation can be varied and increased times yield increased preconcentra- tion and lower detection limits. Figure 2 demonstrates peaks obtained from standards preconcentrated for 180 seconds, using 30 mL of solution.

Figure 2. Peak profiles of mercury in standards and samples

Conclusions

Most current regulatory levels are met satisfactorily with existing methodology. Bromate digestion can increase laboratory productivity and provide less contamination for ultratrace samples. The time-savings aspect may be useful for analyses at all concentration levels and should be further evaluated for incorporation into existing methods. Amalgamation can improve detection limits to measure mercury at ambient water levels. As the move towards a performance-based measurement system continues, the ability to match the available tools more closely to the problem to be solved will be achieved. Techniques for ultratrace analysis require extra care at every step of the collection, sample handling and analysis processes. Although an automated system, such as flow injection, can help tremendously in isolating the sample from sources of contamination, additional skill will be required compared to analyses at higher concentrations.

References

1. S. McInotosh and B. Welz, The Application of Flow Injection Analysis to Automating Cold Vapor Mercury Analyses, ENVA-100, The Perkin-Elmer Corporation, 761 Main Ave, MS-10, Norwalk CT 06859.
2. Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA 821-R-95-027, April 1995.

APPLICATION OF *IN-SITU* GAMMA SPECTROMETRY IN THE REMEDIATION OF RADIOACTIVELY CONTAMINATED SOIL

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ABSTRACT

The Fernald Environmental Management Project (FEMP) is a U.S. Department of Energy site that is undergoing total remediation and closure. Most of the remediation effort entails massive excavation of soil for disposal, both offsite and onsite, at an engineered disposal facility. *In-situ* gamma spectrometry is routinely used to support soil excavation operations to accurately and quickly identify soil areas as being above or below regulatory remediation criteria.

Two different *in-situ* gamma spectrometry systems are used. The first is a sodium iodide (NaI) detector mounted either on a tractor or a jogging stroller, depending on the terrain to be measured. The NaI system allows the collection of a gamma energy spectrum which can be analyzed to identify and quantify radioactive isotopes which are present within the detector's viewing area. Each energy spectrum is tagged by location coordinates provided by an on-board global positioning system (GPS) to precisely locate elevated contamination areas. The second is a tripod-mounted, high purity germanium detector (HPGe) gamma spectrometry system that is functionally similar to the NaI system. The principal advantage of the HPGe is its superior resolution, which allows much more accurate identification and quantification of radionuclide contaminants in soils.

In order to effectively utilize the data quality objective process with these systems, three quality assurance (QA) elements had to be performed. First, method validation studies demonstrated comparability with conventional radiochemistry methods and established performance-based acceptance criteria for key quality control parameters at various data quality levels. The method validation studies for the HPGe system stressed accuracy and comparability, while method validation studies for the NaI systems stressed quantifying measurement uncertainty and detection limits. Second, a "User's Manual" was developed that specifies measurement approaches, provides data interpretation guidelines, and discusses operational and environmental factors that could adversely affect *in-situ* gamma spectrometry measurements. This manual is primarily designed for environmental scientists responsible for remediating soils rather than for analytical chemists who perform the measurements. Third, an *in-situ* gamma spectrometry QA program was implemented to address programmatic QA elements, to ensure legal defensibility of the data, and to specify quality control (QC) criteria, their frequency of measurement, their acceptance limits and whether or not they are to be control charted.

INTRODUCTION

The FEMP is a U.S. Department of Energy site that is undergoing total remediation and closure. Most of the remediation effort entails massive excavation of soil for disposal, both offsite and onsite at an engineered disposal facility. *In-situ* gamma spectrometry is routinely used in support of soil excavation operations to accurately and quickly identify soil areas as being above or below regulatory remediation criteria. Two different *in-situ* gamma spectrometry systems are used. The first is a sodium iodide (NaI) detector system, while the second is a high-purity germanium (HPGe) detector system. The former system is mounted on either a tractor (RTRAK) or a jogging stroller (RSS), depending on the terrain, while the latter system is tripod-mounted.

Both RSS and RTRAK have a measurement system consisting of a 4x4x16 inch NaI detector and associated electronics to provide high-speed pulse height analysis. This system allows the collection of a gamma ray energy spectrum, which can be analyzed to identify and quantify radioactive isotopes that may be present within the detector's viewing area. The RTRAK and RSS are each equipped with a GPS operated in a real-time differential mode to provide location coordinates. Each energy spectrum is tagged with the location coordinates provided by the GPS. All energy and location data are stored on magnetic media by an on-board computer system. This information is used to accurately locate and subsequently map radiological data within the measurement area.

On the RTRAK, the detector is positioned on the tractor horizontal to the ground and perpendicular to the direction of travel at a height of approximately 31 cm above the ground. The detector on the RSS is mounted horizontal to the ground and parallel to the direction of travel at a height of approximately 31 cm. The normal operation of the RTRAK and RSS consists of moving the systems over the measurement area at a predetermined speed. Spectra are continuously collected at regular intervals, typically a few seconds. The viewing area size is a function of the tractor speed, the acquisition time, and the detector's geometrical configuration. For example, for the 4x4x16 inch detector at the 31 cm height, the viewing area is 8.8. m^2 for a single measurement when the system is moving at one mile per hour, with a 4-second data acquisition time (typical operating parameters).

The HPGe detectors are mounted on tripods at heights ranging from 15 cm to 1.0 m above the ground surface. The detectors are connected to 8192 channel multi-channel analyzers which allow the collection of a high resolution gamma ray spectrum. The superior resolution of HPGe detectors relative to NaI detectors allow it to accurately

quantify a wide variety of isotopes with minimal interferences. Data acquisition times typically are 15 minutes. The HPGe field of view ranges from over 100 m^2 at a 1.0 m detector height to 3.1 m^2 at a 15 cm detector height.

METHOD VALIDATION STUDIES

The method validation study for HPGe entails determining the similarity between data generated by HPGe measurements and data generated by laboratory analysis of physical samples. It also delineates acceptance criteria for key QC elements and data quality elements. Three radiological contaminants of concern were measured by HPGe and laboratory methods: total uranium, thorium-232 and radium-226. Method validation studies for NaI systems stressed quantifying measurement uncertainty and detection limits. Such assessments were performed as a function of vehicle speed and data acquisition time in order to determine preferred operating parameters.

HPGe Comparability Studies

One part of the method validation study for HPGe entailed assessing the comparability between HPGe measurements and laboratory data. To accomplish this, a series of physical samples were collected from different areas of widely varying concentrations of contaminants. In each area, samples were collected in a "bullseye" pattern to mimic the averaging done by the field HPGe detector. That is, the area from which physical samples were taken can be envisioned as a circle, with the HPGe detector located above the center. The HPGe detector records gamma ray photons from every point within the circle; however, it records more gamma rays from soil closer to the detector than from soil further from the detector.

For comparison with HPGe measurements, a weighted average (weighted based upon gamma photon fluence contributions) of all laboratory data for a given area was calculated. Figures 1 and 2 show plots of HPGe measurements vs weighted average laboratory data for total uranium and thorium-232. High correlation coefficients (R^2 value), line slopes near one, and line intercepts close to 0.0 demonstrate comparability of data. The width of the error bars for laboratory data in Figures 1 and 2 primarily reflect the degree of heterogeneity among samples in a given area rather than laboratory precision.

NaI Method Validation

A major portion of the method validation studies for NaI systems addressed the total system measurement uncertainty for moving systems. Data were acquired experimentally via repeated measurement profiles, which involved moving the RTRAK or RSS back and forth along a given track for 20 iterations. Each track was divided into segments and the mean and standard deviation of the measurements in each segment was determined. Table 1 shows the results of the precision studies for one area with the RTRAK moving at a speed for 0.5 mph, with a 2-second data acquisition time. Such precision studies were carried out in different areas, using a combination of different speeds and data acquisition times in each area. The results of these studies demonstrated that:

1. The uranium-238 measurements display low degrees of precision. This limits the usability of the data for low-concentration measurements. The low degree of precision (high uncertainty) occurs because of the low photon yield at the energy of interest, the high spectrum background, and interferences from thorium-232 and radium-226 daughter gamma rays.

2. The thorium-232 measurements display the highest degree of precision of the three radionuclides of interest. The high degree of precision (small uncertainty) occurs because of a relatively high photon yield at the energy of interest, the low spectrum background, and because of only limited interference from a low intensity radium-226 peak.

3. The radium-226 measurements display a degree of precision similar to that of uranium or between that of the other two radionuclides of interest. This is in part because both the photon yield and the detection efficiency at the energy of interest fall between those of the thorium and uranium.

Knowledge of the overall precision from studies such as the one outlined above was a key factor in ascertaining *a priori* minimum detectable concentrations, determining error rates, and setting trigger levels.

USER'S MANUAL

Early in the remediation process at the FEMP, it became clear that a critical need existed to bridge the gap between primarily analytical information contained in method validation studies and programmatic remediation design documents. The User's Manual bridges that gap by providing user guidelines, data interpretation guidelines, and measurement strategies and approaches; by discussing operational and technical factors that could adversely affect data; and by delineating strengths and limitations of *in-situ* gamma spectrometry. While the document is beneficial

to anyone involved with any aspect of *in-situ* gamma spectrometry, it is primarily aimed toward FEMP project personnel who:

- plan soil remediation projects;
- collect *in-situ* gamma spectrometry data for soil remediation projects;
- interpret *in-situ* gamma spectrometry data for soil remediation projects;
- integrate *in-situ* gamma spectrometry data with other data sets or into engineering designs; and
- make decisions based upon *in-situ* gamma spectrometry data.

The User's Manual has four sections: 1) Investigation Approaches; 2) Measurement Approaches; 3) Data Interpretation Guidelines; and 4) Technical Issues. Section 1 deals with broader-scale issues such as how *in-situ* gamma spectrometry is used in pre-design investigations and in soil excavation operations. Section 2 deals with smaller-scale issues such as how *in-situ* gamma spectrometry is used to detect, confirm, and identify hot spots. Section 3 addresses such issues as climatic/weather effects upon in-situ gamma measurements, topographic effects, total activity data interpretation, and mapping conventions. Section 4 addresses technical issues such as data review checklists, minimum detectable concentrations, positioning and surveying, and the effects of radon-222 on radium-226 measurements.

QUALITY CONTROL/QUALITY ASSURANCE

All in-situ gamma spectrometry operations, whether method validation studies or field measurements in support of remediation operations, are governed by a comprehensive QA/QC program. The QA program contains all of the same quality elements as a traditional environmental laboratory QA program. It has ten criteria: 1) QA program; 2) personnel training/qualification; 3) quality improvement; 4) documents and records; 5) work processes; 6) method design, 7) procurement/control of materials and services; 8) facilities and equipment/calibration and maintenance; 9) management assessment; and 10) external assessments and audits.

Of particular interest is the QC program, which is centered around performance-based measurements. In this regard, acceptance criteria of key quality control elements are specified, while the mechanism of how such measurements are obtained are not specified in either the QA plan or QC plans. Table 2 contains such criteria for two data quality levels called Analytical Support Levels (ASLs) at the FEMP. ASL B corresponds generally to the US EPA "screening data" category, while ASL D corresponds to the US EPA's "definitive data" category.

Information from the method validation studies, the User's Manual, and the QA/QC plans are incorporated into Project Specific Plans (PSPs) and project Data Quality Objectives (DQOs) to support specific remediation activities. In-situ gamma spectrometry data are validated to ensure that they satisfy the requirements and needs specified by the PSPs and DQOs.

Table 1. RTRAK precision studies at 0.5 MPH with a 2.0 second data acquisition time

		Uranium-238 (pCi/g)			Thorium-232 (pCi/g)			Radium-226 (pCi/g)		
Segment	**No Measurements**	**Mean**	**Std Dev**	**%Std Dev**	**Mean**	**Std Dev**	**%Std Dev**	**Mean**	**Std Dev**	**%Std Dev**
1	129	12.4	9.3	75	0.75	0.26	35	0.72	0.50	70
2	217	14.1	9.1	65	0.77	0.32	42	0.79	0.51	64
3	206	15.6	9.0	58	0.75	0.27	36	0.82	0.47	57
4	205	15.2	8.3	55	0.80	0.31	39	0.76	0.53	70
5	216	16.8	8.7	52	0.73	0.29	40	0.82	0.54	66
6	225	14.5	9.4	65	0.76	0.29	38	0.76	0.52	68
7	200	16.5	9.6	58	0.78	0.31	40	0.80	0.54	68
ROAD	120	12.2	7.3	60	0.48	0.29	60	0.59	0.45	76
8	231	17.0	9.2	54	0.75	0.34	45	0.82	0.59	72
9	232	18.0	9.3	51	0.75	0.32	43	0.87	0.51	58
10	240	17.2	9.8	57	0.73	0.31	42	0.77	0.48	63
11	193	15.2	8.6	56	0.75	0.28	37	0.76	0.50	65
Averages		15.7	9.1	59	0.76	0.30	40	0.79	0.52	66
Minimum		12.4	8.3	51	0.48	0.26	35	0.72	0.45	57
Maximum		18.0	9.8	75	0.80	0.34	60	0.87	0.59	76

SUMMARY
Routine utilization of *in-situ* gamma spectrometry in remediation at Fernald rests upon three programmatic elements. Method validation studies carried out to delineate key measurement quality control elements such as comparability, representativeness, accuracy, uncertainty, and detection limits; a User's Manual which specifies to environmental engineers and scientists how *in-situ* gamma spectrometry should be used in remediation operations; and a comprehensive QA program to ensure that *in-situ* gamma spectrometry data are of sufficient quality for their intended usage and are legally defensible.

Table 2. Tabulation of quality control criteria and requirements

RTRAK and RSS NaI Detector QC Criteria and Requirements

QC Element	Nuclide	Gamma Energy	QC Criteria	Frequency	Control Chart
Energy Calibration	Tl-208 Pb-212	2614.5 keV 238.6 keV	Channel 447±2 Channel 40±2	Days used, prior to and following use	No
Detector Counting Efficiency Check	Tl-208	2614.5 keV	Predetermined check source value (decay corrected) $\bar{x}$ ± 3 sigma	Days used, prior to and following use	Yes

HPGe Detector QC Criteria and Requirements

QC Element	Nuclide	Gamma Energy	QC Criteria	Frequency	Control Chart
Energy Calibration	Am-241 Cs-137 Co-60	59.5 keV 661.6 keV 1332.5 keV	Channel 158±1 Channel 1763±2 Channel 3553±3	Days used, prior to and following use	No
Detector Resolution	Co-60	1332.5	Measured mean value $\bar{x}$ ± 3 sigma	Days used, prior to and following use	Yes
Detector Counting Efficiency Check	Co-60	1332.5	pre-determined check source value (decay corrected) $\bar{x}$ ± 3 sigma	Days used, prior to and following use	Yes

HPGe Field Measurements QC Criteria and Requirements

QC Element	Gamma Energy Nuclide or Basis	QC Acceptance Criteria	Frequency	Control Chart
Field Measurement Interference	1460.8 keV	keV = 1460.8 FWHM ≤ 3.0 keV or Channel = 3895.0 FWHM ≤ 8 Channels	Each time measurements are made	No
Field Control Station	Total U Th-232 Ra-226 K-40	ASL -D measured value ±3 sigma measured value ±3 sigma measured value±3 sigma measured value±3 sigma	On each day measurements are made	Yes
Field Control Station	Temperature Humidity Soil Moisture	No Criteria	Each day measurements are made	No
Minimum Detectable Concentration	Free Release Levels for Nuclides of Concern	For ASL-D 95% UCL[1] <FRLs For ASL-B 90% UCL[1] <FRLs	Quarterly	No

HPGe Field Measurements QC Criteria and Requirements (continued)

QC Element	Gamma Energy Nuclide or Basis	QC Acceptance Criteria	Frequency	Control Chart
Measurement Accuracy	Compared to weighted average of physical samples	ASL-D - weighted average of physical sample ±20% ASL-B - weighted average of physical sample ±35%	Annually	No
Measurement Bias	Compared to weighted average of physical samples	Bias acceptable unless it produces errors resulting in accuracy being exceeded	Annually	No
Precision of Duplicates	At least one per every 20 HPGe measurements.	measured value >(5 x MDC) then RPD ≤±20% measured value <(5 x MDC) then measurement difference ≤ ±MDC	At least one per every 20 HPGe measurements.	No
Detector Counting Efficiency Determination	Determination of conversion (efficiency) factors.	initial conversion factor ±10% for each gamma energy[2]	Annually	No

Note 1. Upper confidence level (UCL) for MDC.

Note 2. Nuclide and Gamma energies measured:

Cs-137	32.2	Eu-152	39.5	Am-241	59.5
Eu-152	121.8	Eu-152	244.7	Eu-152	344.3
Eu-152	411.1	Eu-152	444.0	Cs-137	661.6
Eu-152	778.9	Eu-152	964.0	Co-60	1173.7
Co-60	1332.5	Eu-152	1408.0		

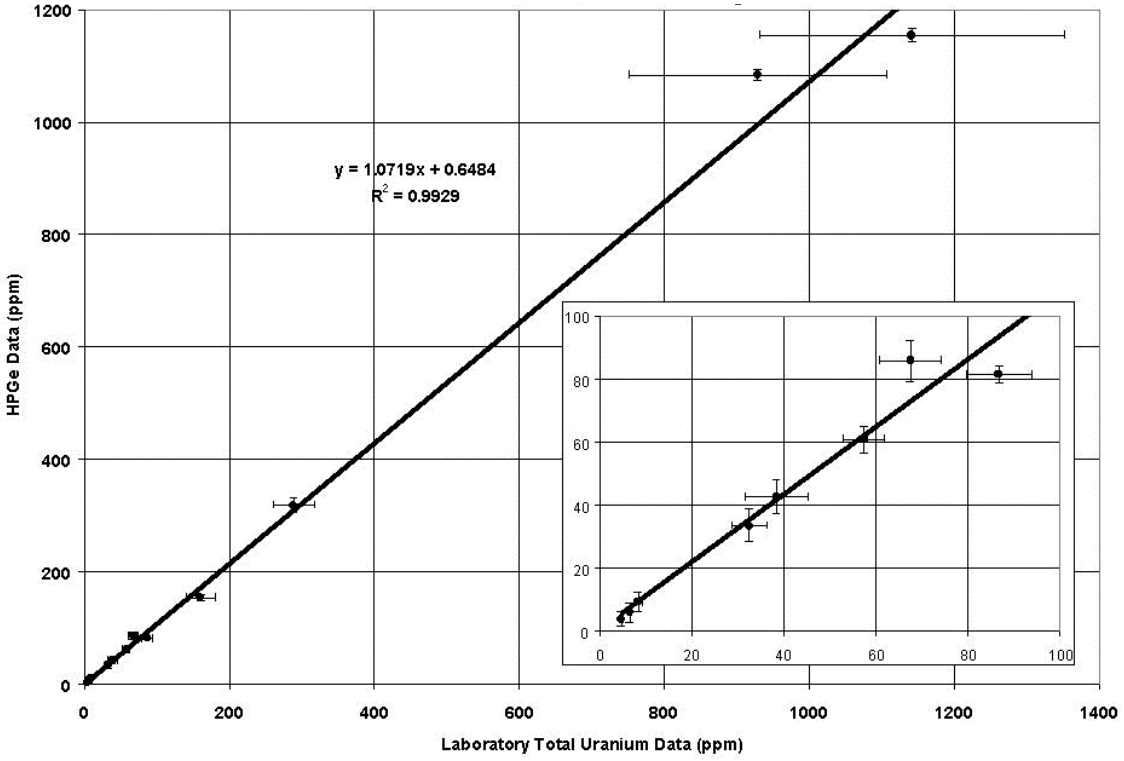

Figure 1. Correlation Between HPGe and Laboratory Data for Total Uranium at a 31 cm Detector Height

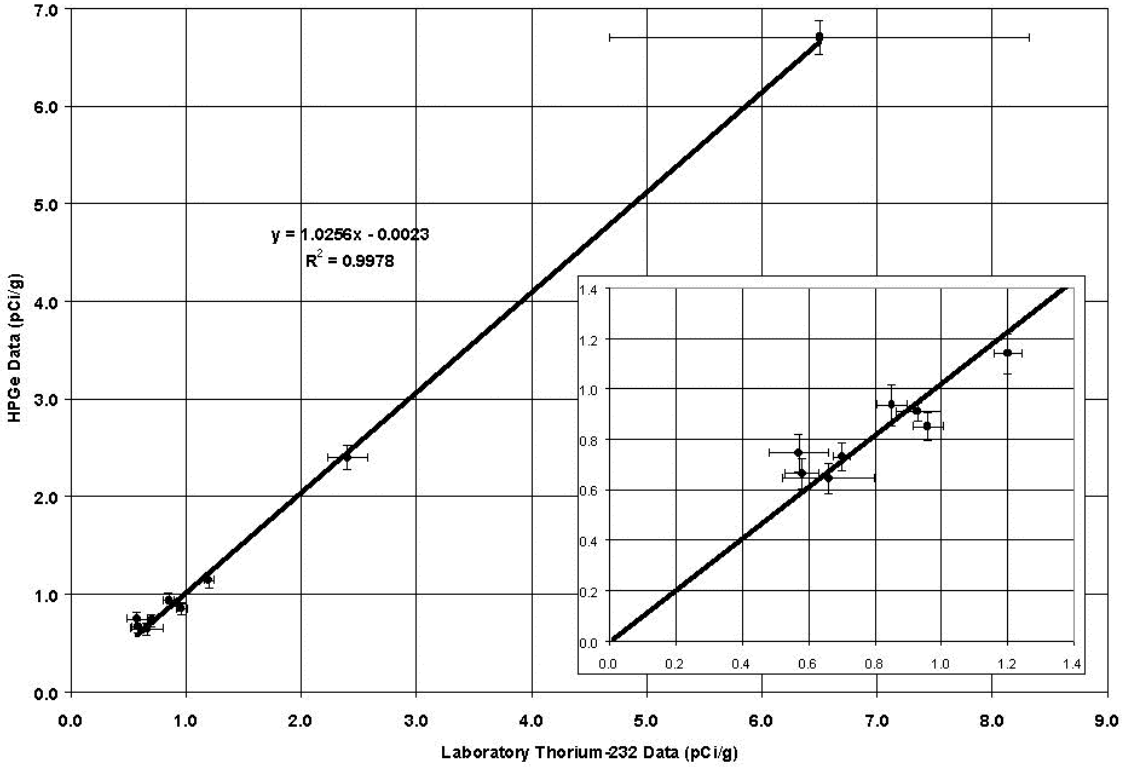

Figure 2. Correlation Between HPGe and Laboratory Data for Th-232 at a 31 cm Detector Height

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EFFECT OF ENVIRONMENTAL VARIABLES UPON *IN-SITU* GAMMA SPECTROMETRY DATA

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ABSTRACT

The Fernald Environmental Management Project (FEMP) is a U.S. Department of Energy site that is undergoing total remediation and closure. Fernald is a former uranium refinery which produced high quality uranium metal. Soil in the Fernald site is pervasively contaminated with uranium and secondarily with thorium and radium isotopes. *In-situ* gamma spectrometry is routinely utilized in soil excavation operations at Fernald to provide high quality and timely analytical data on radionuclide contaminants in soil.

To understand the effect of environmental conditions upon *in-situ* gamma spectrometry measurements, twice daily measurements were made, weather permitting, with a tripod-mounted high purity germanium detector (HPGe) at a single field location (field quality control station) at the Fernald Environmental Management Project. Such measurements are the field analogue of a laboratory control standard. The basic concept is that measurement variations over an extended period of time at a single location can be related to environmental parameters. Trends, peaks, and troughs in data might be correlative to both long-term and short-term environmental conditions. In this paper environmental variables/conditions refer to weather related phenomena such as soil moisture, rainfall, atmospheric humidity, and atmospheric temperature.

Based upon data collected over a year, the effect of soil moisture, humidity, temperature, various weather conditions such as fog, time of day, and season upon HPGe measurements can be delineated. This has resulted in a set of operating guidelines for field personnel and data interpretation guidelines for environmental scientists using HPGe data. Further, the data set allows the long-term measurement uncertainty (precision) for each individual analyte to be ascertained. For example, the mean of 250 total uranium measurements (dry weight basis) taken throughout the

year is 93.4 ppm with a standard deviation of 5.6 ppm. The standard deviation is 6.0% of the mean. Based upon such means and standard deviations for each analyte of interest, control charts have been established in which the warning and control limits are derived from the standard deviations.

Of particular interest is the behavior of radium-226. Because the HPGe actually measures gamma photons emitted by radon-222 daughters to calculate radium-226, weather conditions leading to the buildup and dissipation of radon-222 (a gas) in surface soils greatly affect the concentration of radium-226 determined from HPGe measurements. Typically, morning radium-226 concentrations as determined from HPGe measurements average over 25% higher than afternoon concentrations with a high degree of variability associated with that average.

INTRODUCTION

The Fernald Environmental Management Project (FEMP) is a U.S. Department of Energy site that is undergoing total remediation and closure. Fernald is a former uranium refinery which produced high quality uranium metal. Soil in the Fernald site is pervasively contaminated with uranium and secondarily with thorium and radium isotopes. *In-situ* gamma spectrometry is routinely utilized in soil excavation operations at Fernald to provide high quality and timely analytical data on radionuclide contaminants in soil.

To understand the effect of environmental conditions upon *in-situ* gamma spectrometry measurements, twice daily measurements were made, weather permitting, with a tripod-mounted high purity germanium detector (HPGe) at a single field location (field quality control station, or FCS).

To delineate the effect of weather and climatic conditions upon HPGe measurements, the field analogue of a laboratory control standard was adopted. The basic concept is that measurements over an extended period of time at a single field location can be related to weather and climatic variables. Trends, peaks, and valleys in data may be related to both long term and short term weather and climatic conditions. In this report, such conditions refer to weather related phenomena such as soil moisture, rainfall, atmospheric temperature, and humidity. FCS measurements thus offer the possibility of normalizing all in-situ gamma spectrometry measurements to a standard set of conditions, thereby enabling in-situ gamma spectrometry project personnel to tell when HPGe measurements are "in control."

This paper presents results of twelve months (April 8, 1997 through March 31, 1998) of morning and afternoon HPGe measurements at a FCS. A field location with a total uranium content of approximately 90 to 100 ppm (dry weight basis) was chosen as the FCS. This location was selected over other possible locations because of the closeness of its total uranium concentration to the FEMP final remediation level (FRL) of 82 ppm for total uranium. Measurements were performed at a 1.0 meter detector height using a 15-minute data acquisition time. Data were collected for total uranium, thorium-232, radium-226, and potassium-40. In this paper, only total uranium and radium-226 data are discussed for the sake of brevity.

EFFECT OF SOIL MOISTURE ON HPGe MEASUREMENTS

When total uranium is plotted as a function of soil moisture on a wet weight basis, there is a distinct trend of decreasing concentration with increasing soil moisture. This is not surprising as water acts as a diluent. However, when wet weight concentrations are converted to dry weight concentrations (Figure 1), there is still a slight trend of decreasing dry weight concentrations with increasing soil moisture content. Although the dry weight concentration dependency upon soil moisture is evidenced by a very low correlation coefficient (shown as an R^2 value) of 0.22 in Figure 1, the upper and lower 95% confidence limits for the slope do not bound zero. Hence, the slope of the line in Figure 1 is significantly different than zero. The slight trend of increasing dry weight concentration with decreasing soil moisture content may reflect the fact that a soil moisture depth gradient usually exists. In drying periods, the surface soil is usually drier than soil a few inches deeper. After periods of rain, surface soil is usually wetter than soil a few inches deeper. Because a soil moisture measurement represents an average, the surface soil is usually a little drier or wetter than the average. Since a majority of the gamma photons are emitted from surface soils, it is not surprising that concentrations derived from abundances of these photons still show a residual dependency upon moisture even following correction from wet weight to dry weight.

EFFECT OF ATMOSPHERIC TEMPERATURE ON HPGe MEASUREMENTS

Figure 2 is a plot of total uranium concentration as a function of temperature. A regression line indicates a slight trend of increasing measured HPGe concentrations with increasing temperature. Although the trend in Figure 2 is slight, it is real; the slope of the line of dry weight concentrations vs. temperature is significantly different than zero.

The origin of the trend (albeit slight) of increasing measured concentration with increasing temperature is not clear. Discussions with gamma spectroscopists suggest that it is not instrumental in origin. Speculation is that the trend results from soil moisture gradients. At higher temperatures, more of a gradient between surface soils (drier) and soils at depth (wetter) may exist. At lower temperatures, less of a gradient may exist. Because most of the gamma photons are emitted from surface soils, they reflect radionuclide concentrations less diluted with water than in bulk soils. Hence, higher apparent concentrations are measured at higher temperatures.

To summarize, an average higher temperature will result in higher HPGe measurements. However, the effect is small, and the variation in measured concentrations due to other factors greatly exceeds any temperature effect on measured HPGe concentrations. Thus, for all practical purposes, temperature can be ignored as having a significant effect upon HPGe data.

EFFECT OF HUMIDITY ON HPGe MEASUREMENTS

Regression lines fitted to plots of concentration as a function of humidity for total uranium, thorium-232, potassium-40, and radium-226 have slopes very near zero and extremely low correlation coefficients (expressed as R^2 values). Further, the slopes of concentration vs humidity are generally not significantly different than zero. These facts demonstrate that humidity has little effect upon HPGe measurements.

CONTROL CHART FOR TOTAL URANIUM

Parameters other than temperature, humidity and soil moisture could also possibly affect HPGe measurements. However, rather than collect a voluminous amount of data for multiple parameters, the use of control charts is employed instead to evaluate the cumulative effect of environmental and weather conditions upon HPGe measurements. Initial "means" control charts were constructed using typical conventions (warning limits are ±2 standard deviations from the mean; control limits are ±3 standard deviations from the mean). All of the data collected between April 8, 1997 and March 31, 1998 were utilized in calculating standard deviations in order that the standard deviations represent data collected over a wide range of environmental, climatic, and weather conditions. Table 1 shows values of means, standard deviations, standard deviations as percentages of means, warning limits, and control limits on both a wet weight and dry weight basis.

One significant aspect of the data in Table 1 is that the standard deviation as a percent of the mean for the two radionuclide averages approximately 6% on a dry weight basis. The standard deviations shown in Table 1 are interpreted to represent the long-term total system uncertainty, and this longterm total system uncertainty is very good, typically less than 10%.

An example control chart displaying data resulting from all of the HPGe measurements performed between April 8, 1997 and March 31, 1998 is presented in Figure 3 for total uranium on a dry weight basis. The trends of increasing total uranium concentrations in June and in July, and in August and September, for example, represent the periods of drier soil. Figure 3 also clearly shows that total uranium for the winter months of November, December, January and February is lower than for the summer months. This results from soil moistures being consistently higher for the winter months than for the summer months.

Note that the x axis of Figures 3, 4, and 5 is entitled “Data Index.” A given indice is merely an abbreviation of the date and time the measurements was taken. For example, an indice of 41 signifies April 1. Indices of 513a and 513p indicate that the measurements were made on May 13 in the morning and in the afternoon. Lowercase “a” and “p” in Figures 3, 4, and 5 indicate a.m. and p.m., respectively.

CONTROL CHARTS FOR RADIUM-226

Whereas data points for total uranium, thorium-232, and potassium-40 are predominately within warning and control limits, the situation for radium-226 appears quite different. As shown in Figure 4, numerous radium-226 measurements fall outside warning and control limits.

Table 2 compares the mean and standard deviation of radium-226 measurements taken in the morning and afternoon. Clearly, the means and standard deviations of morning measurements are substantially greater than means and standard deviations of afternoon measurements. More specifically, morning means are 25% higher than afternoon means, and morning standard deviations are approximately three times greater than afternoon standard deviations. “F” tests indicate that morning standard deviations are statistically significantly different than afternoon standard deviations at the 95% confidence level, while “t” tests indicate that differences between morning and

afternoon means are statistically significant at the 95% confidence limits. Examination of an expanded control chart (Figure 5) demonstrates very well that for radium-226 measurements taken on the same day, very often the morning measurements are higher than the afternoon measurements. Because radium-226 is determined from gamma rays emitted by radon-222 daughters, the differences between morning and afternoon measurements are related to radon buildup and its subsequent dissipation from soils. Typically, at the FEMP weather conditions in the morning are favorable for "bad radon days." That is, morning weather conditions are not favorable for the dissipation and dispersion of radon accumulations from very near to the surface of soils to the atmosphere. Conversely, by late morning or early afternoon weather conditions are such that near surface radon has dissipated and dispersed. Usually, mornings with fog also had high measured concentrations of radium-226; thus, one indicator as to whether HPGe measurements for radium-226 should be carried out is the presence of fog.

The effect of environmental influences on measurements for radium-226 is an important issue and has major practical ramifications. Morning measurements for radium-226 can be anomalously high due to radon accumulations near the ground surface, and afternoon radium226 measurements generally have a much lower degree of variation among them than morning measurements (Table 2). These observations were important considerations in developing a methodology to compensate for radon disequilibrium.

SUMMARY

1. Soil moisture has a significant effect upon the magnitude of HPGe measurements when concentrations of radionuclides are calculated on a wet weight basis. Soil moisture has a minor effect upon HPGe measurements when concentrations are calculated on a dry weight basis. This effect is likely related to gradients of moisture from the soil surface to depth (10 inches).
2. Temperature has a minor effect upon HPGe measurements over the range of 14° F to 93° F. This effect may be related to gradients of moisture from the surface of soils to soils at depth (10 inches).
3. Humidity has little observable effect upon HPGe measurements.
4. Weather conditions have significant effects upon HPGe measurements to determine radium-226 concentrations. Because HPGe actually measures gamma photons emitted by radon-222 daughters to calculate radium-226, weather conditions leading to the buildup and dissipation of radon in surface soils greatly affect the concentration of radium-226 calculated from HPGe measurements.
5. Typically, morning radium-226 concentrations are higher than afternoon radium-226 concentrations as calculated from HPGe measurements. From April 8, 1997 through March 31, 1998, morning radium-226 concentrations averaged over 25% higher than afternoon concentrations with a high degree of variability associated with that average.
6. Control charts were established for total uranium based upon the standard deviation of all measurements made at the FCS from April 8, 1997 to March 31, 1998. Excellent long-term precision was observed for this analyte as the standard deviation of the measurement population averaged 6% of the population mean.

Table 1. Statistical calculations for control charts

Parameter	Total Uranium (ppm)		Thorium-232 (pCi/g)	
	Wet wt.	Dry wt.	Wet wt.	Dry wt.
N=	250	250	250	250
Mean=	74.4	93.4	0.91	1.14
Std Dev.=	7.70	5.56	0.09	0.07
Std Dev. as % of Mean	10.4	5.96	10.3	5.83
UCL*=	97.4	110.0	1.19	1.34
UWL*=	89.8	104.5	1.09	1.28
LCL*=	51.2	76.7	0.63	0.94
LWL*=	58.9	82.2	0.72	1.01

* UCL = upper control limit
UWL = upper warning limit
LCL = lower control limit
LWL = lower warning limit

Table 2. Means and standard deviations of morning and afternoon Radium-226 concentrations

Time	Mean, Wet Wt. (pCi/g)	Std Dev., Wet Wt. (pCi/g)	Mean, Dry Wt. (pCi/g)	Std Dev., Dry Wt. (pCi/g)
Morning	1.04	0.28	1.30	0.31
Afternoon	0.84	0.08	1.05	0.10

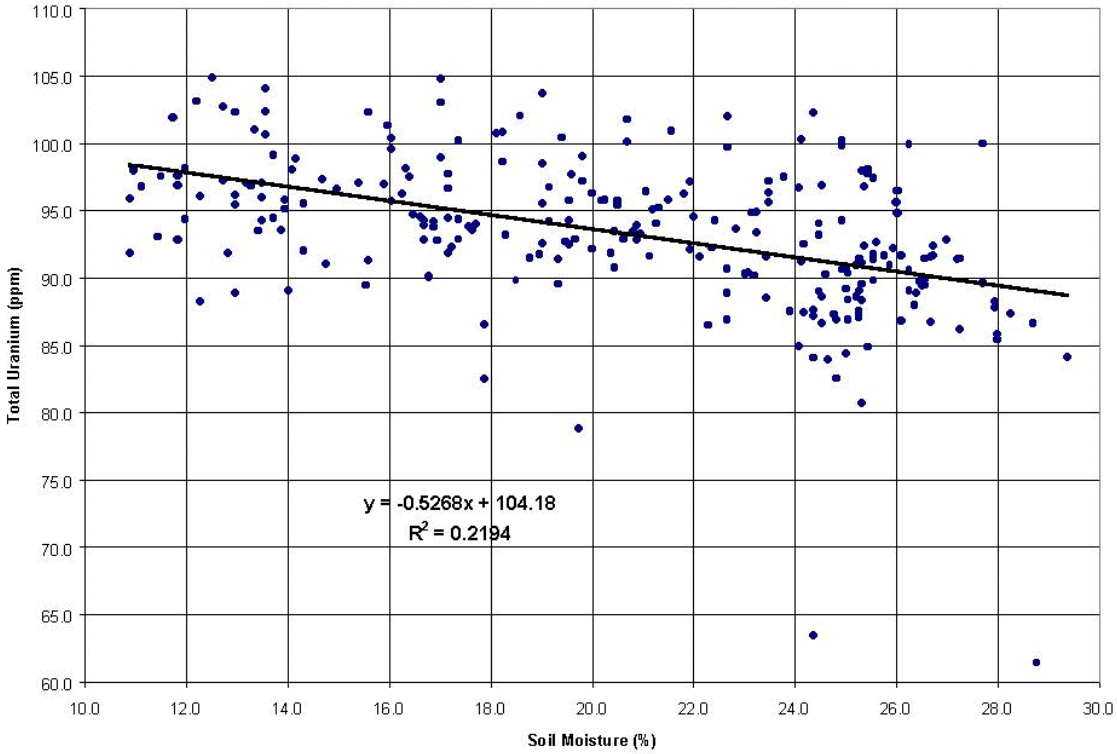

Figure 1. Total Uranium (Dry Wt.) as a Function of Soil Moisture Content

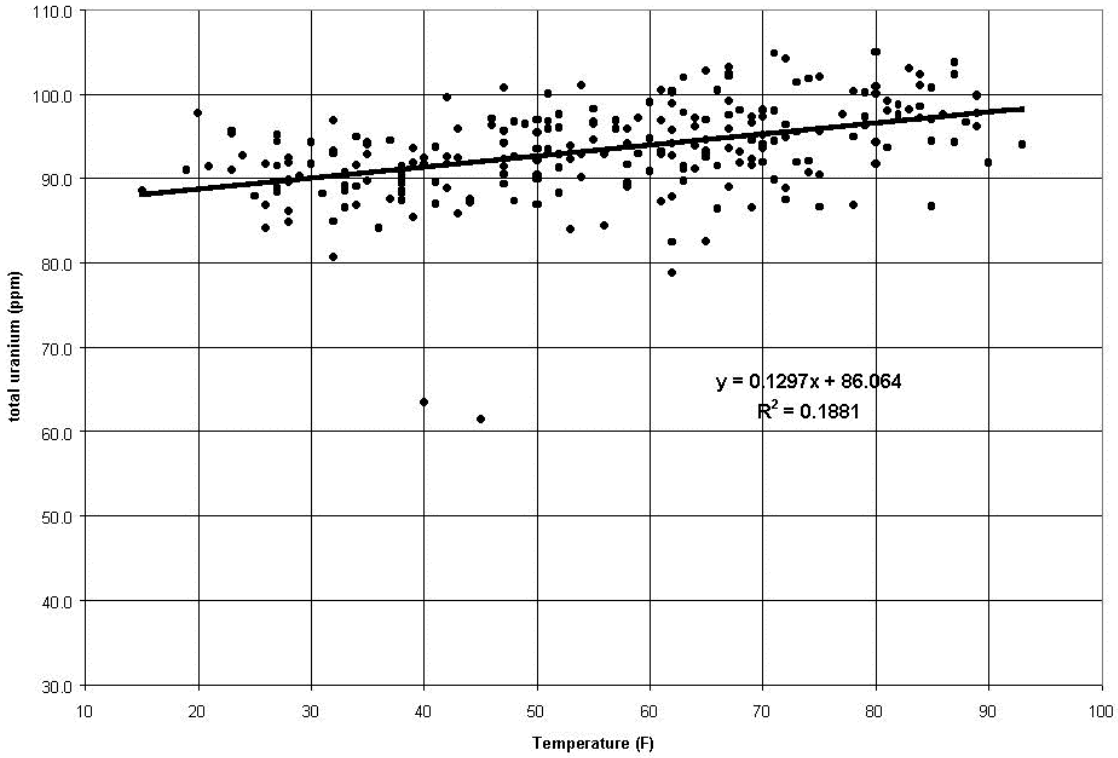

Figure 2. Total Uranium (Dry Wt.) as a Function of Atmospheric Temperature

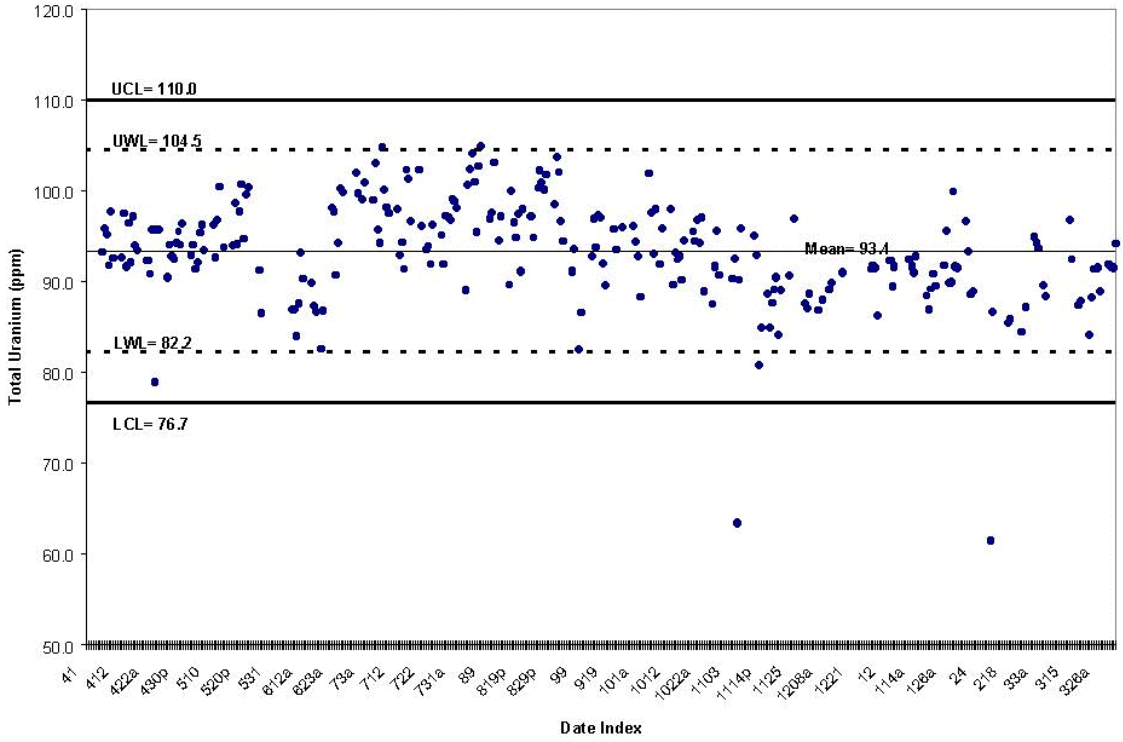

Figure 3. Control Chart for Total Uranium (Dry Wt. Basis)

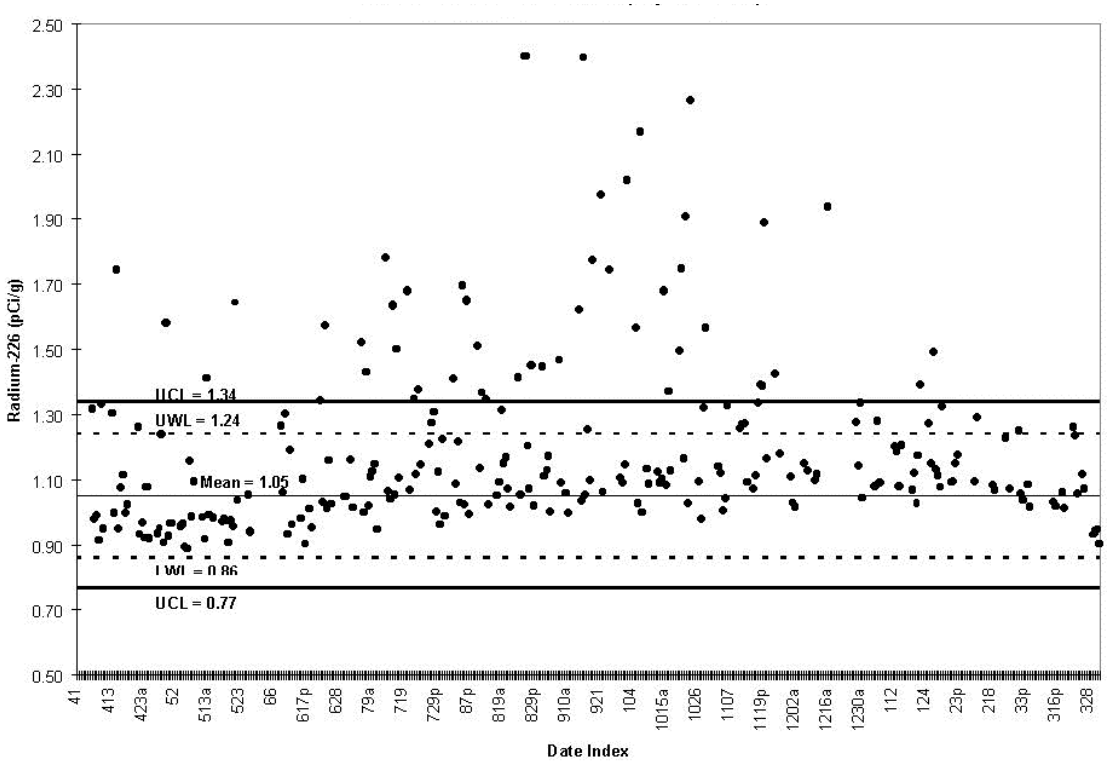

Figure 4. Control Chart for Radium-226 (Dry Wt. Basis)

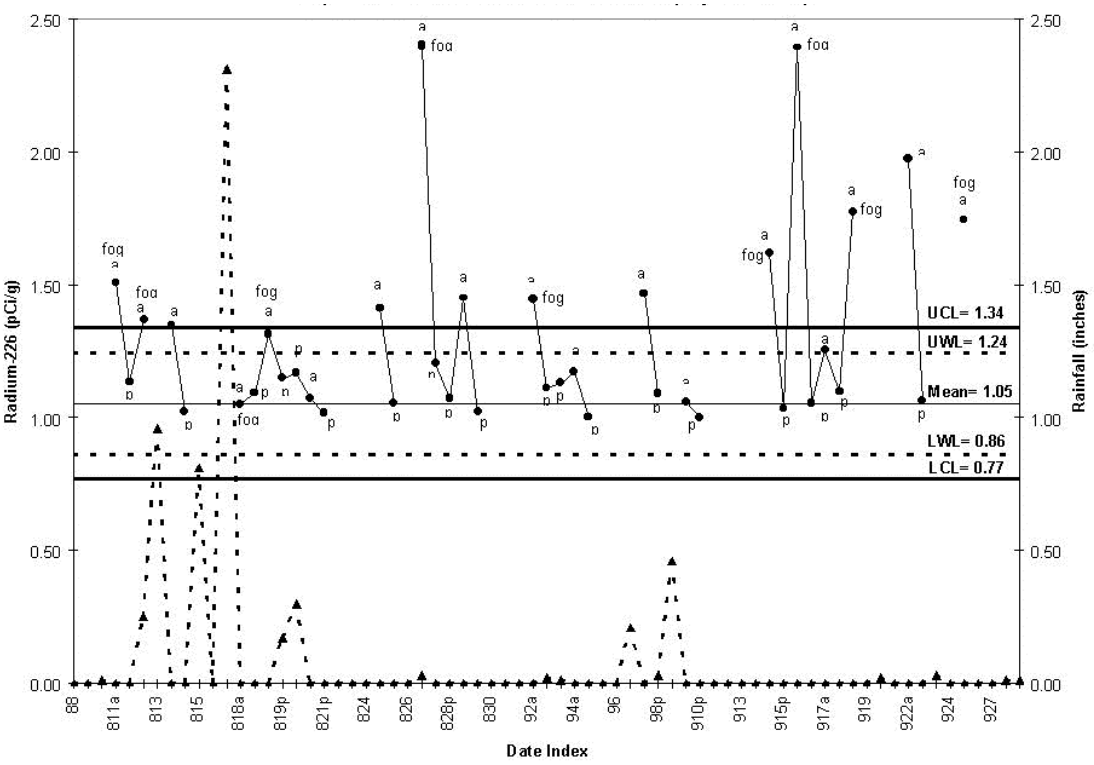

Figure 5. Expanded Control Chart for Radium-226 (Dry Wt. Basis)

USING ACID MINE DRAINAGE TO DETOXIFY HEXAVALENT CHROMIUM LEACHATE FEASIBILITY FOR COAL GENERATED ELECTRIC POWER

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A direct link between the production of Cr (VI) in coal fired electric power generation waste has been established. This is one of the first studies to link the production of Cr (VI) in the process of coal fired electrical power plants to the combustion conditions found in the facility. The study also evaluated aged and buried waste for stability and leaching of Cr (VI). Raw material and cored material were evaluated to assess contribution and species contents including stability. Run-off from many different sources was evaluated for stability and transportation of the chromium species.

Field and bench scale tests, were completed that demonstrated the effectiveness of acid mine drainage (AMD) in remediation. It was demonstrated that this waste stream can be used effectively to reduce the hexavalent chromium in leachate from a coal combustion fly ash landfill. Speciated isotope dilution mass spectrometry (SIDMS), was

used to fully characterize the chromium species in many materials and leachates and to profile the chemical inter-conversions of the chromium species when the leachate and AMD were combined.

Comparison of this remediation scenario against conventional methods like direct chemical treatment or passive wetland treatment proved to be economically and environmentally favorable. The study focuses not only on direct evaluation of the problem but includes the economic and scientific evaluation of the methods of measurement and remediation.

This study may be a useful demonstration of the use of one waste stream to detoxify another that is economically and scientifically feasible. It may be a viable solution for as many as half of the coal fired electrical generation stations each of which have some form of this problem that needs to be addressed in the future.

ENVIRONMENTAL BUSINESS IN THE PBMS PARADIGM

THE SHELL FOR ANALYTICAL CHEMISTRY REQUIREMENTS FOR USACE PROJECTS

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The purpose of the 'Shell' is to establish the basic approach to be used when performance-based methods, especially the SW-846 methods, are employed by the U.S. Army Corps of Engineers (USACE) for the analytical testing of environmental samples. These methods are flexible and can be readily adapted to individual project-specific requirements. The chemistry data generated for USACE projects must be produced by a process or system of known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The 'Shell' outlines such a process. Additionally, the 'Shell' applies the concepts to specific SW-846 methods for relatively critical data uses.

Project-specific data quality objectives (DQOs) must be established for both the field and laboratory operations. Any differences between project DQOs and lab operational criteria must be reconciled before project execution. For each project, data quality must be demonstrated for the analytes of concern at the levels of concern. However, in order to promote flexibility while maintaining some degree of consistency, when no project specific DQOs exist, the 'Shell' is used to establish the project analytical requirements.

Laboratories are required to maintain written, approved SOPs for all methods and operations. The demonstration of method proficiency begins with establishing the basic sensitivity of the method by determining the method detection limit (MDL). The relationship between the MDL, the method quantitation limit, the initial multi-point calibration curve, and the laboratory's method reporting limit is established. A laboratory cannot claim to reliably quantitate values below the low standard or above the high standard. A given method is suitable when the laboratory's low standard is below the site action level for each analyte of concern.

The 'Shell' describes the requirements for instrument calibration, calibration verification with standards from an independent source, and continuing calibration procedures, while maintaining a level of flexibility, which may be exercised, based on analyst judgement. Each preparation batch is to contain a method blank and a laboratory control sample containing all of the project-specific analytes of concern spiked at the levels of concern to monitor laboratory performance. Each preparation batch would typically contain additional QC samples to monitor the effect of the matrix on the method. Corrective actions are carefully detailed and involve interaction with project managers to avoid the generation of a significant amount of flagged or unusable data.

The intent of the 'Shell' is to ensure the generation of chemistry data of known quality. Laboratories employ chemists and others who are experts in the interpretation of analytical data. Much is to be gained by enhancing the interaction between the laboratory and project personnel. The 'Shell' encourages this.

ORGANIC ANALYSIS

QUESTIONABLE PRACTICES IN THE ORGANIC LABORATORY: PART II

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ABSTRACT

During recent environmental 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 manipulation and/or alteration of data, often to achieve or meet method QC criteria. Unfortunately, these practices are still being observed today. In addition, 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.

Examples of some of these practices include the following: (1) Dropping points during initial calibration to meet method criteria. (2) Reporting very tight QC performance ranges when actual lab control charts show a significantly wider range. (3) Dropping points to achieve a lower Method Detection Limit (MDL). (4) Performing tunes by picking the scan or series of scans that will meet the desired criteria after the original tune had failed. (5) Performing initial calibration curves but never verifying that the peaks used for the calibration actually represented the target analyte.

These practices are often described as 'the common approach used by everyone,' yet when described to people within EPA (e.g., the MICE Hotline), the clear response is that these approaches were never intended within the context of SW-846, although not explicitly addressed nor prohibited.

INTRODUCTION

The US Army Corps of Engineers (USACE) currently executes remedial and compliance activities under several environmental regulatory programs. The analytical testing of various environmental samples is often a significant part of these activities. The data must be produced by a process or system of known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. To give the USACE programs the greatest flexibility in the execution of its projects, the SW-846 methods, as published by EPA, are generally the methods employed for the analytical testing of environmental samples. These methods are comprehensive and flexible and can be readily adapted to individual project-specific requirements. As stated in the Final Rule that incorporated the Third Edition of SW-846 (and its updates) into the RCRA regulations, this appendix is required to be used for certain activities in the RCRA program. In other situations, this EPA publication functions as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in satisfying RCRA-related sampling and analysis requirements.

During recent laboratory audits conducted by the USACE, certain 'questionable practices' have been observed, especially in the organic analysis areas. Prior to project execution, the USACE may conduct a review of the laboratory that was proposed for use on that specific project. This review typically consists of three phases: (1) documentation review; (2) analysis of Performance Evaluation (PE) samples; and (3) on-site laboratory audit. Additional follow-up audits can also be conducted. These 'questionable practices' have been noted during all phases of these laboratory reviews.

The concepts of 'dry labbing', '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. Laboratory professionals clearly recognize these practices as inappropriate since no professional reason exits to employ them other than to meet specific contractual requirements and avoid potential penalties. There is no technical basis that can justify the use of these practices. The impact on data usability must be determined on a project by project basis. Unfortunately, these practices are still being observed today. When fraud is detected in conjunction with USACE projects, the Corps is attempting to separate any criminal/civil charges from the actual impact of the fraud on data usability (e.g. to separate legal from technical issues).

As the nation moves away from the use of strict method protocols to a more performance based approach, the

laboratories will have more discretion as to how methods are actually implemented. This will allow the laboratory community to take faster advantage of new technologies to cut costs and improve data quality. This move will place pressure on the laboratory community to employ knowledgeable experts to properly implement these newer technologies in a scientifically justifiable manner and to provide the enhanced documentation that will be needed. Current market over capacity has caused bidding wars and corner cutting. This move will place pressure on the regulator community to properly define what a performance based measurement system is and how its quality should be defined. This move will place pressure on the buyer of analytical services to better define the Data Quality Objectives (DQOs) such that the appropriate data can be obtained for any given project at a fair and appropriate cost. At the present time, issues exist in all these areas that can and are compromising data quality.

During this transition, USACE is observing a new group of 'questionable practices'. Many of these practices involve the selective exclusion of data to achieve or meet current method QC criteria rather than the direct manipulation of any single data point.

QUESTIONABLE PRACTICES

The first example of such 'questionable practices' involves laboratory documentation, including Quality Control Plans and Standard Operating Procedures (SOPs), that do not accurately reflect what the laboratory actually does. Many of these plans contain statements that are misleading, in error, or simply incomplete. These laboratory documents are often directly incorporated into project specific Quality Assurance Project Plans (QAPPs) or Work Plans. Often, these laboratory documents are not carefully read or reviewed before incorporation. They should be. Do misleading, erroneous, or incomplete statements justify these practices? Probably not.

The second example of such 'questionable practices' involves establishing initial calibration curves. Laboratories have been observed running six or more standards for methods that state 'a minimum of five points should be used to establish the initial calibration curve'. Points are then discarded, while maintaining a minimum of five calibration points, throughout 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. This practice is often justified by using the rationalization that a 'better curve' is generated. Another reason heard is that 'everyone is doing it'. Points can only be rejected for inclusion in the curve if a known error was made or if a statistical evaluation indicates that the point can be discarded. When multiple target analytes are included in each calibration standard, it may become necessary to discard selected upper or lower points for individual target analytes. Points can be discarded at the upper end of the curve if the linear range of the detector has been exceeded. For these cases, the laboratory must dilute samples that exceed the highest point of the calibration curve. Points can be discarded at the lower end of the curve if the detector is not producing a response. For these cases, the laboratory quantitation limit must be adjusted accordingly. Under no other circumstances can points be discarded. If QC criteria cannot be met, the instrument system may be unstable or the calibration solutions may be incorrectly prepared. The 'best curve' is obtained when all valid points are included in the initial calibration curve.

The third example of such 'questionable practices' involves the verification of initial calibration curves through the use of continuing calibration verification (CCV) solutions. 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. For example, when method 8021 is used, it is often difficult for laboratories to meet the CCV criteria for many of the gaseous target analytes. Method 8000B states the following: '…, if the average of the responses for all analytes is within 15%, then the calibration has been verified'. This language was chosen to make it easier for laboratories to implement this method when certain problem analytes, i.e. the gases in method 8021, marginally exceed the stated method criteria. It was never intended to allow the inclusion of obviously 'bad' data to make it 'acceptable'. Method 8000B goes on to say: '…, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the 15% limit'. If the QC criteria cannot be met, the instrument system may be unstable or the calibration verification solution may be incorrectly prepared.

The fourth example of such 'questionable practices' involves the reporting of acceptance ranges for laboratory control samples (to include surrogates). Laboratories have been observed reporting a very tight range for these QC samples on laboratory report sheets, indicating that they have good method control. However, an examination of actual control charts maintained by the laboratory shows a significantly wider range, if control charts are even available. This practice is often justified by using the rationalization that 'but the LCS was within the QC range, therefore, it must be okay'. Method 8000B stresses the importance of control charts to track laboratory performance. The

ranges generated should then be compared to method established criteria. If a 'match' is not obtained, then the laboratory should consider modifying their method to improve its performance. Simply reporting data under this circumstance since the LCS 'met the method criteria' is unacceptable since it misleads the user of the data and misrepresents the laboratory's reported data quality. Control chart ranges must also be reasonable. The issue of control charts as related to what analytes need to be charted (all target analytes or just a subset), in what QC samples (LCSs, MSs, LCSs and MSs combined, etc.), at what spiking levels (action levels or mid-level), and appropriate recovery ranges (what would be considered a reasonable range for a given method) needs further clarification in the SW-846 methods. Many laboratories do not understand the significance of these charts and how to properly implement and use them.

The fifth example of such 'questionable practices' involves the reporting of wide matrix spike (MS) recovery ranges. This item is related to the fourth example as given above. Laboratories have been observed reporting very wide ranges for these QC samples on laboratory report sheets. However, an example of the actual ranges as derived in the laboratory shows a significantly narrower range. This practice is often justified by using the rationalization that 'by widening the ranges, less of our data is rejected'. No method is immune to all possible interferences and not all interferences can be predicted. Therefore, it is important to monitor for these effects. The purpose of the matrix spike (MS) is to see if a possible matrix effect is impacting the data quality. When the MS QC range is exceeded, clients would normally be contacted to see if data flagging is appropriate, sample(s) should be rerun, the method should be modified (i.e., add a clean-up step) to better deal with the interference, or a different method chosen that is not affected by the interference. Data users should not penalize a laboratory, or its data, due to the presence of reported potential matrix interferences. At the same time, laboratories should not flag all poor recoveries as possible matrix effects, especially in blanks, LCSs, etc. Good judgment should be used by all parties involved.

The sixth example of such 'questionable practices' involves the determination of the method detection limit (MDL). Laboratories have been observed running eight 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. This practice is often justified by using the rationalization that a 'better (lower) MDL' is generated. Points can only be rejected if a known error was made or if a statistical evaluation indicates that the point can be discarded. Under no other circumstances can points be discarded. The MDL study must be performed at the appropriate level with a reasonable recovery of the target analyte(s) noted. The 'best MDL' is obtained when all valid points are included. It appears that the industry is placing too much emphasis on this concept. Laboratories are being driven to report lower and lower levels of contaminants. Perhaps the industry would be best served by using the performance-based concept to demonstrate what a given method run by a given lab could actually 'see' (the concept of the MDL check sample). The issue of the 'not detected' target analyte has caused great confusion ('detection limit' versus 'quantitation limit' versus 'reporting limit').

The seventh example of such 'questionable practices' involves tuning a GC/MS detector. Laboratories have been observed performing tunes in an inconsistent manner, such as picking a single scan or a series of scans that meet the desired criteria. Single scans have been observed being used at various locations across the peak, including single points being used on the peak tail. The use of an average of two or more scans have been observed over various parts of the peak (front, tail, over apex), to even include more background scans than peak scans in the average. These various schemes would be used when the recommended approach (average of three scans over the peak apex minus a background scan) would fail the desired criteria. No technical justification existed for using these various approaches other than to meet the method QC criteria. This practice is often justified by using the rationalization that 'as long as a scan(s) can be found that passes, the instrument is in tune'. Different tune parameters may be needed to optimize instruments from a given manufacturer. However, a consistent approach must be used to evaluate whether the instrument is 'in tune'. A laboratory cannot simply pick and choose whatever scan(s) happens to meet criteria on any given day.

The eighth example of such 'questionable practices' involves the misidentification of GC/MS peaks during initial calibrations and during continuing calibration verifications. Laboratories have been observed performing these calibrations but never verifying the identity of the peaks observed. These systems can make errors in the identification of target analytes especially when more than one peak is present in the retention time window. As a consequence, laboratories can generate calibration curves for the wrong target analyte. This has been observed for certain Appendix IX compounds and for certain poor performing target analytes in methods 8260 and 8270. Instrument raw data must be reviewed by the analyst to ensure that all peaks have been correctly identified, all peaks are clearly visible

and all peak shapes are appropriate for the target analyte being measured.

The ninth example of such 'questionable practices' involves performing continuing calibration verifications where the majority of the target analytes have missed their assigned retention time windows. Laboratories are performing unnecessary manual integrations to 'find' peaks that have missed these windows. This is very dangerous since peaks can be easily missed during the analysis of samples resulting in the reporting of false negative data. The SW-846 methods directly address retention time window criteria for the internal standards for the GC/MS methods but do not address any requirements for these windows for the target analytes. When such windows are missed, this should be a clear signal to the analyst that the system is out of control and corrective action is required. Such corrective action should include a system inspection along with repeating the initial calibration or updating the retention time windows for the target analytes.

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 (e.g., the MICE Hotline), the clear response is that these approaches were never intended. Potential solutions might include the following: 1) More prescriptive methods (probably not) or more clearly written guidance? 2) Training for lab staff on GLP to include statistics? 3) Rethinking the way laboratory services are contracted for? 4) Collecting additional data from the laboratory for more detailed data validations? 5) The use a standardized data reporting format and better data validation software? 6) Etc.

SUMMARY

The problems/issues noted above are very serious and directly impact on the usability of the data generated. Oftentimes the impact is equivalent to the impacts observed during past demonstrated cases of fraudulent data manipulation. How did we get to this point? There probably is no one single cause. One certain contributing factor is the price paid for these services. It is not uncommon to encounter projects that were bid low simply 'to get one's foot in the Federal door'. Simply put, the price paid for these services was not sufficient to cover the costs of producing the product. The fault lies both with the laboratory community for bidding in this manner and the government for accepting bids based on low price only without considering the quality factor ('best value' procurement strategy). However, this is a free market economy. The age old adages 'let the buyer beware' or 'you get what you pay for' certainly apply here.

Another factor is the level of expertise that now exists at the laboratory level. Some laboratories have let go their most experienced staff since they could no longer 'afford' them. Many people feel that the computer attached to the instrument in use will give them the correct answer without additional thought. If anything, more expertise is needed to evaluate the larger magnitude of data moving through the laboratory and the complexity of today's instrumentation. Laboratories should not be treated as black boxes. It is not uncommon for this author to visit a given laboratory and find that laboratory staff know very little about the fundamental chemistry of the method (or the software) in use. One common phrase heard often is 'but the method doesn't specify the approach to use'. This raises the question as to whether or not very prescriptive methods should be written. Yet each of the SW-846 methods typically state the following: 'This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatography/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a qualitative tool'. Additional training of laboratory staff should be emphasized. Peer review of raw data should also be emphasized. Audit trails should be 'turned on' when available and reviewed on a regular basis.

More review of raw data would be encouraged. Most of the data generated within a laboratory is generated in an electronic format. Yet much of the data is still manually managed and reviewed. A greater emphasis should be placed on receiving data electronically and for the electronic screening/review of this data. To assist this process, standardized electronic data reporting formats should be used. Standard file formats have been developed for several of the instrumental methods that can transfer data electronically in a standard file format between an instrument, or its data station, and a laboratory LIMS system. However, this standard is not often used. No standard file format has been developed for the transfer of information from a laboratory, or its LIMS system, to the data user. The use of a common data dictionary along with a common file structure, such as that proposed by the Department of Energy Environmental Management Electronic Data Deliverable Master Specification (DEEMS) would be encouraged.

Certainly, other contributing factors are involved. The 'CLP' prescriptive mentality is still with us. Data validation is still often performed using a modified version of the National Functional Guidelines. This is not appropriate for the SW-846 methods and further emphasizes the prescriptive, rather than performance based, approach. The move to a

performance based approach for the analysis of environmental samples is a welcome one. This move is also being greeted with uneasiness. The approach will place additional burdens on the laboratory community, regulator community, and the buyer of analytical services. Good communication will be very important to ensure that the needs of everyone involved have been met. The writers of the methods must work together with the users of the methods to minimize misunderstandings. It would be recommended that EPA revise Chapter One of SW-846 to more clearly describe this approach. The 'questionable practices' as described above are serious issues that must be resolved. Their timely resolution will give data users the confidence they need to make appropriate project decisions while at the same time using our tax dollars wisely.

COMPARISON OF FIVE SOIL EXTRACTION TECHNIQUES FOR PESTICIDE AND SEMIVOLATILE ANALYSIS

Rick McMillin, David Spencer, Diane Gregg and Lisa Wool

The objective of this study is to compare some relatively new environmental soil extraction techniques to each other and to the older techniques. This study will be looking at precision and recovery data for each technique using a certified spiked soil sample. This is a continuation of previous work which brought up some questions that are expected to be answered with this new study and a modified experimental design. A sixth procedure will also be included (which is really a modification of a method rather than a completely new method) which will be the abbreviated microwave modification. This simple modification eliminates or reduces the concentration step and has great potential for lab use by significantly reducing extraction time and solvent consumption (pollution prevention).

Certified spiked soils will be extracted in replicate by the various techniques. The replicate extractions will be split over several days with each technique being performed the same day. The single extract from a 10 gram sample will be split between semivolatile and pesticide analysis, effectively resulting in a 5 gram extraction for each. Extraction techniques will include microwave, pressurized fluid extraction (using the ASE™), automated soxhlet (using the Soxtherm™), standard soxhlet, and sonication. Also included will be the abbreviated microwave modification. Extraction and analysis will be by standard EPA methodology. Precision and recovery data will be presented in addition to time comparisons of the different techniques.

FREEZER STORAGE OF SOIL SAMPLES CONTAINING VOLATILE ORGANIC COMPOUNDS

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ABSTRACT
This study evaluates freezer storage (-12±3ºC) as a sample preservation method for volatile organic compounds (VOCs) in soil. Five different soil matrices, spiked with several aromatic and/or chlorinated hydrocarbons at less than 0.2 mg/kg, frequently showed no significant change in concentration after being frozen and stored for up to 12 days. Furthermore, with the exception of garden soil, 88% or more of the analyte concentrations were retained after a two-day transportation period when held at 4±2ºC.

INTRODUCTION
The options that are currently recommended by the U.S. Environmental Protection Agency (EPA) (Method 5035) and the American Society for Testing and Materials (ASTM) (D4547-98) for soil sample collection and preparation/preservation are (1) the immediate infield transfer of a sample into a weighed volatile organic analysis (VOA) vial that either contains VOC-free water acidified to a pH of 2 so that a vapor partitioning (purge-and-trap or headspace) analysis can be performed without re-opening or that contains methanol for analyte extraction in preparation for analysis, or (2) the collection and up to two-day storage of intact samples in an airtight container before initiating one of the aforementioned sample preparation/preservation procedures[1,2]. In both cases samples should be held at 4±2ºC while being transported or stored.

At the time these recommendations were made, two chemical preservation procedures, methanol immersion and

acidification to a pH of 2 or less with sodium bisulfate, received the most attention. It was recommended that methanol preservation be used only when samples were anticipated to contain concentrations of VOCs in excess of 0.2 mg/kg, and acidification be used when the concentrations were expected to be less than this value. Once preserved, the pre-analysis holding period could be extended up to 14 days after sample collection. Other means of biological preservation, such as lowering the storage temperature to below 0ºC, although briefly mentioned, did not receive as much attention as these chemical preservation procedures, because of insufficient validation.

The first sampling option described has the field personnel initiate sample preparation/preservation during the collection activity, and may require that they handle solutions and weigh the sample collection vessels[3]. The second option, which is the focus of this paper, allows for the transportation and storage of samples, so that preparation/preservation can be performed in a laboratory setting. This study evaluates the extended storage of discrete (5-g) samples at -12±3ºC (commercial freezer) as a means of preserving samples prior to either methanol extraction or analysis by vapor partitioning (i.e., purge-and-trap or headspace), subsequent to a 48-hour transportation period during which samples were held at 4±2ºC.

EXPERIMENTAL METHODS

After obtaining 5.0±0.1 g of the soil with a modified syringe, a pilot hole was made with a needle into the middle of the sample plug. Then a 10-µL glass syringe was used to transfer into this cavity a small aliquot of aqueous solution containing approximately 50 mg/L of some or all of the following analytes: trans-1,2-dichloroethene (TDCE), cis-1,2-dichloroethene (CDCE), trichloroethene (TCE), tetrachloroethene (PCE), benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), p-xylene (p-Xyl), and o-xylene (o-Xyl). The resulting sample concentration was less than 0.2 mg/kg for each analyte. Immediately after spiking, the syringe barrel was wiped clean, inserted into the mouth of a 40-mL VOA vial, the sample extruded, and then the vial was capped. For these experiments a variety of soil types, replicate samples, storage periods, and conditions were used (see Table 1).

After all the samples had been prepared, 5.00 mL of methanol was introduced to the first, iniddle, and last replicate samples to estimate the day-zero (D0), extracted within an hour of spiking) concentrations. The methanol was added by piercing each septum with a 23-gauge Luer Lok needle attached to a 5.00-mL glass syringe with a Luer connector. For the remaining samples, methanol was introduced to triplicate samples after various periods of refrigeration, or refrigeration and freezer storage (Table 1).

ANALYSIS

All of the samples were analyzed by equilibrium headspace analysis of a 0.500-mL aliquot of the methanol supemate after a 24-hour extraction period (Method 5021). The preparation of working standards, the instrumentation, and instrumental setting have been reported elsewhere. Samples prepared by methanol extraction were corrected for the increase in extraction solution volume, caused by the soil moisture (10 to 20% by dry wt.). The results of these experiments were evaluated using a one-way analysis of variance (ANOVA) and least significance difference tests (Fishers Protected LSD), at the 95% confidence level (Table 1).

RESULTS

The relative standard deviation for the concentrations established for the sample triplicates was typically less than 5%. Table 1 shows the percent recovery for each analyte after the various holding times and conditions, relative to the D0 (initial concentration or control) values. For all five experiments there was often no significant difference in the established analyte concentrations between the D2 and D14 results. Therefore, independent of soil type, once placed in the freezer, losses were abated even though storage was extended for at least an additional 11 days. With the exception of the fifth experiment, there also was little or no loss of VOCs relative to D0 for the samples held under these two sets of conditions (temperature and storage period). However, there were large losses of both Ben and Tol after 48 hours at 4±2ºC for the garden loam (fifth experiment). The additional refrigerated storage periods (D3 and D5) used in the last two experiments show that there was a slow, continuous decrease of Ben for the CRREL silt/clay, and a fairly rapid loss of all the aromatic compounds for the garden loam, when stored at 4±2ºC.

DISCUSSION

The experiments presented here are part of an ongoing evaluation of various transportation and storage protocols so that VOC samples can be prepared/preserved within a laboratory setting. Previously, it was shown that when samples were stored and transported in either a VOA vial or the En Core Sampler (En Novative Technologies, Inc., Green Bay, Wisconsin), recoveries were often more than 80% after a 48-hour transportation period when held at

4±2ºC. Moreover, often no further significant losses occurred after samples held in these two vessels were preserved by placing in a freezer (-12±3ºC) for up to an additional 12 days[4]. In addition, it was observed that losses due to biological degradation have greater impact (i.e., larger reduction in percentage of the initial concentration) at lower VOC concentrations[4]. This earlier effort, however, assessed only one type of soil (CRREL silt/clay). Here, the CRREL soil and four other soil types were assessed using a VOA vial as a storage vessel (Table 1). Consistent with the earlier experiments, losses of VOCs were abated when samples were frozen, and with the exception of the garden soil, recoveries relative to D0 were more than 80% after a 48-hour transportation period when held at 4±2ºC. The garden soil, however, showed a 50% or greater reduction in Ben and Tol after 48 hours when refrigerated, independent of being initially frozen for 24 hours.

Clearly, samples held in an airtight vessel and stored in a freezer have been effectively preserved in these studies. This method of preservation offers several advantages over the recommended infield chemical preservation option, e.g., no prior knowledge of the VOC concentrations is necessary, few Department of Transportation (DOT) regulatory requirements must be met, and field personnel don't have to handle chemicals or weigh samples. Moreover, preservation by acidification cannot be used indiscriminately; that is, this technique cannot be used with carbonaceous soils or when styrene is a VOC of interest[5]. An additional concern is that by lowering the pH of some matrices, the formation of acetone, a regulated compound itself, has been observed[4].

Based on the findings for the garden soil, it would not be advisable to hold samples for more than 48 hours at 4±2ºC when they are taken from sites where nonhalogenated VOCS are the principal analytes of concern, and where the data quality objectives (DQOs) call for the determination of low analyte concentrations. Indeed, future studies may show that this period should be shortened for samples taken to fulfill these objectives. In particular, it would not be advisable to hold samples for any period of time without chemical or physical (freezing) preservation if taken from a location receiving a biological amendment. Although the experimental evidence was not shown here, for sites where halogenated compounds are the analytes of interest and no biological amendment is being applied, samples are not as susceptible to biodegradation, and therefore would be less likely to be compromised if held for more than two days at 4±2ºC prior to being chemically or physically preserved[4,5]. Additional information on how to incorporate freezing as a method of sample preservation into a site sampling plan can be found elsewhere[4].

SUMMARY

Within the last couple of years new guidance has come from the U.S. EPA and ASTM regarding how soil samples acquired for VOC characterization should be collected and handled in preparation for instrumental analysis. To assist with the implementation of this new guidance, two very different protocols have been developed. In one case, all of the steps leading up to those associated with the analysis process are performed in the field. The other, more traditional approach, has all of the steps associated with sample preparation and analysis occur in a laboratory. The focus of this paper was to continue the process of evaluating secure transporting and storing of samples so that the laboratory protocol could be used. This study showed that, with the exception of a garden soil, the storage of samples in an airtight vessel was found to be consistent with the intent of the new guidance, and in general 80% or greater of the analyte concentrations were retained over a two-day storage period at 4±2ºC. The large losses seen over this period for low concentrations of BTEX compounds in the garden soil, however, indicate that temperate storage conditions are inappropriate for samples removed from sites receiving biological treatment or that have biological characteristics similar to a garden soil. Independent of soil type, samples transferred to a freezer (-12±3ºC) often showed no significant change in VOC concentrations over an additional 11 or 12 days of storage. For several reasons, this method of sample preservation appears to be better suited for VOCs in soil matrices than acidification. For instance, acidification is incompatible with carbonates, causes the decomposition of styrene and perhaps other target analytes, and has the potential to cause the formation of acetone. These findings and observations support the effort to include storage at -12±3ºC as a method of sample preservation in future revisions of these guidance documents.

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REFERENCES

1. U.S. Environmental Protection Agency (1986) Test methods for evaluating solid waste, Vol. 1B, SW-846.
2. American Society for Testing and Materials (in press) Standard guide for sampling waste and soils for volatile organic compounds, ASTM D4547-98.
3. Hewitt, A.D., T.F. Jenkins, and C.L. Grant (1995) Collection, handling, and storage: Keys to improved data quality for volatile organic compounds in soil. American Environmental Laboratory, Vol. 7: 25-28.
4. Hewitt A.D. (in press) Storage and preservation of soil samples for volatile organic compound analysis. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report.
5. Hewitt, A.D. (1995) Enhanced preservation of volatile organic compounds in soil with sodium bisulfate. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 95-26.

Table 1. Storage times, conditions, and % recoveries of analyte concentrations for triplicate samples relative to the DO (initial) values.

Exp.*	Storage (Days)	Soil Type	Storage conditions	Percent recovery								
				TDCE	CDEC	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
Ist	2	Fort Edwards clay	4ºC	97a†	96a,b	100a	103a	101a	98a	100a	99a	102a
	14	Fort Edwards clay	4ºC, 2D**/-12ºC, 12D	82b	90b	95a	94b	94b	89b	95a	93b	98a
2nd	2	WES silt/sand	4ºC	92a	99a	96a	93a	94a	94a	92b	97a	95a
	14	WES silt/sand	4ºC, 2D/-12ºC, 12D	92a	100a	99a	98a	99a	98a	101a	101a	98a
3rd	2	Wisconsin sand	4ºC	97a	98a	97a	97a,b	101a	98a	98a,b	97a	98a,b
	14	Wisconsin sand	4ºC, 2D/-12ºC, 12D	93a	99a	98a	94b	96b	86b	92b	88b	95b
4th	2	CRREL silt/clay	4ºC			91b		98a		101a	98a	
	3	CRREL silt/clay	4ºC			85c		91b		97b	92c	
	5	CRREL silt/clay	4ºC			78d		91b		97b	95b	
	14	CRREL silt/clay	-12ºC, 1D/4ºC, 2D/-12ºC, 11D			92b		102a		100a 98a		
5th	2	Garden loam	4ºC			42b		50b		80b	84b	
	3	Garden loam	4ºC			27d		35c		72c	78b	
	5	Garden loam	4ºC			11		16d		40d	54c	
	14	Garden loam	-12ºC, 1D/4ºC, 2D/-12ºC, 11D			37c		47b		81b	84b	

*Experiment

†Values with common letter are not significantly different at the 95% confidence interval (ANOVA and Fishers protected LSD) for each experiment. The letter "a" was assigned to the D0 values.

** Days

PERFORMANCE OF THE DISPOSABLE EN CORE® SAMPLER FOR STORING SOIL FOR VOLATILE ORGANIC ANALYSIS

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ABSTRACT

Soil sampling and storage practices for volatile organic analysis must minimize loss of volatile organic compounds (VOCs) from samples. The En Core® sampler is designed to collect and store soil samples for volatile organic analysis in a manner that minimizes loss of contaminants due to volatilization and/or biodegradation. The sampler consists of a coring body/storage chamber, O-ring sealed plunger, and O-ring sealed cap, all of which are constructed of an inert composite polymer making the device chemically compatible with soil matrices and contaminants. The devices are designed to collect and hold a soil sample of either 5-grams or 25-grams during shipment to the laboratory for analysis. After the sample is collected in the En Core sampler, the coring body is sealed with the slide-on, locking cap and immediately becomes a sample storage chamber.

The En Core sampler has undergone extensive testing during development to determine design specifications, and after development to evaluate performance under various storage conditions. This paper discusses (1) testing that was performed as part of the developmental work to select an O-ring design to minimize VOC loss from the device; (2) testing that was conducted to generate performance data on the device for inclusion in a new American Society for Testing and Materials (ASTM) standard practice for using the En Core sampler; and (3) testing to evaluate performance of the device to store soils containing low level VOC concentrations. Results show that the En Core sampler performs well for storing VOC-contaminated soil.

INTRODUCTION

A major concern in sampling soil for volatile organic analysis is maintaining sample integrity during collection and shipment of soil samples to the laboratory for analysis. Laboratory data can greatly underestimate volatile organic compound (VOC) concentrations in soil if attention is not paid to sampling and handling techniques. The disposable En Core® device is a soil sampling/storage tool that is designed to collect and store a soil sample for volatile organic analysis in a manner that minimizes loss of contaminants due to volatilization and/or biodegradation. The En Core sampler has three components: (1) the coring body/storage chamber, which is volumetrically designed to collect and store a soil sample of either approximately 5 grams or 25 grams; (2) an O-ring sealed plunger for nondisruptive extrusion of the sample into an appropriate container for analysis or preservation; and (3) a slide-on cap having an O-ring seal and locking arm mechanism. After the sample is collected in the En Core sampler, the coring body is sealed with the slide-on, locking cap and immediately becomes a sample storage chamber. The seals of the device are provided by three Tefon™-coated Viton™ O-rings. There is an American Society for Testing and Materials (ASTM) practice, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis, that gives guidance on using the device and includes an appendix showing data on the performance of the sampler to store VOC-spiked soils[1].

The En Core sampler has undergone extensive testing during development to determine design specifications, and after development to evaluate performance of the device under various storage conditions. This paper discusses (1) testing that was performed as part of the developmental work to select an O-ring design to minimize VOC loss from the device; (2) testing that was conducted to generate performance data on the device for inclusion in the ASTM practice for using the sampler; and (3) testing to evaluate performance of the device to store soils containing low level VOC concentrations.

DISCUSSION OF THE WORK

Performance of Teflon-Coated Viton O-Rings in the En Core Device to Minimize TCE Loss

Testing was performed by Alan Hewitt at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH to evaluate the performance of various O-ring designs based on their ability to minimize loss of trichloroethylene (TCE) from soil samples stored in the 5-gram En Core device[2]. In this study, silty, clay-type soil samples were collected from a site contaminated with TCE. Five soil samples were collected and immediately

transferred to methanol for extraction and analysis. These were the time-zero samples. Samples from the same site were also collected using En Core samplers having various O-ring designs for 48-hour and seven-day storage at 4 ±2°C prior to analysis. For each O-ring design and storage condition, five samples were collected and stored. After storage for the specified length of time, the samples were extruded into methanol and analyzed by automated headspace analysis using an auto sampler coupled to a gas chromatograph with sequential photoionization flame ionization detectors.

To evaluate O-ring performance, the mean concentrations of TCE in the samples stored for 48 hours and seven days at 4 ±2°C were compared to the mean concentrations of TCE in the time-zero samples. This was done by performing a statistical calculation to determine if there is a difference between the mean values at a 95% confidence level. In this evaluation, the actual difference between the time-zero mean concentration of TCE and the mean concentration of TCE in the stored samples (experimental difference) is calculated and compared to a computed difference[3]. If the experimental difference between the mean values is less than the computed threshold difference, it can be concluded that the mean concentration of TCE in the stored samples is statistically the same as the mean concentration of TCE in the time-zero samples, and as a result, the performance of the En Core device is acceptable.

The concentrations of TCE in the time-zero samples and samples stored in the En Core devices having Teflon-coated Viton O-rings, which is the O-ring design selected for the En Core device, are shown in Table 1. The reason the TCE concentrations vary between storage times is because the samples were collected at different depths. The experimental difference and computed difference for the mean values for 48-hour and seven-day storage are also shown in Table 1. For both storage conditions, the mean concentration of TCE in the stored samples is not statistically different from the mean concentration of TCE in the time-zero samples. This shows excellent performance of the Teflon-coated Viton O-rings to minimize loss of TCE from soil collected and stored in the En Core device. Before the O-ring design was finalized, additional testing involving a full list of VOCs was performed to ensure that Teflon-coated Viton O-rings give acceptable performance for use in the En Core device.

Table 1. Evaluation of the Performance of Teflon-Coated Viton O-Rings in the En Core Device to Minimize TCE Loss

TCE Concentrations in Time-Zero Samples, mg/Kg		TCE Concentrations in En Core Samples, mg/Kg
Teflon-Coated Viton O-Rings Used in En Core Device for 48-Hour Storage at 4 ±2°C		
295		295
222		222
280		280
266		266
254	Experimental $\bar{x}_1 - \bar{x}_2 = 20$	254
$\bar{x}_1$: 263	Computed $\bar{x}_1 - \bar{x}_2 = 41$	$\bar{x}_2$: 243
s[a]: 28	20<41	s: 38
	Mean values are not statistically different	
Teflon-Coated Viton O-Ring Used in En Core Device for 7-Day Storage at 4 ±2°C		
400		314
352		352
434		313
364		359
351	Experimental $\bar{x}_1 - \bar{x}_2 = 44$	340
$\bar{x}_1$: 380	Computed $\bar{x}_1 - \bar{x}_2 = 52$	$\bar{x}_2$: 336
s: 36	44<52	s: 28
	Mean values are not statistically different	

[a] s = standard deviation

Testing to Evaluate the Performance of the En Core Sampler for the ASTM Practice

A study was conducted to evaluate the performance of the 5-gram and 25-gram En Core samplers to store three different soil types spiked with an aqueous solution containing nine VOCs. The soils used in the study are representative of different environments and contained native microbial populations. They were (1) a river bank soil having 49% sand, 26% silt, 24% clay, 5.3% organic material, ~14% moisture, and a dehydrogenase (microbial) activity of 22 mg total product formed (TPF)/g/24 hours; (2) a mountain soil having 75% sand, 13% silt, 12% clay, 4.3% organic material, ~12% moisture, and a dehydrogenase activity of 11 mg TPF/g/24 hours; and (3) a prairie soil having 67% sand, 17% silt, 16% clay, 1.5% organic material, ~8% moisture, and a dehydrogenase activity of 17 mg TPF/g/24 hours. The VOCs used in the study were cis-dichloroethylene (CDCE), benzene, TCE, toluene, perchloroethylene (PCE), ethylbenzene, m/p-xylene, o-xylene, and methylethylketone (MEK). These compounds were selected as the analytes of interest because they are representative of halogenated, aromatic, and polar VOCs typically found in contaminated soils.

In the study, soil samples were collected in the En Core samplers from a large container of loose soil and then spiked with an aqueous solution containing the compounds listed above to give an approximate concentration of 2.5 µg/g of each analyte of interest in the samples. This analyte concentration in the soil was selected to limit the influence of the analytical method on the data. After all samples were spiked and capped, five random samples for each soil type were extruded from each size of En Core sampler into methanol for analysis to give time-zero concentrations of the analytes of interest. Five each of the remaining samples were stored under the following storage conditions: on ice at 4 ±2°C for 48 hours; 4 ±2°C for four days (on ice for 48 hours then refrigerated for 48 hours); on ice at 4 ±2°C for 48 hours followed by storage for 5 days in a freezer at -12 ±2°C; and in a freezer at -12 ±2°C for seven days. After the samples were held for the appropriate times, they were extruded into methanol for extraction and analysis. The methanol extracts of the samples were analyzed using EPA Method 8021B[4].

To evaluate the data, the mean values of the analytes of interest in the stored samples were compared to their mean values in the time-zero samples by calculating average percent recovery. The average percent recoveries of the VOCs of interest from samples of the river bank, mountain, and prairie soils stored in the 5-gram and 25-gram En Core samplers for 48 hours at 4 ±2°C are shown in Table 2. These values range from 69 to 102%. The overall average percent recoveries for the analytes of interest from the samples of the three soils stored at 4 ±2°C for 48 hours range from 83 to 98%. The overall average percent recoveries of the nine VOCs of interest from samples of the three soil types stored under the other storage conditions used in the study are shown in Table 3. These values range from 90 to 98% for the river bank soil, 77 to 91% for the mountain soil, and 55 to 79% for the prairie soil. The data generated in this study are included in the appendix of the ASTM practice.

Table 2. Average Percent Recoveries of VOCs from Soil Samples Stored in En Core Samplers for 48 Hrs. at 4 ±2°C

VOCs	River Bank Soil	Mountain Soil	Prairie Soil
CDCE	91[a] (15)[b] / 91[c] (1)[b]	87[a] (10)[b] / 87[c] (8)[b]	82[a] (9)[b] / 76[c] (17)[b]
Benzene	93 (3) / 90 (4)	86 (11) / 90 (11)	75 (13) / 69 (25)
TCE	97 (1) / 92 (3)	91 (8) / 94 (6)	79 (10) / 72 (22)
Toluene	99 (1) / 94 (3)	90 (5) / 93 (6)	82 (8) / 79 (14)
PCE	100 (1) / 96 (3)	96 (4) / 98 (6)	91 (5) / 86 (14)
Ethylbenzene	101 (3) / 98 (3)	92 (7) / 96 (4)	91 (3) / 89 (6)
m\p-Xylene	102 (2) / 98 (1)	92 (2) / 93 (4)	90 (1) / 88 (6)
o-Xylene	99 (1) / 98 (3)	97 (2) / 96 (4)	92 (2) / 94 (4)
MEK	100 (0) / 96 (1)	83 (0) / 86 (2)	92 (0) / 97 (3)
Overall Average % Recovery	98 (4)[d] / 95 (3)[d]	90 (5)[d] / 93 (4)[d]	86 (8)[d] / 83 (12)[d]

[a] Average percent recovery for the 5-gram sampler

[b] Value in parentheses is the percent relative standard deviation of the concentration values in the stored samples. The percent relative standard deviation of the concentration values in the time-zero samples ranged from 0-11%.

[c] Average percent recovery for the 25-gram sampler

[d] Value in parentheses is the percent relative standard deviation of percent recovery values use to calculate overall average percent recovery.

Table 3. Overall Average Percent Recoveries of the Nine VOCs of Interest from Soil Samples Stored in En Core Samplers

Storage Condition	River Bank Soil	Mountain Soil	Prairie Soil
4 ±2°C for 4 Days	98[a] (2)[b] / 97[c] (3)[b]	83[a] (8)[b] / 88[c] (6)[b]	71[a] (25)[b] / 71[c] (21)[b]
4 ±2°C for 48 Hrs. then -12 ±2°C for 5 Days	94 (5) / 90 (7)	83 (10) / 77 (18)	59 (33) / 55 (43)
-12 ±2°C for 5 Days	98 (4) / 97 (6)	91 (11) / 86 (13)	76 (29) / 79 (21)

[a] Overall average percent recovery for the 5-gram sampler

[b] Value in parentheses is the percent relative standard deviation of percent recovery values used to calculate overall average percent recovery.

[c] Overall average percent recovery for the 25-gram sampler

Based on the results of this testing, the following conclusions can be made.

- For storage at 4 ±2°C on ice for 48 hours, the En Core sampler performs well for storing the VOC-spiked river bank, mountain, and prairie soils. Overall average percent recovery values for the analytes of interest range from 83 to 98% (Table 2).
- The En Core sampler performs well for storing the VOC-spiked river bank and mountain soils under all of the storage conditions used in the study. Overall average percent recovery values range from 77 to 98% for the analytes of interest (Table 3).
- Slightly higher percent recovery values for the VOCs of interest from the river bank soil as compared to those for the mountain soil (Tables 2 and 3) are most likely due to the difference in the composition of the soils. The higher percent sand and lower percent clay composition of the mountain soil is a less favorable soil matrix for holding VOCs.
- Percent recovery values for the spiked prairie soil stored in the En Core samplers are generally lower than those for the river bank and mountain soils. It appears that in some cases, loose particles of the drier prairie soil may have scattered when the En Core samplers were capped causing the seals of the device to be compromised. This may be a result of the experimental design of the testing, in which the soil was loose and had no structure when it was collected in the device.

Testing to Evaluate Performance of the En Core Device to Store Soils Containing Low Level VOC Concentrations

Two soils were used in this study, which was performed by En Chem, Inc. One soil was predominantly sand (83% sand, 17% silt and clay, and 7% moisture), and the other was a biologically active loamy garden soil (63% sand, 24% silt, 13% clay, and 12% moisture). Five-gram En Core samplers were filled with soil and frozen. After freezing, the samplers were removed from the freezer and allowed to thaw just enough to allow the spiking solution to be injected. The spiking solution was prepared by saturating deionized water with gasoline and then injecting a VOC stock standard into the gasoline-saturated water. Five replicates of time-zero samples (spiked and immediately extruded into methanol) and five replicates of spiked samples for storage at 4 ±2°C for two and seven days were prepared for each soil type. Low level samples are defined by EPA Method 5035[5] as having concentrations between 1-200 µg/Kg. In this study, all compounds in the soil samples were within this range, except methylene chloride (~210 µg/Kg), benzene (~300 µg/Kg), and toluene (~360 µg/Kg). Benzene and toluene concentrations were high because of their presence in the gasoline-saturated water that was used in the spiking solution.

Average percent recovery values for the VOCs of interest in this study for two-day and seven-day storage are listed in Table 4. For the sandy soil at two-day storage, recovery values range from 82% for vinyl chloride to 94% for bromoform. At seven-day storage, the values range from 66% for vinyl chloride and bromoform to 155% for naphthalene. The lower percent recovery of vinyl chloride is expected because of its low boiling point. The high recovery for naphthalene at seven-day storage is most likely due to analytical factors.

As shown in Table 4, recovery values for the garden soil at two-day storage, range from 76% for benzene to 101% for chloroform. At seven-day storage, the values range from 46% for vinyl chloride to 116% for methylene chloride. Lower percent recovery values for the aromatic compounds, such as benzene and toluene, at seven-day storage are most likely due to biodegradation as chlorinated compounds with similar volatility do not show this loss at seven days. In the near future, data showing the performance of the device to store soil containing low levels of VOCs will be included in the ASTM practice.

Table 4. Average Percent Recovery Values from Soils Spiked with Low Level VOC Concentrations and Stored in En Core Samplers for 2 Days and 7 Days at 4 ±2°C

Compound	Sandy Soil		Garden Soil	
	Average % Recovery for 2-Day Storage	Average % Recovery for 7-Day Storage	Average % Recovery for 2-Day Storage	Average % Recovery for 7-Day Storage
Vinyl Chloride	82 (7)[a]	66 (4)[a]	82 (9)[a]	46 (13)[a]
Methylene Chloride	89 (3)	137 (6)	92 (12)	116 (9)
Methyl tert-butyl Ether	92 (5)	91 (3)	98 (5)	90 (10)
Chloroform	91 (3)	76 (7)	101 (8)	97 (14)
Carbon Tetrachloride	90 (5)	76 (9)	96 (9)	111 (11)
Bromodichloromethane	88 (4)	76 (13)	98 (3)	106 (13)
Benzene	87 (3)	73 (2)	76 (6)	59 (16)
1,1,2-Trichloroethane	90 (8)	93 (11)	95 (3)	107 (11)
Ethyl Dibromide	90 (5)	97 (9)	92 (6)	80 (14)
Toluene	90 (2)	74 (5)	86 (12)	65 (17)
Ethylbenzene	87 (4)	71 (4)	95 (5)	93 (14)
Styrene	83 (4)	67 (6)	86 (7)	65 (13)
Bromoform	94 (8)	66 (20)	83 (21)	91 (6)
m/p-Xylene	90 (2)	77 (1)	96 (6)	89 (12)
o-Xylene	88 (1)	76 (6)	91 (4)	86 (11)
1,3,5-Trimethylbenzene	90 (5)	102 (5)	98 (4)	106 (11)
1,2,4-Trimethylbenzene	89 (3)	112 (3)	99 (5)	102 (9)
Napthalene	86 (8)	155 (10)	96 (10)	108 (8)
Overall Average % Recovery	89 (3)[b]	88 (28)[b]	92 (7)[b]	90 (22)[b]

[a]Value in parentheses is the percent relative standard deviation of the concentration values in the stored samples. The percent relative standard deviation of the concentration values in the time-zero samples ranged from 3-15%.

[b]Value in parentheses is the percent relative standard deviation of the percent recovery values used to calculate overall average percent recovery.

SUMMARY OF RESULTS

Results of the testing described in this paper can be summarized as follows.

- The Teflon-coated Viton O-rings show excellent performance in minimizing loss of TCE from soil collected and stored in the En Core sampler at 4 ±2°C for 48 hours and seven days.
- For storage at 4 ±2°C on ice for 48 hours, the En Core sampler performs well for storing VOC-spiked river bank, mountain, and prairie soils. Overall average percent recovery values for typical VOC contaminants in soil range from 83 to 98%.
- The En Core sampler performs well for storing the VOC-spiked river bank and mountain soils under storage conditions of 4 ±2°C for four days; 4 ±2°C for 48 hours followed by storage for 5 days at -12 ±2°C; and -12 ±2°C for seven days. Overall percent recovery values range from 77 to 98% for typical VOC contaminants in soil.
- Results show that when drier, loose soils are to be stored in the En Core samplers, care should be taken to prevent scattering of particles during capping, which may compromise the seal of the device.
- The En Core sampler performs well for storing sandy and biologically active loamy garden soils containing low levels of 18 VOCs. Overall average percent recovery values for two-day and seven-day storage at 4 ±2°C range from 88 to 92%.

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DISCLAIMER

REFERENCES

1. American Society for Testing and Materials, 1999, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis. In press.
2. Sorini, S.S., and J.F. Schabron, 1998, Validation of a New Soil VOC Sampler: Soil Sampling and Storage Practices for Volatile Organic Analysis. Laramie, WY, WRI Report WRI-98-R007.
3. Skoog, D.A., and D.M. West, 1976, Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston: New York, NY, pp. 67-69.
4. U.S. EPA, 1996, Method 8021B: Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846)*, Vol. 1B, Final Update III.
5. U.S. EPA, 1996, Method 5035: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846)*, Vol. 1B, Proposed Update III.

AN EASY, COST-EFFECTIVE SOLUTION FOR SAMPLING VOLATILE ORGANIC COMPOUNDS IN SOILS

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ABSTRACT

This study evaluates a standard 40-ml vial as a suitable storage container for volatiles when samples are stored at 4±2°C. This method is consistent with SW-846 method 5035, which calls for a "Hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis". Method 5035 further discusses field preservatives as a means of retarding biological degradation. This study also demonstrates that the addition of chemical preservatives such as methanol or acid can be delayed for up to 48 hours without significant losses due to biological degradation. Samples are taken utilizing a coring tool to rapidly delivering an approximate 5-gram sample to a 40-ml vial pretared with stirring bar. Sample preservation and weight determinations are performed at the laboratory.

Introduction

Soil sampling options for volatiles following EPA's Method 5035 or ASTM's D4547-98 can be both time-consuming and expensive. At the time of these recommendations, sample takers typically haul field balances and chemical preservatives to the field or use expensive coring/storing devices which typically add $25-$30 to the cost of each sample. New study data demonstrates that an empty 40-ml vial can be used as a sample storage container for at least 10 days without any significant loss in VOC recoveries due to volatilization. Recoveries of 85 % or more were retained for 55 of 63 analytes tested after a ten-day period when samples were stored at 4°C without preservative. A 10-µl methanol standard was used to spike 13 grams of soil with the 63 volatile analytes. Subsequent studies by Alan Hewitt - U.S. Army Cold Regions Research and Engineering Laboratory and U.S. Analytical suggest that the 10 µl of methanol were enough to sterilize the vial which minimized losses due to biological degradation.

The effects of biological degradation have been studied on several matrixes by both U.S. Analytical - presented here and Alan Hewitt - U.S. Army Cold Regions Research and Engineering Laboratory[2,3]. Results have shown that a 48-hour transportation period where samples were stored at 4±2°C without preservative can be incorporated with at least 73% volatile retention for most soil matrixes.

The focus of this paper is to present data which supports the use of an empty 40-ml VOC vial as a suitable transport/storage container for volatiles and to suggest a sampling protocol, which is less expensive, and more user friendly than the most widely practiced options.

Experimental

Two separate studies were performed to determine the appropriate holding time for soils collected in empty VOC vials. The first study made use of a methanol spiking solution, which is believed to have sterilized the soil, and thus, prevented biological degradation. The significance of this data is that it can be used to show the integrity of a 40-ml vial as a storage container and displays the efficiency of recapturing and extracting volatiles from both dry Ottawa sand and a complex matrix such as garden soil by adding methanol through the vial septum. The second study made use of an aqueous spiking solution of low-level BTEX compounds so as not to sterilize the soil. Results from study two could then be used to determine the level of biological degradation over time in order to determine how long samples can be held without preservation.

For study one, a list of 63 volatiles was chosen that would demonstrate broad range applicability for this procedure. In addition, gasoline was chosen to provide information on a common contamination mixture and to validate the procedure for Wisconsin's GRO method. VOC's were spiked at a low (154 µg/kg) and a high (769 µg/kg) level. The low-level spike would provide information on possible matrix interference and the high level would more accurately determine procedural integrity. The gasoline was spiked at 153 mg/kg. The procedure was tested on both dry Ottawa laboratory sand and biologically active garden soil. The six methanol addition time intervals were 0, 24, 48, 72, 168, and 240 hours. Five replicates were analyzed at each time interval to provide the necessary statistical data. The steps of the procedure are outlined below:

1. Weigh 13 grams of soil matrix into 92- 40ml VOC vials, 30 for VOC low-level spike, 30 for VOC high-level spike, and 30 for gasoline spike, and 2 for blanks.
2. Add 13 mls of methanol to the blanks and cap. Store with all other samples until ready for analysis.
3. Spike 1 replicate for the VOC low-level 0-hour time interval and immediately cap the vial. Add 13 mls of methanol through the septum using a 25-ml Gastight™ syringe equipped with a 22-gauge needle. Holding the plunger down, pull the syringe out, shake the vial for 15 seconds, and vent. Record the time.
4. Repeat step 3 for the remaining 4 VOC low-level 0 hour replicates.
5. Spike the rest of the VOC low-level time intervals, record the time and store at 4±2°C.
6. Repeat steps 3-5 for both the high level and the gasoline middle level spikes.
7. After 24 hours add methanol through the septum to each of the five 24 hour replicates for all three spiking schemes. Repeat this for all other time intervals.
8. Sonicate extract and analyze all VOCs using SW846 method 8260. Sonicate extract and analyze all gasoline spikes using the WDNR GRO September 1995 method.

Samples were spiked as follows:

VOC low-level (154-µg/kg) spike 10 µl of a 200-mg/l solution below the soil surface.
VOC High-level (769 µg/kg) spike 50 µl of a 200-mg/l solution below the soil surface.
Gasoline (154 mg/kg) spike 20 µl of a 100,000 mg/l solution below the soil surface.

For Study two, the list of analytes were the BTEX compounds, benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene. This list of analytes was chosen since the aromatic compounds have been shown to be more susceptible to biological degradation than other VOCs[2]. This study was designed to compare biological degradation in three different soil matrixes. Dry Ottawa sand was used as a baseline to test the experimental procedure. Biologically active garden soil and soil taken from a UST site mildly contaminated with fuel oil were the test soils. After adding 5 g. of soil to an empty 40-ml VOC vial, 30 ul of an approximately 80-mg/l aqueous solution of each analyte were added to the soil subsurface. The resulting sample concentration was less than 400 µg/kg for each analyte. Three different soil types were spiked in duplicate and held from 0-5 days without preservative. Samples were preserved with methanol through the septum using the same procedure as study 1.

Instrumentation

Volatiles, SW846-Method 8260

Hewlett Packard 6890 GC, Hewlett Packard 5973 MSD, Tekmar 3000 Sample Concentrator, Dynatech PTA 30WS Autosampler.

WDNR GRO September 1995
Varian 3400 GC, Tracor PID/FID Detectors, Tekmar LSC 2000 Sample Concentrator, Archon 5100 Autosampler.

Results
Study one results are compiled in Tables 1-25. Study two results are compiled in Table 26.

Discussion
Study one clearly demonstrates that in the absence of biological degradation a Teflon®-lined Silicone Septa 0.125" 40ml VOC vial is an excellent storage container for volatiles. For the Ottawa sand matrix, 58 of 63 analytes recovered at 85% or better at the low-level spike after a 10-day holding period and 59 of 63 analytes recovered at 85% or better at the high-level spike after a 10-day holding period. For the biologically active garden soil, (which probably was partially sterilized by methanol from the spiking solution) 42 of 63 recovered at 85% or better at the low-level spike after a 10-day holding period and 55 of 63 analytes recovered at 85% or better at the high-level spike after a 10-day holding period. Gasoline was recovered at 94% or higher in both Ottawa sand and biologically active garden soil after a 10 day holding period.

High-level biologically active soil recoveries were significantly higher than low-level biologically active soil recoveries. The difference in these recoveries can be attributed to the degree of biological sterilization, which occurred in the study. The amount of methanol used to spike the low-level concentrations was 10 µl, while 50 µl was used for the high-level. Also, biological degradation rates are probably concentration dependent with low concentrations having a shorter half-life than high.

Study two results (Table 28) indicate that soil samples can be held for 48 hours at 4±2°C without a biological preservative. 73% or more of the analyte concentrations were retained after a two-day storage period without preservation. These findings corroborate other recent findings by Alan Hewitt of the U.S. Army Cold Regions Research and Engineering Laboratory. Recoveries of actual subsurface samples may be underestimated, since the soils used in this study were allowed to come in contact with oxygen for several weeks before being used. Studies using freshly exhumed soils should be conducted to determine if there is a necessary acclimation period for the soil bacteria.

Summary with suggested sampling protocol
Over the last few years there has been a lot of discussion regarding the implementation of SW846, Method 5035 for volatiles. Some laboratories and government agencies have been reluctant to implement since; there is both increased costs and new complexities in this procedure Vs the predecessor 5030. Laboratories must invest in new autosamplers which can cost between $20,000-$30,000 each. There are new problems in the field as well, sample takers either use a coring device to collect samples and than either transfer the sample to a 40 ml vial which contains a chemical preservative or they transport the sample in this coring device and than it is up to the laboratory to transfer the sample from the coring device to a 40 ml vial. The first option requires hazardous chemicals to be taken to the field, which is questionable under DOT regulations. The second option of using a coring/transport device typically adds $25-$30 to the cost of each sample. Using an empty VOC vial and an inexpensive coring tool addresses both DOT and cost concerns.

EPA method 5035 was developed to improve volatile data by reducing analyte losses caused by both volatilization and biological degradation. Study one has shown that those analyte losses due to volatilization can virtually be eliminated by using an empty VOC vial as a storage container. Study two indicates that losses due to biological degradation are less significant if samples are preserved within 48 hours. This means preservation can be delayed until back at the laboratory in an environment more conducive to precise measurement. Using the empty VOC vial procedure simplifies a rather complex method and could help facilitate the implementation of method 5035.

If the empty VOC vial option is used, here is U.S. Analytical's recommended sampling protocol. For each sampling point use three 40-ml vials, pre-tare two with stirring bars and one without. Collect 5 g. samples using the Easydraw™ syringe and Powerstop™ handle or equivalent and immediately transfer to the VOC vial. Cap the vials taking care not to get dirt on the threads. Place on ice and ship to the laboratory within 48 hours. Based on studies by Alan Hewitt, it is recommended that the laboratory immediately freeze the two samples with stirring bars and add 5 mls of methanol through the septum of the third. The laboratory has the choice of running either the methanol preserved sample first for medium to high-level contamination or risk gross instrument contamination and run a low-level sample. In either case the methanol-preserved sample is necessary for high level contamination since there is no way to dilute vials collected for low level analysis.

References:

1. U.S. Environmental Protection Agency (1986) Test Methods for Evaluating Solid Waste, Vol. 1B. SW-846.
2. Hewitt, A.D. (8/97) Biodegradation of Volatile Organic Compounds in Soil Samples. American Environmental Laboratory, Vol. 9, Number 7 Pages 1, 5-7.
3. Hewitt, A.D. Freezer Storage of Soil Samples Containing Volatile Organic Compounds. 15th Annual Waste Testing and Quality Assurance Symposium, July 18-22, 1999.

VOC STUDY RESULTS

Table 1

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	Absolute AVG.	Average % REC.	% RSD.
1	*	1,1,2-Trichloroethane	146	95	141	92	151	98	144	94	141	91	144	93.8	2.8
2	*	1,2,4-Trimethylbenzene	156	101	153	99	145	94	145	94	143	93	164	106.6	3.4
3	*	1,3,5-Trimethylbenzene	162	105	150	98	144	93	148	96	150	98	168	109.2	4.0
4	*	Benzene	156	101	154	100	147	95	148	96	149	97	151	97.9	2.5
5	*	Bromodichloromethane	161	105	160	104	150	98	151	98	148	96	154	99.9	4.0
6	*	Bromoform	149	97	151	98	129	84	143	93	136	88	142	92.1	6.5
7	*	Carbon Tetrachloride	186	121	183	119	176	114	173	112	172	112	178	115.5	3.4
8	*	Chloroform	181	117	168	109	167	108	171	111	170	111	171	111.2	3.2
9	*	cis - 1,3 - Dichloropropene	164	107	149	97	149	97	155	101	138	90	151	98.2	6.3
10	*	EDB (1,2-Dibromoethane)	148	96	157	102	140	91	145	94	143	93	146	95.2	4.6
11	*	Ethylbenzene	158	102	154	100	151	98	150	98	147	95	152	98.6	2.8
12	*	Methylene chloride	157	102	162	105	144	93	154	100	164	107	156	101.4	5.1
13	*	MTBE	166	108	167	109	153	99	154	100	153	99	159	103.1	4.5
14	*	m&p-Xylene	320	104	307	100	301	98	299	97	294	95	304	98.8	3.3
15	*	Naphthalene	131	85	127	83	116	75	126	82	116	75	123	80.0	5.7
16	*	o-Xylene	159	103	154	100	145	94	150	98	157	102	153	99.3	3.7
17	*	Styrene	149	97	149	97	144	94	146	95	146	95	147	95.4	1.5
18	*	Toluene	158	103	149	97	150	97	149	97	153	99	152	98.6	2.6
19	*	trans - 1,3 - Dichloropropene	168	109	168	109	158	103	158	103	157	102	162	105.2	3.5
20	*	Vinyl Chloride	135	88	138	90	124	81	128	83	141	92	133	86.6	5.3
21		1,1 - Dichloropropene	187	122	176	114	154	100	167	109	153	99	167	108.8	8.7
22		1,1-Dichloroethane	165	107	166	108	151	98	157	102	149	97	157	102.3	4.9
23		1,1-Dichloroethene	178	116	169	110	152	99	158	103	161	104	163	106.2	6.2
24		1,1,1-Trichloroethane	200	130	191	124	178	116	183	119	185	120	187	121.7	4.5
25		1,1,1,2 - Tetrachloroethane	152	99	149	97	143	93	156	101	150	98	150	97.5	3.2
26		1,1,2,2-Tetrachloroethane	141	92	150	98	133	86	147	95	131	85	140	91.2	6.0
27		1,2-Dibromo-3-Chloropropane	138	90	138	89	129	84	159	103	116	75	136	88.3	11.6
28		1,2-Dichlorobenzene	155	100	145	94	146	95	150	98	137	89	147	95.3	4.4
29		1,2-Dichloroethane	178	115	182	118	172	112	171	111	174	113	175	113.8	2.6
30		1,2-Dichloropropane	141	92	134	87	132	86	133	86	128	83	133	86.7	3.7
31		1,2,3 - Trichloropropane	127	83	147	96	142	92	141	92	141	92	140	90.8	5.4
32		1,2,3-Trichlorobenzene	137	89	140	91	114	74	126	82	123	80	128	83.1	8.2
33		1,2,4-Trichlorobenzene	137	89	135	88	116	75	128	83	108	70	125	81.0	10.1
34		1,3-Dichlorobenzene	149	97	149	97	145	94	142	92	144	93	146	94.7	2.1
35		1,3-Dichloropropane	149	97	148	96	148	96	146	95	145	94	147	95.4	1.0
36		1,4-Dichlorobenzene	142	92	142	92	139	90	145	94	137	89	141	91.4	2.3
37		2-Chlorotoluene	154	100	148	96	138	90	146	95	143	93	146	94.7	4.0
38		2,2-Dichloropropane	192	125	184	120	183	119	176	114	188	122	185	120.0	3.2
39		4-Chlorotoluene	162	105	153	99	151	98	155	100	147	95	153	99.5	3.6
40		Allyl Chloride	156	101	166	108	155	101	152	99	155	101	157	102.0	3.4
41		Bromobenzene	158	103	148	96	142	92	142	92	142	92	146	95.1	4.9
42		Bromochloromethane	169	110	190	124	162	105	155	101	158	103	167	108.5	8.4
43		Chlorobenzene	154	100	149	97	147	95	152	99	146	95	150	97.2	2.3
44		Chloroethane	190	124	179	116	180	117	176	114	189	123	183	118.7	3.6
45		Chloromethane	132	86	119	77	115	75	115	74	119	77	120	77.8	5.8
46		cis-1,2-Dichloroethene	162	105	151	98	147	95	160	104	160	104	156	101.2	4.4
47		Dibromochloromethane	145	94	147	95	148	96	139	90	148	96	145	94.2	2.6
48		Dibromomethane	168	109	157	102	160	104	161	105	154	100	160	104.0	3.3
49		Dichlorofluoromethane	214	139	205	133	223	145	199	129	207	135	210	136.3	4.4
50		Di-Isopropyl ether	150	98	148	96	143	93	142	92	141	92	145	94.1	2.7
51		Ethyl Ether	172	112	178	116	167	109	161	105	173	112	170	110.7	3.8
52		Hexachlorobutadiene	147	96	161	104	170	110	158	102	140	91	155	100.7	7.6
53		Isopropylbenzene	167	109	157	102	148	96	153	99	152	99	155	101.0	4.7
54		n-Butylbenzene	138	90	134	87	136	88	133	86	118	77	132	85.6	6.0
55		n-Propylbenzene	157	102	153	99	147	96	147	96	142	92	149	96.9	3.8
56		p-Isopropyltoluene	156	101	147	95	146	95	145	94	142	92	147	95.5	3.7
57		sec-Butylbenzene	152	99	154	100	143	93	143	93	137	89	146	94.8	4.8
58		tert-Butylbenzene	166	108	159	103	151	98	148	96	145	94	154	99.9	5.6
59		Tetrachloroethene	184	120	165	107	176	114	171	111	160	104	171	111.2	5.4
60		trans-1,2-Dichloroethene	177	115	157	102	155	100	143	93	152	99	156	101.7	7.9
61		Trichloroethene	149	97	144	93	144	94	151	98	157	102	149	96.8	3.7
62		Trichlorofluoromethane	197	128	209	136	185	120	189	123	180	117	192	124.6	5.8
63		Trichlorotrifluoroethane	154	100	164	107	142	92	161	105	142	92	153	99.2	6.8

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 2

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	143	93	147	96	144	93	148	96	137	89	144	99.5	3.0
2	*	1,2,4-Trimethylbenzene	143	93	142	92	148	96	146	95	142	92	144	97.1	1.9
3	*	1,3,5-Trimethylbenzene	147	96	147	96	144	93	146	95	143	93	145	96.5	1.3
4	*	Benzene	148	96	148	96	137	89	139	90	142	92	143	94.7	3.6
5	*	Bromodichloromethane	157	102	142	92	143	93	149	97	141	91	146	95.0	4.5
6	*	Bromoform	143	93	131	85	144	93	127	82	134	87	135	95.6	5.5
7	*	Carbon Tetrachloride	158	102	169	110	179	116	179	116	170	110	171	96.0	5.2
8	*	Chloroform	173	112	164	107	180	117	163	106	161	104	168	98.2	4.9
9	*	cis - 1,3 - Dichloropropene	144	93	141	92	148	96	149	97	146	95	145	96.2	2.1
10	*	EDB (1,2-Dibromoethane)	142	92	155	100	142	92	149	97	133	86	144	98.2	5.8
11	*	Ethylbenzene	149	97	150	98	151	98	146	95	145	94	148	97.6	1.8
12	*	Methylene chloride	154	100	152	99	153	99	157	102	157	102	155	99.1	1.6
13	*	MTBE	158	102	163	106	157	102	154	100	159	103	158	99.6	2.0
14	*	m&p-Xylene	299	97	293	95	295	96	281	91	289	94	291	95.8	2.4
15	*	Naphthalene	109	71	111	72	115	75	112	72	113	73	112	90.7	2.0
16	*	o-Xylene	145	94	157	102	150	97	143	93	148	96	148	97.2	3.7
17	*	Styrene	146	95	144	93	145	94	143	93	144	93	144	98.0	0.8
18	*	Toluene	149	97	146	95	144	94	151	98	143	93	146	96.5	2.3
19	*	trans - 1,3 - Dichloropropene	157	102	148	96	146	95	137	89	153	99	148	91.5	5.0
20	*	Vinyl Chloride	124	80	115	75	123	80	127	83	123	80	122	91.7	3.6
21		1,1 - Dichloropropene	153	99	146	95	152	99	151	98	153	99	151	90.1	1.9
22		1,1-Dichloroethane	154	100	150	98	150	98	154	100	145	94	151	95.7	2.4
23		1,1-Dichloroethene	144	93	159	103	149	97	152	99	161	104	153	93.5	4.6
24		1,1,1-Trichloroethane	170	111	185	120	183	119	177	115	174	113	178	94.9	3.5
25		1,1,1,2 - Tetrachloroethane	155	100	148	96	146	95	137	89	153	99	148	98.5	4.7
26		1,1,2,2-Tetrachloroethane	120	78	130	85	132	86	124	80	129	84	127	90.4	3.8
27		1,2-Dibromo-3-Chloropropane	129	84	127	83	136	88	121	78	131	85	129	94.7	4.3
28		1,2-Dichlorobenzene	144	94	144	93	141	92	141	91	143	93	142	97.1	1.1
29		1,2-Dichloroethane	167	108	172	112	169	110	178	116	168	109	171	97.5	2.6
30		1,2-Dichloropropane	127	82	124	81	135	88	125	81	123	80	127	95.0	3.8
31		1,2,3 - Trichloropropane	139	90	129	84	142	92	142	92	141	92	139	99.3	4.0
32		1,2,3-Trichlorobenzene	120	78	117	76	127	82	115	74	123	80	120	93.9	4.0
33		1,2,4-Trichlorobenzene	121	78	116	75	125	81	124	81	118	76	121	96.7	3.4
34		1,3-Dichlorobenzene	138	90	136	88	140	91	139	90	152	99	141	96.7	4.5
35		1,3-Dichloropropane	141	92	147	96	145	94	140	91	144	93	143	97.5	2.1
36		1,4-Dichlorobenzene	142	92	130	84	133	86	132	86	145	94	136	96.7	5.0
37		2-Chlorotoluene	142	92	143	93	141	92	135	88	141	91	140	96.3	2.2
38		2,2-Dichloropropane	156	101	169	110	162	105	151	98	154	100	158	85.5	4.5
39		4-Chlorotoluene	146	95	141	91	148	96	144	94	143	93	144	94.2	1.9
40		Allyl Chloride	145	94	157	102	145	94	144	93	148	96	148	94.1	3.7
41		Bromobenzene	146	95	141	91	142	92	135	88	141	91	141	96.2	2.8
42		Bromochloromethane	159	103	165	107	166	108	163	106	159	103	162	97.2	2.1
43		Chlorobenzene	149	97	147	95	147	95	145	94	138	89	145	96.9	2.9
44		Chloroethane	182	118	178	116	177	115	170	111	174	113	176	96.4	2.5
45		Chloromethane	109	71	114	74	106	69	116	75	105	68	110	91.5	4.4
46		cis-1,2-Dichloroethene	144	93	159	103	151	98	158	102	147	96	152	97.3	4.4
47		Dibromochloromethane	147	96	145	94	146	95	144	93	144	93	145	99.9	1.0
48		Dibromomethane	155	100	142	92	137	89	151	98	137	89	144	90.2	5.6
49		Dichlorofluoromethane	201	131	210	137	213	138	197	128	208	135	206	98.1	3.3
50		Di-Isopropyl ether	139	90	141	91	137	89	139	90	142	92	139	96.3	1.2
51		Ethyl Ether	156	101	163	106	160	104	165	107	163	106	161	94.7	2.1
52		Hexachlorobutadiene	142	92	150	98	150	97	139	90	150	97	146	94.2	3.7
53		Isopropylbenzene	148	96	142	92	149	97	144	94	144	94	145	93.5	2.1
54		n-Butylbenzene	132	86	122	79	130	85	123	80	123	80	126	95.5	3.9
55		n-Propylbenzene	139	90	137	89	142	92	139	90	139	90	139	93.2	1.2
56		p-Isopropyltoluene	139	90	135	87	144	93	137	89	137	89	138	93.9	2.5
57		sec-Butylbenzene	135	88	136	88	143	93	140	91	132	86	137	93.9	3.2
58		tert-Butylbenzene	149	97	150	97	149	97	147	95	143	93	147	95.8	1.8
59		Tetrachloroethene	157	102	152	99	155	101	151	98	149	97	153	89.2	2.2
60		trans-1,2-Dichloroethene	136	88	142	92	142	92	134	87	132	86	137	87.4	3.4
61		Trichloroethene	149	97	145	94	150	97	149	97	143	93	147	98.7	2.1
62		Trichlorofluoromethane	182	118	195	126	181	118	191	124	182	118	186	97.1	3.3
63		Trichlorotrifluoroethane	143	93	159	103	147	96	151	98	148	96	150	98.0	4.0

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 3

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	129	84	omitted		136	88	174	113	144	93	146	100.8	13.5
2	*	1,2,4-Trimethylbenzene	139	90	omitted		140	91	143	93	144	93	141	95.3	1.7
3	*	1,3,5-Trimethylbenzene	136	88	omitted		144	93	140	91	140	91	140	92.8	2.2
4	*	Benzene	132	86	omitted		143	93	147	96	143	93	141	93.7	4.5
5	*	Bromodichloromethane	151	98	omitted		143	93	136	88	154	100	146	94.7	5.6
6	*	Bromoform	129	84	omitted		133	86	138	89	154	100	138	97.5	8.1
7	*	Carbon Tetrachloride	160	104	omitted		166	108	174	113	179	116	169	95.3	4.9
8	*	Chloroform	164	106	omitted		158	103	169	110	177	115	167	97.5	4.9
9	*	cis - 1,3 - Dichloropropene	135	87	omitted		141	91	138	89	147	95	140	92.5	3.7
10	*	EDB (1,2-Dibromoethane)	158	103	omitted		137	89	137	89	147	95	144	98.6	7.1
11	*	Ethylbenzene	139	90	omitted		148	96	150	97	146	95	145	95.8	3.4
12	*	Methylene chloride	144	93	omitted		156	101	151	98	168	109	155	99.1	6.7
13	*	MTBE	144	94	omitted		154	100	155	101	162	105	154	97.0	4.8
14	*	m&p-Xylene	278	90	omitted		290	94	272	88	292	95	283	93.0	3.4
15	*	Naphthalene	106	69	omitted		113	73	109	71	119	77	111	90.5	5.0
16	*	o-Xylene	134	87	omitted		138	90	143	93	151	98	141	92.5	5.0
17	*	Styrene	138	90	omitted		147	95	141	92	144	94	142	97.0	2.6
18	*	Toluene	132	86	omitted		143	93	143	93	150	97	142	93.4	5.3
19	*	trans - 1,3 - Dichloropropene	128	83	omitted		141	91	149	97	139	90	139	85.8	6.4
20	*	Vinyl Chloride	105	68	omitted		119	77	131	85	125	81	120	90.1	9.3
21		1,1 - Dichloropropene	133	86	omitted		150	98	163	106	165	107	153	91.2	9.8
22		1,1-Dichloroethane	148	96	omitted		149	97	151	98	169	110	154	97.9	6.5
23		1,1-Dichloroethene	138	89	omitted		159	103	157	102	156	101	152	93.2	6.5
24		1,1,1-Trichloroethane	172	112	omitted		180	117	187	121	195	126	183	97.8	5.3
25		1,1,1,2 - Tetrachloroethane	139	90	omitted		151	98	156	101	144	94	147	98.1	5.1
26		1,1,2,2-Tetrachloroethane	127	83	omitted		130	85	118	76	138	89	128	91.3	6.5
27		1,2-Dibromo-3-Chloropropane	111	72	omitted		113	73	151	98	130	84	126	92.7	14.7
28		1,2-Dichlorobenzene	133	86	omitted		139	90	137	89	147	95	139	94.6	4.1
29		1,2-Dichloroethane	161	104	omitted		171	111	166	108	168	109	166	95.0	2.6
30		1,2-Dichloropropane	112	73	omitted		130	85	120	78	126	82	122	91.5	6.4
31		1,2,3 - Trichloropropane	124	81	omitted		145	94	138	90	133	86	135	96.6	6.4
32		1,2,3-Trichlorobenzene	122	79	omitted		123	80	109	71	134	87	122	95.4	8.4
33		1,2,4-Trichlorobenzene	117	76	omitted		120	78	121	78	127	82	121	97.0	3.4
34		1,3-Dichlorobenzene	134	87	omitted		140	91	137	89	142	92	138	94.8	2.3
35		1,3-Dichloropropane	129	84	omitted		143	93	135	87	146	95	138	94.1	5.6
36		1,4-Dichlorobenzene	128	83	omitted		133	86	131	85	135	88	131	93.4	2.4
37		2-Chlorotoluene	133	86	omitted		137	89	132	86	138	90	135	92.5	2.3
38		2,2-Dichloropropane	140	91	omitted		146	95	143	93	147	96	144	77.8	2.4
39		4-Chlorotoluene	135	88	omitted		141	92	137	89	146	95	140	91.2	3.3
40		Allyl Chloride	131	85	omitted		143	93	141	91	139	90	138	88.1	3.9
41		Bromobenzene	137	89	omitted		136	88	138	89	142	92	138	94.4	2.0
42		Bromochloromethane	147	95	omitted		156	101	166	108	180	117	162	97.1	8.7
43		Chlorobenzene	136	88	omitted		142	92	143	93	147	96	142	94.8	3.2
44		Chloroethane	166	108	omitted		179	116	201	131	173	112	179	98.2	8.6
45		Chloromethane	98	64	omitted		109	71	114	74	113	73	108	90.5	6.8
46		cis-1,2-Dichloroethene	142	92	omitted		144	93	153	99	166	108	151	96.9	7.3
47		Dibromochloromethane	137	89	omitted		145	94	138	89	147	96	142	97.7	3.5
48		Dibromomethane	136	88	omitted		147	96	147	96	149	97	145	90.4	4.0
49		Dichlorofluoromethane	190	123	omitted		212	138	218	142	211	137	207	98.9	6.0
50		Di-Isopropyl ether	126	82	omitted		138	89	137	89	147	95	137	94.4	6.1
51		Ethyl Ether	150	97	omitted		151	98	165	107	172	112	159	93.6	6.7
52		Hexachlorobutadiene	143	93	omitted		126	82	124	80	152	99	136	87.9	10.1
53		Isopropylbenzene	138	89	omitted		146	95	140	91	143	93	142	91.2	2.6
54		n-Butylbenzene	117	76	omitted		128	83	121	79	127	82	123	93.6	4.1
55		n-Propylbenzene	137	89	omitted		139	90	134	87	139	90	137	91.8	1.7
56		p-Isopropyltoluene	131	85	omitted		141	92	136	88	140	91	137	93.2	3.4
57		sec-Butylbenzene	129	84	omitted		138	90	135	88	134	87	134	91.9	2.8
58		tert-Butylbenzene	136	88	omitted		148	96	137	89	139	90	140	91.0	3.8
59		Tetrachloroethene	138	89	omitted		159	103	156	101	166	108	154	90.2	7.7
60		trans-1,2-Dichloroethene	119	77	omitted		137	89	135	88	158	102	137	87.7	11.5
61		Trichloroethene	142	92	omitted		146	95	165	107	162	105	153	103.0	7.4
62		Trichlorofluoromethane	178	115	omitted		175	114	212	138	177	115	185	96.6	9.5
63		Trichlorotrifluoroethane	120	78	omitted		126	82	170	111	150	97	141	92.5	16.4

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 4

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	150	98	150	98	136	88	144	94	149	97	146	101.0	4.1
2	*	1,2,4-Trimethylbenzene	135	88	142	92	136	88	141	91	150	98	141	95.1	4.2
3	*	1,3,5-Trimethylbenzene	143	93	145	94	142	92	136	88	145	94	142	94.4	2.6
4	*	Benzene	139	90	153	99	144	93	150	97	152	99	147	97.8	4.1
5	*	Bromodichloromethane	143	93	149	97	140	91	145	94	151	98	146	94.7	3.0
6	*	Bromoform	130	85	126	82	137	89	130	85	136	88	132	92.9	3.3
7	*	Carbon Tetrachloride	170	110	173	112	165	107	181	117	169	110	171	96.4	3.4
8	*	Chloroform	160	104	176	114	157	102	175	113	169	110	167	97.7	5.2
9	*	cis - 1,3 - Dichloropropene	140	91	142	92	130	84	140	91	137	89	138	91.1	3.5
10	*	EDB (1,2-Dibromoethane)	138	90	145	94	137	89	138	90	153	99	142	97.1	4.8
11	*	Ethylbenzene	146	95	145	94	141	91	142	92	154	100	145	95.7	3.5
12	*	Methylene chloride	136	88	145	94	146	95	144	93	148	96	144	92.2	3.2
13	*	MTBE	159	103	163	106	147	95	165	107	162	105	159	100.3	4.6
14	*	m&p-Xylene	292	95	289	94	283	92	287	93	313	102	293	96.3	4.0
15	*	Naphthalene	104	67	124	81	100	65	115	74	115	74	111	90.4	8.6
16	*	o-Xylene	142	92	139	90	141	91	147	95	149	97	143	93.8	3.0
17	*	Styrene	144	93	144	93	139	90	142	92	147	96	143	97.3	2.1
18	*	Toluene	147	95	145	94	147	96	146	95	158	102	148	97.8	3.5
19	*	trans - 1,3 - Dichloropropene	139	90	151	98	140	91	145	94	150	97	145	89.5	3.8
20	*	Vinyl Chloride	120	78	128	83	125	81	131	85	110	72	123	92.0	6.7
21		1,1 - Dichloropropene	144	94	151	98	164	107	150	97	158	102	153	91.5	5.0
22		1,1-Dichloroethane	148	96	154	100	147	95	161	104	164	106	154	98.2	4.9
23		1,1-Dichloroethene	155	101	156	101	160	104	145	94	160	104	155	95.0	4.0
24		1,1,1-Trichloroethane	181	118	188	122	176	114	177	115	177	115	180	96.0	2.8
25		1,1,1,2 - Tetrachloroethane	147	95	151	98	151	98	146	95	154	100	150	99.7	2.2
26		1,1,2,2-Tetrachloroethane	121	79	141	91	113	73	127	82	122	79	124	88.7	8.3
27		1,2-Dibromo-3-Chloropropane	106	69	122	79	116	75	143	93	111	72	120	88.0	12.0
28		1,2-Dichlorobenzene	140	91	142	92	136	88	138	89	140	91	139	94.9	1.7
29		1,2-Dichloroethane	164	107	175	114	173	112	170	111	182	118	173	98.7	3.8
30		1,2-Dichloropropane	124	81	143	93	120	78	126	82	139	90	130	97.7	7.6
31		1,2,3 - Trichloropropane	135	88	145	94	129	84	142	92	132	86	136	97.7	4.9
32		1,2,3-Trichlorobenzene	118	77	126	82	123	80	132	86	132	86	126	98.6	4.7
33		1,2,4-Trichlorobenzene	102	66	126	82	111	72	126	82	121	79	117	94.0	8.9
34		1,3-Dichlorobenzene	138	90	139	90	134	87	138	90	143	93	138	94.9	2.2
35		1,3-Dichloropropane	135	87	146	95	127	83	145	94	148	96	140	95.4	6.4
36		1,4-Dichlorobenzene	132	86	132	86	128	83	132	86	143	93	133	94.7	4.1
37		2-Chlorotoluene	133	86	137	89	131	85	136	88	144	93	136	93.3	3.6
38		2,2-Dichloropropane	161	105	147	95	145	94	140	91	146	95	148	79.8	5.4
39		4-Chlorotoluene	137	89	141	92	138	89	145	94	148	96	142	92.4	3.4
40		Allyl Chloride	138	89	145	94	134	87	144	94	151	98	142	90.6	4.7
41		Bromobenzene	142	92	143	93	135	88	137	89	138	90	139	95.1	2.4
42		Bromochloromethane	163	106	163	106	165	107	164	106	168	109	164	98.5	1.3
43		Chlorobenzene	146	95	143	93	141	91	147	95	147	95	145	96.7	1.8
44		Chloroethane	181	118	189	123	185	120	176	114	170	110	180	98.6	4.2
45		Chloromethane	109	71	117	76	113	73	118	76	116	75	114	95.5	3.2
46		cis-1,2-Dichloroethene	148	96	144	94	151	98	153	99	161	104	151	97.0	4.1
47		Dibromochloromethane	140	91	153	99	133	86	152	99	158	102	147	101.4	6.9
48		Dibromomethane	134	87	149	97	142	92	158	102	176	114	152	94.7	10.6
49		Dichlorofluoromethane	192	125	220	143	212	138	223	145	221	143	213	101.8	6.0
50		Di-Isopropyl ether	140	91	143	93	133	86	140	91	143	93	140	96.5	2.9
51		Ethyl Ether	140	91	171	111	165	107	161	104	170	110	161	94.5	7.8
52		Hexachlorobutadiene	136	88	137	89	135	88	135	88	132	86	135	87.1	1.5
53		Isopropylbenzene	143	93	141	92	145	94	142	92	147	96	144	92.4	1.6
54		n-Butylbenzene	115	75	118	77	120	78	122	79	126	82	120	91.2	3.3
55		n-Propylbenzene	136	88	136	88	133	86	139	90	143	93	137	92.1	2.7
56		p-Isopropyltoluene	130	84	134	87	134	87	140	91	149	97	137	93.5	5.5
57		sec-Butylbenzene	132	86	133	86	131	85	138	89	140	91	135	92.4	2.9
58		tert-Butylbenzene	142	92	143	93	142	92	146	95	151	98	144	93.9	2.7
59		Tetrachloroethene	155	101	158	102	145	94	146	95	153	99	151	88.5	3.7
60		trans-1,2-Dichloroethene	141	91	134	87	139	90	149	97	151	98	143	91.1	5.0
61		Trichloroethene	147	95	152	99	157	102	157	102	155	100	153	103.0	2.9
62		Trichlorofluoromethane	173	112	174	113	197	128	197	128	188	122	186	96.9	6.3
63		Trichlorotrifluoroethane	142	92	143	93	154	100	145	94	150	98	147	96.1	3.3

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 5

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	141	91	146	95	152	99	133	86	132	86	141	97.4	6.0
2	*	1,2,4-Trimethylbenzene	144	93	146	95	154	100	138	89	132	86	142	96.2	5.7
3	*	1,3,5-Trimethylbenzene	144	94	150	98	151	98	136	88	134	87	143	94.8	5.6
4	*	Benzene	145	94	143	93	153	99	133	86	127	82	140	93.0	7.3
5	*	Bromodichloromethane	134	87	139	90	155	101	122	79	134	87	137	88.8	8.9
6	*	Bromoform	128	83	126	82	136	88	121	78	126	82	127	89.7	4.3
7	*	Carbon Tetrachloride	138	90	145	94	158	103	129	84	140	91	142	79.8	7.6
8	*	Chloroform	148	96	148	96	160	104	138	90	143	93	147	86.0	5.4
9	*	cis - 1,3 - Dichloropropene	138	89	143	93	163	106	135	88	144	93	144	95.5	7.5
10	*	EDB (1,2-Dibromoethane)	134	87	141	92	154	100	136	88	140	91	141	96.2	5.7
11	*	Ethylbenzene	135	88	145	94	153	99	130	85	133	86	139	91.7	6.8
12	*	Methylene chloride	147	96	150	97	149	97	131	85	134	87	142	91.1	6.2
13	*	MTBE	149	97	152	99	157	102	135	88	134	87	145	91.5	7.1
14	*	m&p-Xylene	282	92	274	89	296	96	260	84	254	83	273	89.8	6.1
15	*	Naphthalene	127	82	127	82	121	78	123	80	111	72	121	98.6	5.4
16	*	o-Xylene	149	97	143	93	148	96	130	85	134	87	140	91.9	5.9
17	*	Styrene	137	89	135	88	142	92	132	86	127	82	134	91.4	4.2
18	*	Toluene	138	89	145	94	156	101	132	86	142	92	142	93.8	6.2
19	*	trans - 1,3 - Dichloropropene	140	91	144	93	157	102	133	86	137	89	142	87.6	6.4
20	*	Vinyl Chloride	124	80	128	83	126	82	104	68	108	70	118	88.5	9.4
21		1,1 - Dichloropropene	148	96	147	95	158	102	133	86	127	82	142	85.0	8.7
22		1,1-Dichloroethane	142	92	154	100	162	105	135	88	137	89	146	92.8	7.9
23		1,1-Dichloroethene	130	84	142	92	154	100	126	82	125	81	135	82.7	9.3
24		1,1,1-Trichloroethane	152	99	165	107	161	105	148	96	148	96	155	82.6	5.0
25		1,1,1,2 - Tetrachloroethane	143	93	146	95	162	105	139	90	135	88	145	96.5	7.0
26		1,1,2,2-Tetrachloroethane	132	86	121	78	137	89	119	77	112	73	124	88.4	8.1
27		1,2-Dibromo-3-Chloropropane	124	80	174	113	137	89	129	84	119	77	136	100.3	16.1
28		1,2-Dichlorobenzene	139	90	143	93	150	97	136	88	129	84	139	95.1	5.5
29		1,2-Dichloroethane	143	93	144	94	151	98	131	85	133	86	140	80.1	5.9
30		1,2-Dichloropropane	132	86	147	96	155	101	120	78	128	83	136	102.2	10.7
31		1,2,3 - Trichloropropane	154	100	138	90	149	97	143	93	127	83	142	101.7	7.3
32		1,2,3-Trichlorobenzene	132	86	136	88	137	89	130	85	125	81	132	103.1	3.6
33		1,2,4-Trichlorobenzene	121	79	132	86	135	88	124	80	117	76	126	100.7	6.1
34		1,3-Dichlorobenzene	135	87	134	87	144	93	127	83	127	82	133	91.3	5.2
35		1,3-Dichloropropane	150	98	141	92	152	99	128	83	137	89	141	96.3	6.9
36		1,4-Dichlorobenzene	128	83	128	83	137	89	128	83	120	78	128	91.0	4.6
37		2-Chlorotoluene	137	89	143	93	149	97	130	84	133	86	138	94.8	5.7
38		2,2-Dichloropropane	135	87	139	90	141	91	120	78	119	77	130	70.6	8.0
39		4-Chlorotoluene	139	90	138	90	152	99	134	87	139	90	140	91.6	4.9
40		Allyl Chloride	154	100	158	103	159	103	146	95	136	88	150	96.0	6.3
41		Bromobenzene	132	86	141	91	151	98	135	87	133	86	138	94.5	5.8
42		Bromochloromethane	141	92	158	102	162	105	128	83	129	84	143	86.0	10.9
43		Chlorobenzene	142	92	138	90	150	98	130	84	129	84	138	92.0	6.4
44		Chloroethane	123	80	141	92	144	94	131	85	128	83	133	72.9	6.8
45		Chloromethane	117	76	124	80	128	83	110	71	97	63	115	96.0	10.5
46		cis-1,2-Dichloroethene	150	97	148	96	157	102	129	84	135	87	143	92.1	8.0
47		Dibromochloromethane	138	90	136	88	151	98	131	85	127	83	136	94.1	6.6
48		Dibromomethane	147	96	156	101	160	104	137	89	140	91	148	92.3	6.6
49		Dichlorofluoromethane	148	96	156	101	168	109	150	97	153	99	95	83.6	8.4
50		Di-Isopropyl ether	145	94	148	96	151	98	130	85	130	85	155	73.8	5.2
51		Ethyl Ether	149	97	150	97	160	104	133	86	129	84	141	97.2	7.1
52		Hexachlorobutadiene	140	91	157	102	152	99	152	99	126	82	144	84.4	9.0
53		Isopropylbenzene	146	95	152	99	162	105	146	95	138	89	145	93.7	8.7
54		n-Butylbenzene	134	87	137	89	142	92	129	84	123	80	149	95.8	6.1
55		n-Propylbenzene	140	91	142	92	150	97	135	87	131	85	133	100.9	5.7
56		p-Isopropyltoluene	139	90	145	94	147	96	130	85	132	86	139	93.5	5.1
57		sec-Butylbenzene	142	92	148	96	152	99	139	90	135	88	139	94.3	5.5
58		tert-Butylbenzene	146	95	149	97	155	100	142	92	137	89	143	98.0	4.7
59		Tetrachloroethene	141	91	148	96	161	105	135	88	140	91	146	94.7	4.7
60		trans-1,2-Dichloroethene	131	85	141	92	148	96	116	75	121	78	145	84.7	7.0
61		Trichloroethene	158	103	161	104	175	113	141	91	155	100	131	83.8	10.4
62		Trichlorofluoromethane	118	77	137	89	154	100	127	82	138	89	158	105.8	7.7
63		Trichlorotrifluoroethane	124	81	130	85	148	96	128	83	126	82	135	70.2	10.0

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 6

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	135	87	143	93	135	88	148	96	150	98	142	98.3	5.0
2	*	1,2,4-Trimethylbenzene	140	91	136	88	132	86	132	86	141	92	136	91.9	3.2
3	*	1,3,5-Trimethylbenzene	139	90	135	88	130	84	134	87	141	91	136	90.1	3.2
4	*	Benzene	145	94	152	99	135	87	147	95	156	101	147	97.4	5.4
5	*	Bromodichloromethane	140	91	139	90	125	81	134	87	139	90	135	87.8	4.6
6	*	Bromoform	130	85	128	83	130	85	125	81	130	84	129	90.7	1.7
7	*	Carbon Tetrachloride	160	104	145	94	134	87	157	102	160	104	151	85.1	7.6
8	*	Chloroform	154	100	154	100	143	93	153	99	156	101	152	88.7	3.3
9	*	cis - 1,3 - Dichloropropene	138	89	141	92	130	84	135	88	143	93	137	90.9	3.9
10	*	EDB (1,2-Dibromoethane)	145	94	141	91	128	83	148	96	143	93	141	96.1	5.6
11	*	Ethylbenzene	143	93	138	90	130	85	139	90	142	92	138	91.2	3.7
12	*	Methylene chloride	151	98	149	97	133	86	144	93	150	98	145	93.0	5.2
13	*	MTBE	159	103	151	98	140	91	158	102	158	102	153	96.4	5.1
14	*	m&p-Xylene	281	91	269	87	254	83	262	85	280	91	269	88.5	4.3
15	*	Naphthalene	121	79	115	74	121	79	119	77	122	79	119	97.0	2.5
16	*	o-Xylene	144	94	140	91	128	83	138	90	140	91	138	90.4	4.3
17	*	Styrene	137	89	136	88	127	82	138	89	138	89	135	91.8	3.5
18	*	Toluene	148	96	147	95	137	89	151	98	148	96	146	96.1	3.8
19	*	trans - 1,3 - Dichloropropene	139	90	137	89	131	85	144	94	131	85	136	84.2	4.3
20	*	Vinyl Chloride	122	79	134	87	111	72	125	81	124	81	123	92.5	6.7
21		1,1 - Dichloropropene	154	100	153	99	138	89	158	103	163	106	153	91.3	6.2
22		1,1-Dichloroethane	150	98	153	99	139	90	150	98	159	103	150	95.4	4.7
23		1,1-Dichloroethene	159	103	141	92	138	90	148	96	143	93	146	89.2	5.7
24		1,1,1-Trichloroethane	165	107	166	108	148	96	169	110	170	111	164	87.3	5.4
25		1,1,1,2 - Tetrachloroethane	139	90	151	98	123	80	143	93	141	91	139	92.7	7.2
26		1,1,2,2-Tetrachloroethane	120	78	111	72	115	75	105	68	117	76	113	80.9	5.1
27		1,2-Dibromo-3-Chloropropane	148	96	108	70	124	81	153	99	152	99	137	100.7	14.8
28		1,2-Dichlorobenzene	137	89	135	88	130	85	138	89	138	90	136	92.5	2.4
29		1,2-Dichloroethane	150	98	158	102	145	94	153	99	158	102	153	87.1	3.6
30		1,2-Dichloropropane	141	92	140	91	123	80	144	93	136	88	137	102.5	5.9
31		1,2,3 - Trichloropropane	147	96	148	96	139	90	142	92	147	95	145	103.5	2.7
32		1,2,3-Trichlorobenzene	127	82	128	83	130	85	133	86	140	91	131	102.7	4.0
33		1,2,4-Trichlorobenzene	112	72	117	76	112	72	114	74	126	82	116	93.0	5.0
34		1,3-Dichlorobenzene	132	86	133	86	133	86	129	84	134	87	132	90.6	1.4
35		1,3-Dichloropropane	147	96	149	97	131	85	142	92	145	94	142	97.0	5.0
36		1,4-Dichlorobenzene	126	82	127	82	127	83	123	80	127	83	126	89.5	1.3
37		2-Chlorotoluene	138	90	137	89	127	82	136	88	139	90	135	92.8	3.7
38		2,2-Dichloropropane	137	89	138	90	126	82	138	90	129	84	133	72.1	4.4
39		4-Chlorotoluene	136	88	138	89	130	84	131	85	138	90	134	87.7	3.0
40		Allyl Chloride	149	97	159	103	132	86	153	99	161	105	151	96.0	7.7
41		Bromobenzene	141	91	137	89	126	82	127	83	141	91	134	91.7	5.5
42		Bromochloromethane	162	105	158	102	134	87	161	104	155	100	154	92.0	7.5
43		Chlorobenzene	138	90	142	92	124	80	134	87	142	92	136	90.9	5.7
44		Chloroethane	151	98	168	109	143	93	161	105	159	103	156	85.5	6.3
45		Chloromethane	127	83	121	78	108	70	118	76	130	84	121	100.7	7.0
46		cis-1,2-Dichloroethene	149	97	151	98	127	82	146	95	156	101	146	93.4	7.7
47		Dibromochloromethane	139	90	136	88	123	80	139	90	143	93	136	93.7	5.5
48		Dibromomethane	139	90	151	98	138	90	152	99	152	99	146	91.4	4.8
49		Dichlorofluoromethane	168	109	172	112	155	100	164	106	186	121	169	80.4	6.8
50		Di-Isopropyl ether	149	97	150	98	135	88	145	94	149	97	146	100.6	4.2
51		Ethyl Ether	165	107	160	104	142	92	162	105	156	101	157	92.1	5.8
52		Hexachlorobutadiene	140	91	127	83	156	101	137	89	147	95	141	91.1	7.6
53		Isopropylbenzene	150	97	148	96	141	92	140	91	148	96	145	93.5	3.0
54		n-Butylbenzene	130	84	121	79	120	78	123	80	129	84	125	94.6	3.6
55		n-Propylbenzene	141	91	138	90	134	87	136	88	141	91	138	92.4	2.1
56		p-Isopropyltoluene	137	89	138	90	136	88	131	85	141	91	136	92.8	2.7
57		sec-Butylbenzene	145	94	140	91	138	89	139	90	143	93	141	96.5	2.1
58		tert-Butylbenzene	152	99	147	96	145	94	141	92	151	98	147	95.6	2.9
59		Tetrachloroethene	144	94	144	94	133	86	142	92	145	94	142	82.8	3.5
60		trans-1,2-Dichloroethene	136	88	132	86	124	80	146	95	140	91	136	86.6	6.3
61		Trichloroethene	161	105	172	112	146	95	169	110	175	114	164	110.4	7.2
62		Trichlorofluoromethane	146	95	157	102	144	94	152	99	149	97	149	77.9	3.4
63		Trichlorotrifluoroethane	141	91	138	90	119	77	151	98	142	92	138	90.4	8.5

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 7

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	0 Hour Absol.	Rec. %	0 Hour Absol.	Rec. %	0 Hour Absol.	Rec. %	0 Hour Absol.	Rec. %	0 Hour Absol.	Rec. %	Absolute AVG.	Average % REC.	% RSD.
1	*	1,1,2-Trichloroethane	772	100	774	101	812	106	745	97	777	101	776	100.8	3.1
2	*	1,2,4-Trimethylbenzene	734	95	771	100	767	100	720	94	758	98	750	97.5	2.9
3	*	1,3,5-Trimethylbenzene	742	96	767	100	766	100	723	94	769	100	753	97.9	2.7
4	*	Benzene	762	99	772	100	776	101	729	95	766	100	761	98.9	2.5
5	*	Bromodichloromethane	819	106	810	105	842	109	795	103	827	107	818	106.4	2.2
6	*	Bromoform	674	88	692	90	727	95	675	88	683	89	690	89.7	3.2
7	*	Carbon Tetrachloride	876	114	840	109	867	113	829	108	873	113	857	111.4	2.5
8	*	Chloroform	844	110	853	111	863	112	812	105	864	112	847	110.1	2.5
9	*	cis - 1,3 - Dichloropropene	792	103	805	105	826	107	769	100	781	102	795	103.3	2.8
10	*	EDB (1,2-Dibromoethane)	818	106	821	107	826	107	776	101	824	107	813	105.7	2.6
11	*	Ethylbenzene	781	102	774	101	798	104	734	95	790	103	775	100.8	3.2
12	*	Methylene chloride	788	102	780	101	807	105	752	98	787	102	782	101.7	2.5
13	*	MTBE	817	106	796	103	826	107	770	100	810	105	803	104.4	2.7
14	*	m&p-Xylene	1503	98	1524	99	1568	102	1465	95	1555	101	1523	99.0	2.7
15	*	Naphthalene	689	90	689	90	718	93	659	86	709	92	693	90.0	3.3
16	*	o-Xylene	758	99	780	101	790	103	737	96	777	101	768	99.9	2.7
17	*	Styrene	764	99	776	101	773	100	732	95	779	101	765	99.4	2.5
18	*	Toluene	768	100	791	103	802	104	731	95	783	102	775	100.7	3.6
19	*	trans - 1,3 - Dichloropropene	802	104	814	106	818	106	774	101	811	105	804	104.5	2.2
20	*	Vinyl Chloride	681	89	673	87	678	88	664	86	681	88	675	87.8	1.1
21		1,1 - Dichloropropene	822	107	821	107	832	108	779	101	823	107	815	106.0	2.6
22		1,1-Dichloroethane	829	108	813	106	830	108	790	103	814	106	815	105.9	2.0
23		1,1-Dichloroethene	768	100	784	102	784	102	779	101	810	105	785	102.0	2.0
24		1,1,1-Trichloroethane	874	114	886	115	895	116	843	110	885	115	876	113.9	2.3
25		1,1,1,2 - Tetrachloroethane	805	105	828	108	842	109	786	102	842	109	820	106.6	3.0
26		1,1,2,2-Tetrachloroethane	542	70	642	83	576	75	541	70	578	75	576	74.8	7.1
27		1,2-Dibromo-3-Chloropropane	788	102	823	107	811	105	782	102	810	105	803	104.4	2.1
28		1,2-Dichlorobenzene	702	91	725	94	728	95	688	89	709	92	710	92.3	2.3
29		1,2-Dichloroethane	846	110	842	109	870	113	796	103	858	111	842	109.5	3.3
30		1,2-Dichloropropane	735	96	760	99	752	98	714	93	746	97	741	96.4	2.4
31		1,2,3 - Trichloropropane	738	96	769	100	737	96	694	90	757	98	739	96.0	3.9
32		1,2,3-Trichlorobenzene	735	96	773	100	745	97	693	90	748	97	739	96.0	4.0
33		1,2,4-Trichlorobenzene	696	90	736	96	724	94	672	87	719	93	709	92.2	3.6
34		1,3-Dichlorobenzene	703	91	715	93	722	94	670	87	722	94	706	91.8	3.1
35		1,3-Dichloropropane	766	100	786	102	775	101	740	96	783	102	770	100.1	2.4
36		1,4-Dichlorobenzene	696	90	710	92	702	91	659	86	696	90	692	90.0	2.9
37		2-Chlorotoluene	703	91	722	94	721	94	679	88	724	94	710	92.2	2.7
38		2,2-Dichloropropane	686	89	672	87	686	89	618	80	659	86	664	86.3	4.3
39		4-Chlorotoluene	745	97	755	98	754	98	720	94	749	97	744	96.8	1.9
40		Allyl Chloride	649	84	652	85	641	83	615	80	651	85	641	83.4	2.4
41		Bromobenzene	697	91	732	95	738	96	676	88	744	97	717	93.2	4.1
42		Bromochloromethane	883	115	893	116	901	117	838	109	906	118	884	114.9	3.1
43		Chlorobenzene	761	99	765	99	790	103	727	95	771	100	763	99.1	3.0
44		Chloroethane	791	103	768	100	779	101	778	101	765	99	776	100.9	1.3
45		Chloromethane	631	82	628	82	641	83	610	79	629	82	628	81.6	1.8
46		cis-1,2-Dichloroethene	789	103	818	106	818	106	772	100	817	106	803	104.3	2.6
47		Dibromochloromethane	821	107	872	113	890	116	813	106	856	111	850	110.5	3.9
48		Dibromomethane	853	111	841	109	849	110	827	107	836	109	841	109.3	1.2
49		Dichlorofluoromethane	841	109	845	110	861	112	837	109	852	111	847	110.1	1.1
50		Di-Isopropyl ether	758	99	767	100	770	100	733	95	768	100	759	98.6	2.0
51		Ethyl Ether	823	107	844	110	854	111	805	105	768	100	818	106.4	4.2
52		Hexachlorobutadiene	724	94	738	96	766	100	706	92	728	95	732	95.2	3.0
53		Isopropylbenzene	770	100	784	102	787	102	742	96	788	102	774	100.6	2.5
54		n-Butylbenzene	714	93	732	95	740	96	678	88	712	93	715	93.0	3.4
55		n-Propylbenzene	734	95	755	98	751	98	709	92	755	98	740	96.3	2.7
56		p-Isopropyltoluene	750	97	762	99	772	100	720	94	757	98	752	97.7	2.6
57		sec-Butylbenzene	740	96	761	99	774	101	720	94	761	99	751	97.6	2.8
58		tert-Butylbenzene	767	100	795	103	790	103	740	96	784	102	775	100.8	2.9
59		Tetrachloroethene	814	106	827	107	827	108	774	101	817	106	812	105.5	2.7
60		trans-1,2-Dichloroethene	777	101	803	104	843	110	758	99	823	107	801	104.1	4.3
61		Trichloroethene	967	126	893	116	953	124	914	119	948	123	935	121.5	3.3
62		Trichlorofluoromethane	773	100	723	94	792	103	760	99	774	101	764	99.3	3.4
63		Trichlorotrifluoroethane	664	86	649	84	723	94	685	89	682	89	680	88.4	4.1

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 8

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	24 Hour Absol.	Rec. %	24 Hour Absol.	Rec. %	24 Hour Absol.	Rec. %	24 Hour Absol.	Rec. %	24 Hour Absol.	Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	745	97	741	96	728	95	746	97	743	743	740.4	95.4	1.0
2	*	1,2,4-Trimethylbenzene	731	95	715	93	720	94	707	92	733	733	721.1	96.2	1.5
3	*	1,3,5-Trimethylbenzene	708	92	719	93	721	94	729	95	739	739	722.9	96.0	1.6
4	*	Benzene	715	93	712	92	602	78	704	92	722	722	690.7	90.8	7.2
5	*	Bromodichloromethane	797	104	793	103	754	98	817	106	803	803	792.4	96.8	3.0
6	*	Bromoform	649	84	703	91	660	86	682	89	668	668	672.3	97.4	3.1
7	*	Carbon Tetrachloride	878	114	888	115	695	90	859	112	843	843	832.5	97.2	9.5
8	*	Chloroform	815	106	824	107	716	93	819	106	841	841	802.9	94.8	6.2
9	*	cis - 1,3 - Dichloropropene	799	104	758	98	801	104	789	103	745	745	778.1	97.9	3.3
10	*	EDB (1,2-Dibromoethane)	756	98	749	97	732	95	761	99	765	765	752.3	92.6	1.7
11	*	Ethylbenzene	744	97	740	96	709	92	707	92	744	744	728.6	94.0	2.6
12	*	Methylene chloride	714	93	759	99	564	73	711	92	749	749	699.2	89.4	11.3
13	*	MTBE	762	99	779	101	624	81	759	99	780	780	740.7	92.2	8.9
14	*	m&p-Xylene	1492	97	1481	96	1432	93	1408	92	1460	95	1454.2	95.5	2.4
15	*	Naphthalene	643	84	686	89	678	88	614	80	682	682	660.4	95.4	4.7
16	*	o-Xylene	744	97	735	96	724	94	693	90	739	739	726.8	94.6	2.8
17	*	Styrene	700	91	741	96	711	92	725	94	711	711	717.3	93.8	2.2
18	*	Toluene	729	95	730	95	681	89	738	96	735	735	722.5	93.3	3.3
19	*	trans - 1,3 - Dichloropropene	818	106	794	103	795	103	802	104	781	781	797.7	99.3	1.7
20	*	Vinyl Chloride	617	80	629	82	363	47	620	81	613	613	568.3	84.2	20.2
21		1,1 - Dichloropropene	750	97	779	101	757	98	765	99	737	737	757.2	92.9	2.1
22		1,1-Dichloroethane	770	100	783	102	614	80	747	97	780	780	738.5	90.6	9.7
23		1,1-Dichloroethene	746	97	741	96	508	66	723	94	749	749	693.1	88.3	15.0
24		1,1,1-Trichloroethane	876	114	869	113	723	94	845	110	875	875	837.3	95.5	7.8
25		1,1,1,2 - Tetrachloroethane	781	101	782	102	781	101	807	105	757	757	781.2	95.3	2.3
26		1,1,2,2-Tetrachloroethane	633	82	685	89	622	81	628	82	641	641	641.5	111.5	3.9
27		1,2-Dibromo-3-Chloropropane	739	96	843	110	721	94	786	102	774	774	772.4	96.2	6.1
28		1,2-Dichlorobenzene	692	90	697	91	702	91	676	88	687	687	690.4	97.2	1.4
29		1,2-Dichloroethane	804	105	810	105	728	95	802	104	830	830	794.6	94.3	4.9
30		1,2-Dichloropropane	701	91	694	90	636	83	696	90	697	697	684.6	92.4	4.0
31		1,2,3 - Trichloropropane	665	86	703	91	676	88	703	91	686	686	686.3	92.9	2.4
32		1,2,3-Trichlorobenzene	709	92	729	95	740	96	697	91	740	740	722.9	97.9	2.7
33		1,2,4-Trichlorobenzene	697	91	704	92	717	93	679	88	733	733	705.6	99.5	2.9
34		1,3-Dichlorobenzene	681	89	691	90	691	90	677	88	683	683	684.5	96.9	0.9
35		1,3-Dichloropropane	713	93	747	97	705	92	719	93	729	729	722.4	93.8	2.2
36		1,4-Dichlorobenzene	665	86	677	88	683	89	659	86	679	679	672.4	97.1	1.5
37		2-Chlorotoluene	683	89	683	89	680	88	682	89	690	690	683.5	96.3	0.6
38		2,2-Dichloropropane	805	105	795	103	626	81	744	97	740	740	741.8	111.7	9.6
39		4-Chlorotoluene	715	93	716	93	710	92	703	91	722	722	713	95.8	1.0
40		Allyl Chloride	602	78	624	81	588	76	609	79	584	584	601.1	93.7	2.7
41		Bromobenzene	687	89	694	90	681	88	671	87	701	701	686.6	95.7	1.7
42		Bromochloromethane	784	102	829	108	803	104	831	108	777	777	804.6	91.0	3.1
43		Chlorobenzene	742	96	726	94	710	92	721	94	735	735	726.6	95.3	1.7
44		Chloroethane	723	94	710	92	467	61	760	99	716	716	674.9	87.0	17.5
45		Chloromethane	531	69	534	69	313	41	534	69	552	552	492.6	78.5	20.5
46		cis-1,2-Dichloroethene	762	99	770	100	644	84	745	97	770	770	738.1	92.0	7.3
47		Dibromochloromethane	841	109	842	109	837	109	835	109	852	852	841.2	99.0	0.8
48		Dibromomethane	824	107	781	101	807	105	826	107	766	766	800.6	95.2	3.3
49		Dichlorofluoromethane	854	111	842	109	819	106	857	111	800	800	834	98.5	2.9
50		Di-Isopropyl ether	717	93	722	94	620	81	699	91	714	714	694.2	91.5	6.1
51		Ethyl Ether	781	102	798	104	773	100	825	107	736	736	782.5	95.6	4.2
52		Hexachlorobutadiene	747	97	807	105	758	98	738	96	718	718	753.4	102.9	4.4
53		Isopropylbenzene	738	96	740	96	724	94	728	95	752	752	736	95.1	1.5
54		n-Butylbenzene	710	92	709	92	700	91	679	88	715	715	702.3	98.2	2.0
55		n-Propylbenzene	697	91	708	92	711	92	701	91	717	717	706.5	95.4	1.2
56		p-Isopropyltoluene	732	95	743	97	740	96	721	94	744	744	735.9	97.9	1.3
57		sec-Butylbenzene	727	94	746	97	723	94	710	92	731	731	727	96.8	1.8
58		tert-Butylbenzene	747	97	749	97	740	96	734	95	752	752	744.3	96.0	1.0
59		Tetrachloroethene	775	101	771	100	708	92	797	104	756	756	761	93.8	4.4
60		trans-1,2-Dichloroethene	742	96	734	95	567	74	708	92	740	740	698	87.2	10.7
61		Trichloroethene	806	105	801	104	742	96	847	110	816	816	802.2	85.8	4.8
62		Trichlorofluoromethane	825	107	836	109	495	64	795	103	785	785	747	97.7	19.1
63		Trichlorotrifluoroethane	644	84	666	87	680	88	666	87	617	617	654.3	96.2	3.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 9

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	48 Hour Absol.	Rec. %	48 Hour Absol.	Rec. %	48 Hour Absol.	Rec. %	48 Hour Absol.	Rec. %	48 Hour Absol.	Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	730	95	744	97	751	98	757	98	712	93	739	95.2	2.4
2	*	1,2,4-Trimethylbenzene	711	92	726	94	723	751	727	94	690	90	715	95.4	2.2
3	*	1,3,5-Trimethylbenzene	727	95	730	95	715	93	729	95	708	92	722	95.8	1.3
4	*	Benzene	691	90	708	92	701	91	703	91	673	87	695	91.4	2.0
5	*	Bromodichloromethane	821	107	784	102	835	109	813	106	754	98	801	97.9	4.0
6	*	Bromoform	649	84	703	91	660	86	682	89	668	87	672	97.4	3.1
7	*	Carbon Tetrachloride	825	107	849	110	821	107	885	115	803	104	836	97.6	3.8
8	*	Chloroform	812	106	824	107	802	104	806	105	801	104	809	95.5	1.1
9	*	cis - 1,3 - Dichloropropene	799	104	758	98	801	104	789	103	745	97	778	97.9	3.3
10	*	EDB (1,2-Dibromoethane)	762	99	788	102	760	99	766	100	730	95	761	93.7	2.7
11	*	Ethylbenzene	726	94	742	96	718	93	748	97	709	92	728	93.9	2.2
12	*	Methylene chloride	720	94	753	98	710	92	737	96	691	90	722	92.3	3.3
13	*	MTBE	749	97	776	101	725	94	781	102	750	97	756	94.1	3.0
14	*	m&p-Xylene	1395	91	1466	95	1419	92	1452	94	1430	93	1432	94.1	2.0
15	*	Naphthalene	638	83	684	89	644	84	672	87	650	85	657	94.9	3.0
16	*	o-Xylene	704	91	744	97	718	93	737	96	706	92	722	93.9	2.5
17	*	Styrene	700	91	741	96	711	92	725	94	711	92	717	93.8	2.2
18	*	Toluene	731	95	729	95	731	95	745	97	699	91	727	93.8	2.3
19	*	trans - 1,3 - Dichloropropene	818	106	794	103	795	103	802	104	781	102	798	99.3	1.7
20	*	Vinyl Chloride	588	76	582	76	571	74	620	81	545	71	581	86.0	4.7
21		1,1 - Dichloropropene	750	97	779	101	757	98	765	99	737	96	757	92.9	2.1
22		1,1-Dichloroethane	758	98	768	100	746	97	764	99	738	96	754	92.6	1.7
23		1,1-Dichloroethene	720	94	702	91	712	93	732	95	658	85	704	89.8	4.0
24		1,1,1-Trichloroethane	829	108	842	109	844	110	865	112	826	107	841	96.0	1.8
25		1,1,1,2 - Tetrachloroethane	781	101	782	102	781	101	807	105	757	98	781	95.3	2.3
26		1,1,2,2-Tetrachloroethane	676	88	743	97	690	90	762	99	680	88	710	123.3	5.6
27		1,2-Dibromo-3-Chloropropane	696	90	754	98	702	91	771	100	737	96	732	91.2	4.5
28		1,2-Dichlorobenzene	670	87	668	87	683	89	668	87	648	84	667	94.0	1.8
29		1,2-Dichloroethane	807	105	799	104	785	102	822	107	775	101	797	94.7	2.3
30		1,2-Dichloropropane	714	93	675	88	702	91	702	91	663	86	691	93.2	3.1
31		1,2,3 - Trichloropropane	665	86	703	91	676	88	703	91	686	89	686	92.9	2.4
32		1,2,3-Trichlorobenzene	719	93	731	95	718	93	725	94	709	92	720	97.5	1.1
33		1,2,4-Trichlorobenzene	707	92	692	90	678	88	695	90	686	89	691	97.5	1.6
34		1,3-Dichlorobenzene	668	87	667	87	681	89	676	88	659	86	670	94.9	1.3
35		1,3-Dichloropropane	741	96	745	97	729	95	743	97	696	90	731	94.9	2.8
36		1,4-Dichlorobenzene	654	85	663	86	648	84	660	86	642	83	653	94.3	1.3
37		2-Chlorotoluene	659	86	676	88	688	89	682	89	652	85	671	94.6	2.3
38		2,2-Dichloropropane	800	104	793	103	780	101	787	102	731	95	778	117.1	3.5
39		4-Chlorotoluene	699	91	715	93	702	91	713	93	694	90	704	94.6	1.3
40		Allyl Chloride	602	78	624	81	588	76	609	79	584	76	601	93.7	2.7
41		Bromobenzene	673	87	680	88	685	89	697	91	664	86	680	94.8	1.8
42		Bromochloromethane	784	102	829	108	803	104	831	108	777	101	805	91.0	3.1
43		Chlorobenzene	712	92	730	95	712	93	731	95	706	92	718	94.2	1.6
44		Chloroethane	743	97	738	96	736	96	749	97	684	89	730	94.1	3.6
45		Chloromethane	529	69	543	71	521	68	561	73	506	66	532	84.7	3.9
46		cis-1,2-Dichloroethene	734	95	768	100	739	96	765	99	722	94	745	92.9	2.7
47		Dibromochloromethane	838	109	820	107	840	109	868	113	790	103	831	97.8	3.5
48		Dibromomethane	824	107	781	101	807	105	826	107	766	100	801	95.2	3.3
49		Dichlorofluoromethane	854	111	842	109	819	106	857	111	800	104	834	98.5	2.9
50		Di-Isopropyl ether	712	92	701	91	697	91	704	92	685	89	700	92.2	1.4
51		Ethyl Ether	781	102	798	104	773	100	825	107	736	96	783	95.6	4.2
52		Hexachlorobutadiene	727	95	729	95	729	95	693	90	719	93	719	98.2	2.1
53		Isopropylbenzene	731	95	738	96	734	95	747	97	709	92	732	94.5	1.9
54		n-Butylbenzene	695	90	688	89	692	90	692	90	678	88	689	96.3	0.9
55		n-Propylbenzene	686	89	699	91	708	92	705	92	676	88	694	93.8	1.9
56		p-Isopropyltoluene	713	93	727	94	730	95	725	94	695	90	718	95.5	2.0
57		sec-Butylbenzene	710	92	716	93	707	92	724	94	694	90	710	94.5	1.6
58		tert-Butylbenzene	714	93	737	96	729	95	736	96	692	90	721	93.1	2.6
59		Tetrachloroethene	776	101	798	104	795	103	794	103	727	94	778	95.8	3.8
60		trans-1,2-Dichloroethene	721	94	733	95	715	93	710	92	710	92	718	89.6	1.4
61		Trichloroethene	784	102	714	93	747	97	731	95	723	94	739	79.1	3.7
62		Trichlorofluoromethane	752	98	715	93	745	97	780	101	692	90	737	96.4	4.6
63		Trichlorotrifluoroethane	644	84	666	87	680	88	666	87	617	80	654	96.2	3.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 10

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	781	101	713	93	730	98	747	97	759	99	746	96.1	3.5
2	*	1,2,4-Trimethylbenzene	728	95	710	92	711	751	709	92	722	94	716	95.5	1.2
3	*	1,3,5-Trimethylbenzene	744	97	718	93	713	93	715	93	723	94	722	95.9	1.8
4	*	Benzene	717	93	695	90	711	92	683	89	712	92	703	92.5	2.0
5	*	Bromodichloromethane	849	110	758	98	833	108	803	104	816	106	812	99.2	4.3
6	*	Bromoform	684	89	669	87	668	87	677	88	719	93	683	99.0	3.0
7	*	Carbon Tetrachloride	882	115	836	109	844	110	833	108	889	116	857	100.0	3.1
8	*	Chloroform	838	109	801	104	843	110	803	104	844	110	826	97.5	2.6
9	*	cis - 1,3 - Dichloropropene	823	107	743	97	788	102	770	100	785	102	782	98.4	3.7
10	*	EDB (1,2-Dibromoethane)	775	101	742	96	760	99	774	101	764	99	763	93.8	1.8
11	*	Ethylbenzene	741	96	719	93	735	95	722	94	756	98	734	94.7	2.0
12	*	Methylene chloride	723	94	696	90	721	94	709	92	725	94	714	91.3	1.7
13	*	MTBE	782	102	762	99	754	98	759	99	793	103	770	95.8	2.2
14	*	m&p-Xylene	1457	95	1422	92	1456	95	1417	92	1509	98	1452	95.4	2.5
15	*	Naphthalene	653	85	666	87	618	80	655	85	703	91	659	95.1	4.6
16	*	o-Xylene	748	97	711	92	722	94	711	92	764	99	731	95.1	3.3
17	*	Styrene	711	92	711	92	728	95	700	91	759	99	722	94.4	3.2
18	*	Toluene	746	97	710	92	744	97	718	93	752	98	734	94.7	2.5
19	*	trans - 1,3 - Dichloropropene	820	107	751	98	799	104	779	101	792	103	788	98.1	3.3
20	*	Vinyl Chloride	611	79	598	78	612	80	560	73	606	79	597	88.4	3.6
21		1,1 - Dichloropropene	806	105	773	100	772	100	740	96	759	99	770	94.5	3.1
22		1,1-Dichloroethane	773	100	743	97	772	100	749	97	786	102	765	93.8	2.4
23		1,1-Dichloroethene	778	101	726	94	747	97	696	90	706	92	731	93.1	4.5
24		1,1,1-Trichloroethane	886	115	840	109	879	114	840	109	892	116	867	99.0	2.9
25		1,1,1,2 - Tetrachloroethane	798	104	756	98	813	106	774	101	798	104	788	96.0	2.9
26		1,1,2,2-Tetrachloroethane	696	90	740	96	667	87	666	87	702	91	694	120.5	4.4
27		1,2-Dibromo-3-Chloropropane	725	94	771	100	748	97	743	97	770	100	751	93.6	2.6
28		1,2-Dichlorobenzene	682	89	677	88	687	89	665	86	697	91	681	95.9	1.8
29		1,2-Dichloroethane	811	105	793	103	815	106	811	105	825	107	811	96.3	1.4
30		1,2-Dichloropropane	737	96	654	85	700	91	690	90	688	89	693	93.6	4.3
31		1,2,3 - Trichloropropane	675	88	710	92	660	86	693	90	720	94	691	93.6	3.6
32		1,2,3-Trichlorobenzene	712	93	710	92	682	89	703	91	746	97	711	96.2	3.2
33		1,2,4-Trichlorobenzene	702	91	674	88	685	89	699	91	712	92	694	97.9	2.1
34		1,3-Dichlorobenzene	682	89	672	87	675	88	663	86	686	89	675	95.6	1.3
35		1,3-Dichloropropane	754	98	715	93	747	97	717	93	753	98	737	95.8	2.6
36		1,4-Dichlorobenzene	665	86	661	86	668	87	656	85	679	88	666	96.1	1.3
37		2-Chlorotoluene	689	90	673	87	667	87	674	88	677	88	676	95.3	1.2
38		2,2-Dichloropropane	769	100	734	95	734	95	698	91	739	96	734	110.6	3.5
39		4-Chlorotoluene	718	93	707	92	717	93	719	93	716	93	715	96.1	0.7
40		Allyl Chloride	605	79	604	78	605	79	588	76	634	82	607	94.6	2.8
41		Bromobenzene	695	90	700	91	687	89	717	93	683	89	696	97.1	1.9
42		Bromochloromethane	836	109	795	103	831	108	818	106	855	111	827	93.5	2.7
43		Chlorobenzene	740	96	699	91	721	94	712	93	744	97	723	94.8	2.6
44		Chloroethane	767	100	715	93	747	97	745	97	771	100	749	96.5	3.0
45		Chloromethane	523	68	536	70	512	67	529	69	524	68	525	83.6	1.6
46		cis-1,2-Dichloroethene	767	100	743	97	762	99	754	98	784	102	762	94.9	2.0
47		Dibromochloromethane	866	113	814	106	842	109	832	108	861	112	843	99.1	2.5
48		Dibromomethane	832	108	764	99	825	107	782	102	840	109	808	96.2	4.2
49		Dichlorofluoromethane	871	113	836	109	864	112	837	109	871	113	856	101.1	2.1
50		Di-Isopropyl ether	726	94	685	89	716	93	697	91	727	94	710	93.6	2.6
51		Ethyl Ether	793	103	771	100	787	102	784	102	809	105	789	96.3	1.8
52		Hexachlorobutadiene	751	98	714	93	715	93	706	92	736	96	724	98.9	2.5
53		Isopropylbenzene	749	97	732	95	742	96	737	96	726	94	737	95.2	1.2
54		n-Butylbenzene	712	92	685	89	684	89	690	90	698	91	693	97.0	1.7
55		n-Propylbenzene	720	94	696	90	706	92	703	91	700	91	705	95.2	1.3
56		p-Isopropyltoluene	743	97	738	96	725	94	720	94	746	97	734	97.6	1.5
57		sec-Butylbenzene	734	95	722	94	703	91	712	93	727	95	720	95.8	1.7
58		tert-Butylbenzene	764	99	743	97	728	95	722	94	736	96	738	95.3	2.2
59		Tetrachloroethene	808	105	747	97	794	103	781	102	817	106	789	97.2	3.4
60		trans-1,2-Dichloroethene	732	95	689	90	736	96	753	98	741	96	730	91.2	3.3
61		Trichloroethene	808	105	686	89	801	104	788	102	782	102	773	82.7	6.4
62		Trichlorofluoromethane	856	111	794	103	809	105	770	100	788	102	803	105.1	4.1
63		Trichlorotrifluoroethane	757	98	711	92	718	93	663	86	704	91	710	104.4	4.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 11

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	7 Day Absol.	Rec. %	7 Day Absol.	Rec. %	7 Day Absol.	Rec. %	7 Day Absol.	Rec. %	7 Day Absol.	Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	650	85	729	95	702	98	699	91	739	96	704	90.7	4.9
2	*	1,2,4-Trimethylbenzene	604	78	724	94	661	751	695	90	712	92	679	90.5	7.1
3	*	1,3,5-Trimethylbenzene	611	79	731	95	661	86	690	90	713	93	681	90.4	6.9
4	*	Benzene	586	76	698	91	663	86	585	76	706	92	647	85.1	9.1
5	*	Bromodichloromethane	711	92	776	101	790	103	744	97	780	101	760	92.9	4.3
6	*	Bromoform	582	76	684	89	659	86	650	84	667	87	648	93.9	6.0
7	*	Carbon Tetrachloride	707	92	863	112	834	108	695	90	836	109	787	91.8	10.1
8	*	Chloroform	714	93	805	105	776	101	708	92	810	105	762	90.0	6.4
9	*	cis - 1,3 - Dichloropropene	705	92	759	99	743	97	681	88	754	98	728	91.6	4.7
10	*	EDB (1,2-Dibromoethane)	653	85	751	98	728	95	715	93	754	98	720	88.6	5.7
11	*	Ethylbenzene	605	79	735	96	677	88	678	88	721	94	683	88.1	7.4
12	*	Methylene chloride	614	80	713	93	690	90	551	72	720	94	657	84.0	11.1
13	*	MTBE	643	84	769	100	731	95	630	82	758	99	706	87.9	9.3
14	*	m&p-Xylene	1192	77	1426	93	1315	85	1328	86	1426	93	1337	87.8	7.2
15	*	Naphthalene	555	72	708	92	599	78	625	81	675	88	632	91.3	9.6
16	*	o-Xylene	600	78	713	93	662	86	667	87	725	94	673	87.6	7.4
17	*	Styrene	617	80	720	94	668	87	667	87	712	92	677	88.5	6.1
18	*	Toluene	614	80	707	92	686	89	660	86	718	93	677	87.4	6.1
19	*	trans - 1,3 - Dichloropropene	679	88	757	98	748	97	726	94	741	96	730	90.9	4.2
20	*	Vinyl Chloride	481	63	585	76	573	74	379	49	583	76	520	77.0	17.3
21		1,1 - Dichloropropene	625	81	764	99	723	94	628	82	750	98	698	85.6	9.6
22		1,1-Dichloroethane	647	84	747	97	725	94	597	78	747	97	692	85.0	9.8
23		1,1-Dichloroethene	593	77	741	96	718	93	528	69	718	93	659	84.0	14.2
24		1,1,1-Trichloroethane	703	91	881	115	821	107	698	91	863	112	793	90.5	11.0
25		1,1,1,2 - Tetrachloroethane	675	88	798	104	746	97	762	99	777	101	751	91.6	6.3
26		1,1,2,2-Tetrachloroethane	544	71	667	87	569	74	640	83	597	78	603	104.8	8.3
27		1,2-Dibromo-3-Chloropropane	638	83	816	106	671	87	774	101	719	93	724	90.1	10.1
28		1,2-Dichlorobenzene	577	75	679	88	623	81	657	85	668	87	641	90.2	6.4
29		1,2-Dichloroethane	689	90	802	104	768	100	714	93	809	105	756	89.8	7.0
30		1,2-Dichloropropane	597	78	662	86	674	88	607	79	662	86	640	86.4	5.6
31		1,2,3 - Trichloropropane	604	78	728	95	623	81	690	90	687	89	666	90.2	7.7
32		1,2,3-Trichlorobenzene	624	81	733	95	658	85	693	90	735	95	688	93.2	7.0
33		1,2,4-Trichlorobenzene	622	81	700	91	652	85	661	86	693	90	665	93.8	4.8
34		1,3-Dichlorobenzene	584	76	686	89	635	83	668	87	677	88	650	92.0	6.4
35		1,3-Dichloropropane	574	75	684	89	629	82	643	84	669	87	639	83.0	6.7
36		1,4-Dichlorobenzene	631	82	721	94	673	87	668	87	692	90	677	97.8	4.9
37		2-Chlorotoluene	563	73	665	86	603	78	640	83	665	86	627	88.4	7.0
38		2,2-Dichloropropane	571	74	686	89	624	81	658	86	661	86	640	96.4	6.9
39		4-Chlorotoluene	576	75	694	90	639	83	542	70	649	84	620	83.3	9.7
40		Allyl Chloride	598	78	718	93	658	85	697	91	695	90	673	104.9	7.1
41		Bromobenzene	497	65	606	79	571	74	442	57	590	77	541	75.4	12.8
42		Bromochloromethane	702	91	818	106	769	100	694	90	841	109	765	86.5	8.7
43		Chlorobenzene	606	79	729	95	669	87	676	88	714	93	679	89.0	7.0
44		Chloroethane	654	85	760	99	729	95	513	67	758	99	683	88.0	15.3
45		Chloromethane	414	54	526	68	496	64	327	43	522	68	457	72.8	18.7
46		cis-1,2-Dichloroethene	633	82	733	95	740	96	621	81	721	94	689	85.9	8.4
47		Dibromochloromethane	734	95	823	107	789	103	788	102	808	105	788	92.7	4.3
48		Dibromomethane	706	92	778	101	766	100	715	93	803	104	753	89.6	5.5
49		Dichlorofluoromethane	773	100	820	107	826	107	650	85	824	107	779	91.9	9.7
50		Di-Isopropyl ether	602	78	696	90	669	87	590	77	702	91	652	85.9	8.1
51		Ethyl Ether	685	89	792	103	757	98	608	79	812	105	731	89.3	11.5
52		Hexachlorobutadiene	642	83	730	95	688	89	703	91	760	99	705	96.2	6.3
53		Isopropylbenzene	614	80	740	96	671	87	715	93	727	95	693	89.6	7.4
54		n-Butylbenzene	579	75	702	91	627	82	659	86	708	92	655	91.6	8.2
55		n-Propylbenzene	585	76	711	92	643	84	673	87	691	90	660	89.2	7.4
56		p-Isopropyltoluene	608	79	741	96	665	86	698	91	718	93	686	91.2	7.6
57		sec-Butylbenzene	606	79	727	94	651	85	699	91	711	92	679	90.3	7.3
58		tert-Butylbenzene	613	80	752	98	667	87	712	92	729	95	694	89.6	8.0
59		Tetrachloroethene	642	83	744	97	745	97	693	90	752	98	715	88.1	6.6
60		trans-1,2-Dichloroethene	598	78	696	90	682	89	535	69	679	88	638	79.6	10.9
61		Trichloroethene	693	90	762	99	784	102	712	93	814	106	753	80.5	6.6
62		Trichlorofluoromethane	705	92	782	102	805	105	581	75	763	99	727	95.1	12.4
63		Trichlorotrifluoroethane	546	71	709	92	698	91	523	68	680	88	631	92.8	14.2

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 12

Matrix - Clean Laboratory Sand

VOC METHOD 8260 STANDARD 769.2 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	685	89	713	93	682	98	662	86	672	87	683	88.0	2.8
2	*	1,2,4-Trimethylbenzene	686	89	697	91	658	751	626	81	653	85	664	88.6	4.2
3	*	1,3,5-Trimethylbenzene	697	91	712	92	679	88	648	84	662	86	679	90.2	3.8
4	*	Benzene	691	90	704	92	677	88	634	82	673	87	676	88.8	3.9
5	*	Bromodichloromethane	764	99	797	104	767	100	720	94	746	97	759	92.7	3.7
6	*	Bromoform	681	89	700	91	655	85	579	75	628	82	648	94.0	7.3
7	*	Carbon Tetrachloride	847	110	901	117	893	116	822	107	883	115	869	101.4	3.9
8	*	Chloroform	812	105	849	110	795	103	746	97	798	104	800	94.4	4.6
9	*	cis - 1,3 - Dichloropropene	763	99	772	100	725	94	688	89	719	93	733	92.3	4.7
10	*	EDB (1,2-Dibromoethane)	720	94	752	98	681	89	670	87	692	90	703	86.5	4.7
11	*	Ethylbenzene	717	93	735	96	696	90	653	85	691	90	698	90.1	4.4
12	*	Methylene chloride	712	92	741	96	667	87	659	86	684	89	692	88.5	4.9
13	*	MTBE	759	99	814	106	722	94	682	89	751	98	746	92.8	6.5
14	*	m&p-Xylene	1415	92	1434	93	1371	89	1294	84	1346	87	1372	90.1	4.1
15	*	Naphthalene	564	73	659	86	606	79	583	76	603	78	603	87.1	5.9
16	*	o-Xylene	717	93	725	94	692	90	659	86	700	91	698	90.9	3.7
17	*	Styrene	712	92	726	94	690	90	649	84	674	88	690	90.2	4.4
18	*	Toluene	698	91	703	91	691	90	651	85	686	89	686	88.5	3.0
19	*	trans - 1,3 - Dichloropropene	785	102	811	105	748	97	701	91	733	95	755	94.0	5.7
20	*	Vinyl Chloride	609	79	610	79	595	77	560	73	612	80	597	88.4	3.7
21		1,1 - Dichloropropene	759	99	792	103	768	100	699	91	768	100	757	92.8	4.6
22		1,1-Dichloroethane	743	97	783	102	723	94	699	91	733	95	736	90.3	4.2
23		1,1-Dichloroethene	761	99	739	96	727	94	686	89	752	98	733	93.4	4.0
24		1,1,1-Trichloroethane	906	118	919	119	885	115	806	105	867	113	876	100.0	5.1
25		1,1,1,2 - Tetrachloroethane	785	102	774	101	765	99	699	91	745	97	754	91.9	4.5
26		1,1,2,2-Tetrachloroethane	662	86	745	97	647	84	657	85	655	85	673	116.9	6.0
27		1,2-Dibromo-3-Chloropropane	693	90	774	101	650	84	668	87	724	94	701	87.4	7.0
28		1,2-Dichlorobenzene	652	85	671	87	631	82	607	79	645	84	641	90.3	3.8
29		1,2-Dichloroethane	816	106	860	112	765	99	759	99	795	103	799	94.8	5.2
30		1,2-Dichloropropane	641	83	682	89	627	81	594	77	609	79	630	85.0	5.4
31		1,2,3 - Trichloropropane	621	81	668	87	606	79	604	79	640	83	628	85.0	4.3
32		1,2,3-Trichlorobenzene	655	85	726	94	664	86	633	82	679	88	671	90.9	5.2
33		1,2,4-Trichlorobenzene	639	83	677	88	674	88	605	79	651	85	649	91.5	4.5
34		1,3-Dichlorobenzene	648	84	658	86	618	80	603	78	638	83	633	89.6	3.5
35		1,3-Dichloropropane	691	90	700	91	669	87	618	80	649	84	665	86.4	5.0
36		1,4-Dichlorobenzene	629	82	660	86	623	81	585	76	621	81	623	90.0	4.3
37		2-Chlorotoluene	648	84	647	84	647	84	601	78	631	82	635	89.4	3.2
38		2,2-Dichloropropane	877	114	983	128	917	119	853	111	888	115	904	136.0	5.5
39		4-Chlorotoluene	685	89	698	91	666	87	629	82	666	87	669	89.8	3.9
40		Allyl Chloride	599	78	668	87	616	80	575	75	635	82	618	96.4	5.7
41		Bromobenzene	663	86	661	86	649	84	609	79	633	82	643	89.7	3.5
42		Bromochloromethane	807	105	854	111	757	98	739	96	799	104	791	89.5	5.7
43		Chlorobenzene	701	91	711	92	680	88	644	84	690	90	685	89.8	3.8
44		Chloroethane	842	109	818	106	771	100	743	97	810	105	797	102.7	4.9
45		Chloromethane	564	73	550	72	499	65	486	63	528	69	525	83.6	6.3
46		cis-1,2-Dichloroethene	741	96	743	97	715	93	666	87	710	92	715	89.1	4.4
47		Dibromochloromethane	827	108	835	109	766	100	752	98	774	101	791	93.0	4.8
48		Dibromomethane	799	104	799	104	730	95	725	94	730	95	756	89.9	5.1
49		Dichlorofluoromethane	992	129	951	124	901	117	852	111	925	120	924	109.1	5.7
50		Di-Isopropyl ether	678	88	715	93	663	86	632	82	665	86	670	88.4	4.5
51		Ethyl Ether	818	106	840	109	776	101	730	95	795	103	792	96.7	5.3
52		Hexachlorobutadiene	702	91	720	94	763	99	684	89	731	95	720	98.3	4.2
53		Isopropylbenzene	697	91	700	91	693	90	645	84	681	88	683	88.2	3.3
54		n-Butylbenzene	673	87	673	87	663	86	626	81	647	84	656	91.7	3.1
55		n-Propylbenzene	671	87	678	88	663	86	627	81	647	84	657	88.7	3.1
56		p-Isopropyltoluene	701	91	712	93	682	89	658	85	673	87	685	91.1	3.2
57		sec-Butylbenzene	691	90	689	90	672	87	637	83	665	86	671	89.3	3.3
58		tert-Butylbenzene	703	91	699	91	694	90	658	86	673	87	685	88.4	2.8
59		Tetrachloroethene	767	100	786	102	732	95	691	90	726	94	740	91.2	5.0
60		trans-1,2-Dichloroethene	710	92	721	94	673	87	629	82	678	88	682	85.1	5.3
61		Trichloroethene	692	90	723	94	681	88	623	81	683	89	680	72.7	5.3
62		Trichlorofluoromethane	919	119	824	107	934	121	834	108	870	113	876	114.6	5.6
63		Trichlorotrifluoroethane	669	87	651	85	744	97	674	88	717	93	691	101.5	5.5

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

Table 13

GASOLINE STANDARD (153.8) MG/KG or 3077 UG/L

Matrix - Clean Laboratory Sand

	Unspiked		0 Hour		24 Hour		48 Hour		72 Hour		7 Day		10 Day	
	Absolute	% Rec.	Absolute	% Rec.	Absolute	% Rec.	Absolute	% Rec.	Absolute	% Rec.	Absolute	% Rec.	Absolute	% Rec.
Rep. #1	0.21	NA	95.9	62.3	98.2	63.8	99.4	64.6	97.4	63.3	97.3	63.3	95.6	62.1
Rep. #2	0.4	NA	94.8	61.6	100	65.1	101	65.7	98.9	64.3	97.7	63.5	97.8	63.6
Rep. #3	NR	NA	97.4	63.3	100	65.3	101	65.8	102	66.2	96.8	62.9	91.6	59.5
Rep. #4	NR	NA	98.2	63.8	102	66.2	103	66.7	101	65.4	101	65.7	93.3	60.6
Rep. #5	NR	NA	95.6	62.2	102	66.1	103	66.9	99.6	64.7	98.4	64.0	95.8	62.3
Average		NA	96.3	62.6	100	65.3	101	65.9	99.6	64.8	98.2	63.9	94.8	61.6
% Recovery of 0 Hour.		NA		NA		104		105		104		102		98
% RSD		NA		1.4		1.5		1.4		1.7		1.7		2.6

x:/users/mike/agasvial

NR = Not Run

NA = Not Applicable

GASOLINE STANDARD (153.8) MG/KG or 3077 UG/L

Matrix - Biologically Active Garden Soil

	Unspiked		0 Hour		24 Hour		48 Hour		72 Hour		7 Day		10 Day	
	Absolute	% Rec. *	Absolute	% Rec. *	Absolute	% Rec. *	Absolute	% Rec. *	Absolute	% Rec. *	Absolute	% Rec. *	Absolute	% Rec. *
Rep. #1	0.2	NA	87.0	70.8	84.6	68.9	85.8	69.8	83.2	67.7	84.4	68.7	80.3	65.4
Rep. #2	NR	NA	85.7	69.7	82.2	66.9	61.5	50.1	87.5	71.2	85.8	69.9	80.3	65.4
Rep. #3	NR	NA	84.2	68.5	82.9	67.5	87.1	70.9	83.8	68.2	84.5	68.8	81.3	66.1
Rep. #4	NR	NA	87.8	71.5	85.2	69.3	86.6	70.4	87.4	71.2	84.9	69.1	82.8	67.4
Rep. #5	NR	NA	86.2	70.2	83.9	68.3	82.1	66.8	85.2	69.3	85.9	69.9	81.5	66.3
Average		NA	86.2	70.1	83.8	68.2	80.6	65.6	85.4	69.5	85.1	69.3	81.3	66.1
% Recovery of 0 Hour.		NA		NA		97.3		93.6		99.2		98.8		94.3
% RSD		NA		1.6		1.5		13.4		2.3		0.9		1.3

X:/users/Mike/bigasvia

* % Recoveries were corrected for moisture using a dry weight value of 79.9 %. (See Table 14).

NR = Not Run

NA = Not Applicable

VOC STUDY RESULTS

Table 14

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
			0 Hour		0 Hour		0 Hour		0 Hour		0 Hour		Absolute	Average	%
		ANALYTE	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	AVG.	% REC. **	RSD.
1	*	1,1,2-Trichloroethane	133	86	126	82	144	94	138	90	130	85	134	109.1	5.2
2	*	1,2,4-Trimethylbenzene	130	84	119	77	135	87	134	87	138	89	131	106.5	5.5
3	*	1,3,5-Trimethylbenzene	134	87	123	80	138	90	138	89	138	89	134	109.0	4.7
4	*	Benzene	136	88	129	84	140	91	138	90	139	90	136	110.8	3.1
5	*	Bromodichloromethane	123	80	112	73	130	84	129	84	125	81	124	100.5	5.9
6	*	Bromoform	115	75	102	66	111	72	108	70	109	71	109	88.6	4.4
7	*	Carbon Tetrachloride	116	75	122	79	126	82	120	78	128	83	122	99.5	4.1
8	*	Chloroform	133	86	122	79	137	89	139	90	138	89	133	108.6	5.2
9	*	cis - 1,3 - Dichloropropene	127	83	115	75	126	82	124	81	125	81	123	100.3	3.8
10	*	EDB (1,2-Dibromoethane)	131	85	121	78	132	86	136	88	132	86	130	105.9	4.4
11	*	Ethylbenzene	134	87	123	80	139	90	137	89	134	87	133	108.3	4.7
12	*	Methylene Chloride	130	85	123	80	143	93	138	90	141	91	135	109.6	6.2
13	*	MTBE	136	88	128	83	146	95	145	94	133	86	137	111.8	5.5
14	*	m&p-Xylene	268	87	249	81	275	89	278	90	275	89	269	109.4	4.4
15	*	Naphthalene	109	71	100	65	111	72	112	73	103	67	107	86.9	4.9
16	*	o-Xylene	134	87	123	80	137	89	136	88	133	86	132	107.8	4.1
17	*	Styrene	125	81	115	75	128	83	131	85	126	82	125	101.5	4.7
18	*	Toluene	132	86	123	80	145	94	136	88	136	88	134	109.3	5.9
19	*	trans - 1,3 - Dichloropropene	127	83	117	76	132	86	127	83	130	84	126	102.8	4.6
20	*	Vinyl Chloride	166	108	106	69	106	69	103	67	105	68	117	95.1	23.3
21		1,1 - Dichloropropene	126	82	123	80	138	90	133	86	138	89	132	107.0	5.1
22		1,1-Dichloroethane	131	85	125	81	145	94	136	88	139	90	135	110.0	5.5
23		1,1-Dichloroethene	119	77	130	84	128	83	133	86	132	86	128	104.2	4.4
24		1,1,1-Trichloroethane	127	82	124	81	136	88	132	86	136	88	131	106.5	4.1
25		1,1,1,2 - Tetrachloroethane	121	78	115	75	128	83	127	83	129	84	124	100.7	4.8
26		1,1,2,2-Tetrachloroethane	131	85	118	77	121	79	129	84	114	74	122	99.6	5.7
27		1,2-Dibromo-3-Chloropropane	143	93	115	74	132	86	125	81	122	79	127	103.4	8.4
28		1,2-Dichlorobenzene	133	86	121	78	135	88	134	87	134	87	131	106.8	4.6
29		1,2-Dichloroethane	135	87	123	80	139	90	135	88	135	87	133	108.2	4.6
30		1,2-Dichloropropane	132	86	122	79	139	90	140	91	132	86	133	108.0	5.4
31		1,2,3 - Trichloropropane	138	90	124	81	143	93	133	86	134	87	134	109.2	5.1
32		1,2,3-Trichlorobenzene	119	77	110	72	125	81	123	80	115	75	118	96.2	5.0
33		1,2,4-Trichlorobenzene	112	73	106	69	119	77	121	79	119	77	115	93.8	5.5
34		1,3-Dichlorobenzene	127	83	122	79	135	87	137	89	133	86	131	106.2	4.8
35		1,3-Dichloropropane	134	87	122	79	138	89	138	89	134	87	133	108.2	4.8
36		1,4-Dichlorobenzene	128	83	122	79	131	85	131	85	131	85	128	104.3	3.1
37		2-Chlorotoluene	131	85	121	78	133	86	137	89	136	88	131	106.9	4.9
38		2,2-Dichloropropane	118	76	109	71	120	78	119	77	118	77	117	94.8	3.7
39		4-Chlorotoluene	133	86	125	81	135	87	137	89	135	88	133	108.2	3.5
40		Allyl Chloride	128	83	123	80	134	87	137	89	134	87	131	106.7	4.3
41		Bromobenzene	129	84	119	77	131	85	133	86	132	86	128	104.5	4.3
42		Bromochloromethane	132	86	117	76	130	84	137	89	136	88	130	106.0	6.2
43		Chlorobenzene	127	83	123	80	133	86	134	87	137	89	131	106.2	4.3
44		Chloroethane	182	118	124	80	122	79	106	69	121	78	131	106.4	22.6
45		Chloromethane	167	108	93	60	103	67	101	66	101	66	113	91.8	26.8
46		cis-1,2-Dichloroethene	134	87	128	83	140	91	142	92	138	89	136	110.7	4.2
47		Dibromochloromethane	114	74	103	67	113	73	116	75	117	76	112	91.5	4.9
48		Dibromomethane	131	85	119	77	137	89	138	89	133	86	131	106.9	5.6
49		Dichlorofluoromethane	199	129	103	67	117	76	106	69	104	67	125	102.0	32.9
50		Di-isopropyl Ether	135	87	128	83	144	93	143	93	141	91	138	112.1	4.9
51		Ethyl Ether	140	91	126	82	143	93	143	93	139	90	138	112.2	5.0
52		Hexachlorobutadiene	138	89	122	79	140	91	130	85	132	86	132	107.6	5.3
53		Isopropylbenzene	135	88	125	81	138	90	136	88	142	92	135	110.0	4.6
54		n-Butylbenzene	131	85	123	80	140	91	133	86	132	86	132	107.0	4.5
55		n-Propylbenzene	132	86	125	81	138	90	135	88	139	90	134	108.7	4.2
56		p-Isopropyltoluene	130	85	119	77	139	90	134	87	135	88	131	106.8	5.7
57		sec-Butylbenzene	132	86	123	80	138	90	135	88	137	89	133	108.1	4.7
58		tert-Butylbenzene	133	86	123	80	137	89	137	89	139	90	134	108.7	4.7
59		Tetrachloroethene	128	83	124	81	135	87	138	90	132	86	131	106.9	4.2
60		trans-1,2-Dichloroethene	125	81	125	81	137	89	134	87	142	92	132	107.6	5.7
61		Trichloroethene	143	93	135	87	153	99	144	94	149	97	145	117.7	4.7
62		Trichlorofluoromethane	170	111	114	74	107	70	107	69	112	73	122	99.2	22.2
63		Trichlorotrifluoroethane	175	113	105	68	97	63	98	63	100	65	115	93.3	29.3

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

** Recoveries have been corrected for % moisture using a dry weight value of 79.9%.

x:/users/mike/lbvoc0hr

VOC STUDY RESULTS

Table 15

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	135	88	135	87	128	83	128	83	130	84	131	97.7	2.7
2	*	1,2,4-Trimethylbenzene	127	83	131	85	125	81	125	81	125	81	126	96.6	2.0
3	*	1,3,5-Trimethylbenzene	132	86	133	86	126	82	129	84	132	86	130	97.2	2.2
4	*	Benzene	124	81	128	83	122	79	124	80	126	82	125	91.5	1.7
5	*	Bromodichloromethane	123	80	124	81	114	74	117	76	126	82	121	97.6	4.2
6	*	Bromoform	102	66	103	67	99	64	97	63	98	64	100	91.4	2.4
7	*	Carbon Tetrachloride	116	75	119	77	120	78	113	73	115	75	116	95.2	2.3
8	*	Chloroform	128	83	139	90	133	86	131	85	135	88	133	99.8	3.1
9	*	cis - 1,3 - Dichloropropene	45	29	49	32	43	28	41	27	38	24	43	34.8	9.7
10	*	EDB (1,2-Dibromoethane)	118	77	119	77	114	74	111	72	120	78	116	89.4	3.2
11	*	Ethylbenzene	122	79	128	83	120	78	118	76	123	80	122	91.6	3.1
12	*	Methylene Chloride	124	81	129	84	125	81	121	78	124	81	124	92.3	2.3
13	*	MTBE	140	91	137	89	131	85	134	87	135	88	135	98.4	2.7
14	*	m&p-Xylene	254	82	255	83	241	78	243	79	248	81	248	92.3	2.6
15	*	Naphthalene	110	71	105	68	109	71	107	70	107	69	107	100.4	1.8
16	*	o-Xylene	134	87	132	86	125	81	122	79	128	83	128	96.7	3.7
17	*	Styrene	100	65	101	65	95	61	96	62	100	65	98	78.7	2.7
18	*	Toluene	122	79	122	79	118	77	114	74	120	78	119	88.7	3.0
19	*	trans - 1,3 - Dichloropropene	81	52	83	54	76	49	77	50	79	51	79	62.4	3.5
20	*	Vinyl Chloride	89	58	97	63	101	66	86	56	91	59	93	79.2	6.7
21		1,1 - Dichloropropene	133	86	130	84	123	80	114	74	129	84	126	95.4	6.1
22		1,1-Dichloroethane	131	85	135	88	127	82	130	84	135	87	131	97.1	2.7
23		1,1-Dichloroethene	111	72	117	76	117	76	109	71	118	76	114	89.1	3.7
24		1,1,1-Trichloroethane	127	83	126	82	127	83	124	80	125	81	126	96.1	1.2
25		1,1,1,2 - Tetrachloroethane	121	79	121	78	119	77	118	76	124	81	120	97.3	2.0
26		1,1,2,2-Tetrachloroethane	134	87	116	75	115	74	109	71	112	73	117	95.6	8.4
27		1,2-Dibromo-3-Chloropropane	121	79	121	79	110	72	117	76	123	80	118	93.1	4.4
28		1,2-Dichlorobenzene	129	84	131	85	123	80	127	82	129	84	128	97.2	2.5
29		1,2-Dichloroethane	133	86	130	84	123	80	128	83	129	84	128	96.5	2.8
30		1,2-Dichloropropane	133	86	132	86	129	84	129	84	134	87	131	98.8	1.7
31		1,2,3 - Trichloropropane	139	90	133	86	130	84	127	83	134	87	132	98.5	3.3
32		1,2,3-Trichlorobenzene	122	79	122	79	127	83	121	79	120	78	122	103.6	2.2
33		1,2,4-Trichlorobenzene	116	75	112	73	113	73	112	73	111	72	113	97.7	1.6
34		1,3-Dichlorobenzene	128	83	129	84	122	79	126	82	126	82	126	96.6	2.0
35		1,3-Dichloropropane	133	86	134	87	127	82	127	82	129	84	130	97.6	2.8
36		1,4-Dichlorobenzene	124	81	125	81	121	78	121	79	121	79	122	95.4	1.7
37		2-Chlorotoluene	126	82	129	84	124	81	124	80	128	83	126	95.9	1.7
38		2,2-Dichloropropane	106	69	108	70	102	66	101	65	102	66	104	88.9	3.1
39		4-Chlorotoluene	125	81	128	83	121	79	120	78	124	81	123	92.8	2.4
40		Allyl Chloride	109	71	105	68	99	64	92	60	100	65	101	77.0	6.4
41		Bromobenzene	127	82	131	85	121	79	123	80	125	81	125	97.5	3.1
42		Bromochloromethane	127	82	126	82	122	79	124	80	127	83	125	95.9	1.7
43		Chlorobenzene	127	83	130	84	125	81	123	80	128	83	126	96.8	2.0
44		Chloroethane	113	73	104	68	119	77	87	57	111	72	107	81.6	11.4
45		Chloromethane	77	50	82	53	83	54	80	52	80	52	80	70.8	2.9
46		cis-1,2-Dichloroethene	131	85	131	85	125	81	121	79	127	82	127	93.1	3.2
47		Dibromochloromethane	106	69	110	71	103	67	103	67	106	69	105	93.7	2.8
48		Dibromomethane	138	89	133	86	137	89	134	87	133	86	135	102.7	1.6
49		Dichlorofluoromethane	99	64	106	69	104	67	96	62	108	70	102	81.7	4.9
50		Di-isopropyl Ether	138	90	136	88	132	86	131	85	132	86	134	97.1	2.4
51		Ethyl Ether	134	87	134	87	129	84	123	80	133	86	130	94.6	3.6
52		Hexachlorobutadiene	133	86	136	88	120	78	122	79	121	79	126	95.5	5.9
53		Isopropylbenzene	132	86	131	85	126	82	125	81	129	84	128	95.0	2.3
54		n-Butylbenzene	111	72	115	75	109	71	108	70	110	71	110	84.0	2.5
55		n-Propylbenzene	122	79	124	81	117	76	117	76	121	79	120	89.7	2.5
56		p-Isopropyltoluene	113	73	114	74	111	72	108	70	111	72	111	85.0	2.1
57		sec-Butylbenzene	127	82	128	83	122	79	121	78	126	82	125	93.8	2.6
58		tert-Butylbenzene	128	83	133	86	127	82	125	81	130	84	128	96.1	2.4
59		Tetrachloroethene	130	84	129	84	124	81	118	76	124	80	125	94.9	3.8
60		trans-1,2-Dichloroethene	120	78	122	79	123	80	118	76	124	81	121	91.7	2.2
61		Trichloroethene	140	91	144	93	141	92	138	90	147	96	142	98.1	2.5
62		Trichlorofluoromethane	92	60	96	62	106	69	96	62	103	67	98	80.7	5.6
63		Trichlorotrifluoroethane	95	61	82	53	101	66	85	55	91	59	91	79.1	8.3

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 16

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	127	82	129	84	133	86	136	88	129	84	131	97.3	2.7
2	*	1,2,4-Trimethylbenzene	130	84	119	77	124	81	126	82	123	80	124	95.0	3.1
3	*	1,3,5-Trimethylbenzene	134	87	129	84	125	81	128	83	128	83	129	96.1	2.6
4	*	Benzene	122	79	120	78	123	80	122	79	122	79	122	89.5	0.9
5	*	Bromodichloromethane	120	78	118	76	119	77	120	78	120	78	119	96.5	0.9
6	*	Bromoform	92	60	97	63	91	59	97	63	93	60	94	86.0	2.8
7	*	Carbon Tetrachloride	117	76	114	74	119	77	118	76	115	75	116	95.2	1.7
8	*	Chloroform	136	88	128	83	132	86	134	87	129	84	132	98.7	2.4
9	*	cis - 1,3 - Dichloropropene	21	13	33	21	30	19	24	16	32	20	28	22.4	18.7
10	*	EDB (1,2-Dibromoethane)	114	74	109	71	116	75	119	77	116	75	115	88.1	3.1
11	*	Ethylbenzene	117	76	118	76	120	78	119	77	116	75	118	88.6	1.4
12	*	Methylene Chloride	127	83	123	80	126	82	129	84	131	85	127	94.4	2.3
13	*	MTBE	139	90	129	84	133	86	137	89	134	87	134	97.5	2.9
14	*	m&p-Xylene	244	79	242	79	248	81	245	79	243	79	244	90.8	1.0
15	*	Naphthalene	114	74	104	67	100	65	101	66	100	65	104	97.0	5.5
16	*	o-Xylene	128	83	123	80	127	83	131	85	129	84	127	96.2	2.3
17	*	Styrene	87	57	85	55	87	56	85	55	87	57	86	69.0	1.2
18	*	Toluene	118	76	118	77	119	77	119	77	119	77	118	88.2	0.6
19	*	trans - 1,3 - Dichloropropene	62	40	65	42	62	40	65	42	66	43	64	50.5	3.1
20	*	Vinyl Chloride	89	58	93	60	97	63	85	55	87	56	90	77.0	5.6
21		1,1 - Dichloropropene	114	74	114	74	123	80	113	73	107	70	114	86.7	5.0
22		1,1-Dichloroethane	127	82	129	84	133	86	128	83	124	80	128	94.6	2.6
23		1,1-Dichloroethene	112	73	113	73	118	77	107	69	105	68	111	86.5	4.7
24		1,1,1-Trichloroethane	130	84	124	80	131	85	130	84	128	83	128	97.9	2.2
25		1,1,1,2 - Tetrachloroethane	119	77	122	79	119	77	122	79	125	81	121	97.9	2.2
26		1,1,2,2-Tetrachloroethane	120	78	123	80	109	71	122	79	108	70	116	94.9	6.3
27		1,2-Dibromo-3-Chloropropane	131	85	123	80	122	79	118	76	108	70	120	94.4	7.0
28		1,2-Dichlorobenzene	129	84	125	81	127	83	129	84	125	81	127	96.7	1.7
29		1,2-Dichloroethane	128	83	127	82	132	86	128	83	127	83	128	96.4	1.7
30		1,2-Dichloropropane	130	84	128	83	128	83	128	83	129	84	128	96.8	0.6
31		1,2,3 - Trichloropropane	132	86	130	84	133	86	134	87	127	82	131	97.6	2.3
32		1,2,3-Trichlorobenzene	129	84	123	80	117	76	117	76	118	77	121	101.9	4.2
33		1,2,4-Trichlorobenzene	120	78	105	68	108	70	106	69	111	72	110	95.1	5.5
34		1,3-Dichlorobenzene	130	84	123	80	124	81	124	81	126	82	125	96.0	2.1
35		1,3-Dichloropropane	131	85	128	83	130	84	137	89	128	83	131	98.3	2.7
36		1,4-Dichlorobenzene	128	83	121	78	125	81	124	80	125	81	124	96.8	2.0
37		2-Chlorotoluene	127	82	126	82	121	79	125	81	125	81	124	94.7	1.7
38		2,2-Dichloropropane	96	62	91	59	93	60	90	59	89	58	92	78.8	3.0
39		4-Chlorotoluene	121	79	119	77	121	79	123	80	123	80	121	91.1	1.4
40		Allyl Chloride	99	64	97	63	104	68	94	61	99	64	98	75.0	3.9
41		Bromobenzene	123	80	119	77	125	81	129	84	127	83	124	96.9	3.0
42		Bromochloromethane	132	86	121	78	126	82	130	85	126	82	127	97.3	3.5
43		Chlorobenzene	125	81	123	80	126	82	128	83	126	82	126	96.2	1.4
44		Chloroethane	108	70	109	71	118	76	119	77	111	72	113	86.3	4.5
45		Chloromethane	68	44	71	46	76	49	67	43	74	48	71	62.7	5.4
46		cis-1,2-Dichloroethene	128	83	123	80	127	83	126	82	128	83	126	92.8	1.8
47		Dibromochloromethane	109	71	103	67	104	67	105	68	105	68	105	93.1	2.2
48		Dibromomethane	145	94	138	90	145	94	139	90	136	88	141	106.9	2.9
49		Dichlorofluoromethane	105	68	109	71	102	66	107	69	105	68	105	84.0	2.5
50		Di-isopropyl Ether	132	86	130	85	135	88	132	86	130	85	132	95.6	1.6
51		Ethyl Ether	134	87	124	80	131	85	129	84	129	84	129	93.7	2.9
52		Hexachlorobutadiene	137	89	122	79	126	82	123	80	119	77	125	94.7	5.6
53		Isopropylbenzene	128	83	124	80	126	82	126	82	125	81	125	92.8	1.2
54		n-Butylbenzene	105	68	101	65	102	66	100	65	101	65	101	77.1	1.8
55		n-Propylbenzene	116	75	112	73	113	73	113	73	114	74	114	85.0	1.3
56		p-Isopropyltoluene	111	72	103	67	103	67	102	66	102	66	104	79.3	3.8
57		sec-Butylbenzene	126	82	119	77	123	80	122	79	120	78	122	91.7	2.3
58		tert-Butylbenzene	129	84	124	80	128	83	127	82	126	82	126	94.6	1.6
59		Tetrachloroethene	123	80	122	79	127	83	127	82	128	83	125	95.2	2.2
60		trans-1,2-Dichloroethene	124	81	123	80	128	83	119	77	122	79	123	93.1	2.8
61		Trichloroethene	139	90	129	84	146	95	134	87	139	90	137	94.8	4.6
62		Trichlorofluoromethane	100	65	104	67	109	71	98	64	93	60	101	82.5	5.8
63		Trichlorotrifluoroethane	86	56	92	60	99	64	94	61	86	56	91	79.6	6.0

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 17

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
			72 Hour		72 Hour		72 Hour		72 Hour		72 Hour		Absolute	AVG. % REC	%
		ANALYTE	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	AVG.	of 0 Hour	RSD.
1	*	1,1,2-Trichloroethane	133	86	130	84	123	80	136	88	137	89	132	98.1	4.5
2	*	1,2,4-Trimethylbenzene	128	83	128	83	126	82	125	81	125	81	126	96.3	1.2
3	*	1,3,5-Trimethylbenzene	138	89	130	84	134	87	135	87	134	87	134	100.0	2.1
4	*	Benzene	128	83	128	83	124	80	126	82	126	82	126	92.6	1.4
5	*	Bromodichloromethane	119	77	124	80	121	79	127	83	127	82	123	99.8	2.9
6	*	Bromoform	91	59	88	57	89	58	93	60	90	58	90	82.6	2.1
7	*	Carbon Tetrachloride	123	80	122	79	125	81	125	81	126	82	124	101.5	1.5
8	*	Chloroform	137	89	140	91	135	87	140	91	140	91	138	103.5	1.7
9	*	cis - 1,3 - Dichloropropene	11	7.2	19	12	18	12	19	12	15	9.4	16	13.1	20.5
10	*	EDB (1,2-Dibromoethane)	107	70	116	75	108	70	113	73	105	68	110	84.2	4.0
11	*	Ethylbenzene	117	76	119	77	120	78	122	79	121	78	120	89.9	1.6
12	*	Methylene Chloride	134	87	123	80	130	84	133	86	134	87	131	96.9	3.5
13	*	MTBE	141	91	137	89	131	85	135	88	133	86	135	98.2	2.8
14	*	m&p-Xylene	244	79	242	79	242	79	249	81	248	81	245	91.0	1.4
15	*	Naphthalene	102	66	101	65	94	61	104	67	97	63	99	92.9	4.0
16	*	o-Xylene	127	82	130	85	128	83	133	86	131	85	130	97.8	1.8
17	*	Styrene	80	52	78	50	72	46	77	50	76	49	76	61.2	3.9
18	*	Toluene	118	76	122	79	120	78	121	79	125	81	121	89.9	2.1
19	*	trans - 1,3 - Dichloropropene	56	36	61	39	55	36	62	40	56	36	58	45.8	5.4
20	*	Vinyl Chloride	89	58	99	64	91	59	98	64	91	59	94	80.0	4.9
21		1,1 - Dichloropropene	114	74	132	86	115	75	121	79	120	78	120	91.6	5.9
22		1,1-Dichloroethane	132	86	138	90	133	86	139	90	130	85	134	99.2	2.9
23		1,1-Dichloroethene	121	78	123	80	120	78	121	78	122	79	121	94.5	1.1
24		1,1,1-Trichloroethane	136	88	136	88	134	87	139	90	140	91	137	104.7	1.7
25		1,1,1,2 - Tetrachloroethane	126	82	124	81	123	80	123	80	124	80	124	100.1	1.0
26		1,1,2,2-Tetrachloroethane	139	90	135	87	133	86	137	89	127	83	134	109.4	3.3
27		1,2-Dibromo-3-Chloropropane	119	77	112	73	111	72	123	80	120	78	117	91.8	4.5
28		1,2-Dichlorobenzene	132	86	130	85	131	85	131	85	132	86	131	99.8	0.6
29		1,2-Dichloroethane	131	85	132	86	129	84	135	87	129	84	131	98.4	1.9
30		1,2-Dichloropropane	131	85	136	88	134	87	137	89	132	86	134	100.7	1.9
31		1,2,3 - Trichloropropane	139	90	136	88	130	85	132	86	132	86	133	99.4	2.6
32		1,2,3-Trichlorobenzene	120	78	122	79	115	75	120	78	118	76	119	100.3	2.1
33		1,2,4-Trichlorobenzene	111	72	106	69	104	67	110	72	109	71	108	93.6	2.8
34		1,3-Dichlorobenzene	131	85	132	86	128	83	128	83	128	83	129	98.8	1.6
35		1,3-Dichloropropane	131	85	131	85	130	84	131	85	134	87	131	98.8	1.3
36		1,4-Dichlorobenzene	125	81	128	83	124	80	126	82	126	82	126	98.0	1.2
37		2-Chlorotoluene	134	87	129	84	123	80	134	87	133	86	131	99.4	3.7
38		2,2-Dichloropropane	137	89	137	89	135	87	137	89	133	86	136	116.3	1.5
39		4-Chlorotoluene	123	80	123	80	123	80	126	82	126	82	124	93.2	1.2
40		Allyl Chloride	87	57	92	59	97	63	97	63	87	56	92	69.9	5.3
41		Bromobenzene	129	84	132	86	131	85	134	87	128	83	130	101.5	1.8
42		Bromochloromethane	127	83	132	86	133	86	127	83	126	82	129	98.9	2.4
43		Chlorobenzene	127	82	131	85	127	83	131	85	132	86	129	99.1	1.9
44		Chloroethane	121	79	127	82	115	75	121	79	128	83	122	93.5	4.1
45		Chloromethane	62	40	67	43	61	40	67	43	64	42	64	56.6	4.1
46		cis-1,2-Dichloroethene	127	83	125	81	128	83	132	86	129	84	128	94.0	2.0
47		Dibromochloromethane	106	69	108	70	103	67	108	70	109	71	106	94.7	2.1
48		Dibromomethane	143	93	141	91	141	92	141	92	142	92	141	107.5	0.5
49		Dichlorofluoromethane	105	68	122	79	114	74	112	73	111	72	113	89.8	5.3
50		Di-isopropyl Ether	136	88	140	91	134	87	139	90	134	87	136	99.0	2.0
51		Ethyl Ether	138	89	130	85	129	84	134	87	134	87	133	96.4	2.6
52		Hexachlorobutadiene	132	86	136	88	127	82	130	84	134	87	131	99.4	2.7
53		Isopropylbenzene	131	85	130	84	129	84	132	86	132	86	130	96.5	0.9
54		n-Butylbenzene	99	64	99	64	97	63	101	65	97	63	98	74.7	1.6
55		n-Propylbenzene	114	74	115	75	120	78	118	76	116	75	116	87.1	1.9
56		p-Isopropyltoluene	107	69	100	65	100	65	102	66	100	65	102	77.4	2.9
57		sec-Butylbenzene	128	83	124	80	126	82	126	82	125	81	125	94.4	1.1
58		tert-Butylbenzene	134	87	131	85	132	86	133	86	133	86	132	99.1	0.8
59		Tetrachloroethene	130	84	133	86	132	86	129	84	139	90	132	100.8	3.1
60		trans-1,2-Dichloroethene	123	80	126	82	123	80	134	87	129	84	127	96.0	3.7
61		Trichloroethene	136	88	134	87	126	82	137	89	138	90	134	92.7	3.5
62		Trichlorofluoromethane	113	73	117	76	114	74	119	77	121	78	117	95.6	2.8
63		Trichlorotrifluoroethane	108	70	105	68	102	66	110	71	103	67	105	91.8	3.2

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 18

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
			7 Day		7 Day		7 Day		7 Day		7 Day		Absolute	AVG. % REC	%
		ANALYTE	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	AVG.	of 0 Hour	RSD.
1	*	1,1,2-Trichloroethane	omitted		136	88	130	84	133	86	124	81	130	97.2	3.8
2	*	1,2,4-Trimethylbenzene	omitted		119	77	116	75	115	75	112	73	115	88.0	2.3
3	*	1,3,5-Trimethylbenzene	omitted		129	84	129	84	132	86	126	82	129	96.1	2.1
4	*	Benzene	omitted		124	80	122	79	121	79	119	77	121	89.1	1.7
5	*	Bromodichloromethane	omitted		119	77	122	79	126	82	119	77	121	98.1	2.8
6	*	Bromoform	omitted		77	50	72	46	70	46	75	49	73	67.3	4.1
7	*	Carbon Tetrachloride	omitted		121	78	124	80	127	82	120	78	123	100.3	2.5
8	*	Chloroform	omitted		141	91	137	89	140	91	131	85	137	102.7	3.4
9	*	cis - 1,3 - Dichloropropene	omitted		12	7.5	4	2.3	2	1.3	5	2.9	5	4.4	78.3
10	*	EDB (1,2-Dibromoethane)	omitted		105	68	93	60	89	58	94	61	95	73.0	7.0
11	*	Ethylbenzene	omitted		111	72	109	71	110	72	109	71	110	82.4	1.0
12	*	Methylene Chloride	omitted		127	83	121	78	130	84	122	79	125	92.5	3.5
13	*	MTBE	omitted		133	86	131	85	130	85	127	83	130	94.7	1.8
14	*	m&p-Xylene	omitted		232	75	229	74	229	74	224	73	229	85.0	1.5
15	*	Naphthalene	omitted		98	63	100	65	91	59	86	56	93	87.4	6.8
16	*	o-Xylene	omitted		127	82	123	80	123	80	121	79	123	93.1	1.9
17	*	Styrene	omitted		51	33	41	26	40	26	40	26	37	28.1	24.2
18	*	Toluene	omitted		116	75	114	74	120	78	114	74	116	86.3	2.5
19	*	trans - 1,3 - Dichloropropene	omitted		44	28	27	17	25	16	30	19	31	24.5	27.7
20	*	Vinyl Chloride	omitted		91	59	91	59	94	61	83	54	90	76.6	5.5
21		1,1 - Dichloropropene	omitted		127	82	134	87	130	85	131	85	130	99.0	2.2
22		1,1-Dichloroethane	omitted		135	88	130	85	139	90	124	80	132	97.6	5.1
23		1,1-Dichloroethene	omitted		114	74	117	76	122	79	112	73	116	90.6	3.6
24		1,1,1-Trichloroethane	omitted		133	86	133	86	138	89	128	83	133	101.4	2.9
25		1,1,1,2 - Tetrachloroethane	omitted		124	81	125	81	123	80	121	79	123	99.6	1.4
26		1,1,2,2-Tetrachloroethane	omitted		136	88	138	89	137	89	134	87	136	111.0	1.1
27		1,2-Dibromo-3-Chloropropane	omitted		115	75	121	78	121	78	108	70	116	91.3	5.1
28		1,2-Dichlorobenzene	omitted		127	83	130	84	127	82	124	80	127	96.5	1.9
29		1,2-Dichloroethane	omitted		127	82	134	87	130	85	131	85	130	97.8	2.2
30		1,2-Dichloropropane	omitted		131	85	131	85	131	85	128	83	130	98.0	1.3
31		1,2,3 - Trichloropropane	omitted		134	87	135	87	137	89	130	84	134	99.5	2.2
32		1,2,3-Trichlorobenzene	omitted		115	75	117	76	112	73	109	71	113	95.7	2.9
33		1,2,4-Trichlorobenzene	omitted		107	70	104	68	102	66	99	64	103	89.3	3.5
34		1,3-Dichlorobenzene	omitted		127	83	128	83	131	85	128	83	128	98.4	1.4
35		1,3-Dichloropropane	omitted		130	85	131	85	129	84	126	82	129	96.9	1.6
36		1,4-Dichlorobenzene	omitted		125	81	123	80	124	80	120	78	123	95.5	1.8
37		2-Chlorotoluene	omitted		126	82	126	82	129	84	127	83	127	96.5	1.3
38		2,2-Dichloropropane	omitted		127	83	125	81	122	79	120	78	124	106.0	2.5
39		4-Chlorotoluene	omitted		117	76	117	76	118	77	117	76	117	87.9	0.6
40		Allyl Chloride	omitted		85	55	68	44	64	42	75	48	73	55.6	12.6
41		Bromobenzene	omitted		125	81	125	81	127	83	123	80	125	97.2	1.3
42		Bromochloromethane	omitted		127	82	129	84	131	85	128	83	129	98.6	1.5
43		Chlorobenzene	omitted		127	83	126	82	127	83	124	80	126	96.3	1.3
44		Chloroethane	omitted		120	78	112	73	130	84	111	72	118	90.3	7.4
45		Chloromethane	omitted		44	28	40	26	41	27	38	24	41	35.9	6.1
46		cis-1,2-Dichloroethene	omitted		129	84	124	81	130	84	125	81	127	93.3	2.2
47		Dibromochloromethane	omitted		102	66	101	65	104	68	101	66	102	90.5	1.5
48		Dibromomethane	omitted		154	100	156	101	165	107	148	96	155	118.2	4.5
49		Dichlorofluoromethane	omitted		120	78	121	79	124	80	111	72	119	94.7	4.8
50		Di-isopropyl Ether	omitted		132	86	132	86	134	87	130	85	132	95.8	1.3
51		Ethyl Ether	omitted		125	81	130	84	131	85	124	81	127	92.4	2.7
52		Hexachlorobutadiene	omitted		131	85	120	78	127	82	112	72	122	92.4	6.8
53		Isopropylbenzene	omitted		125	81	125	81	126	82	122	79	124	92.0	1.4
54		n-Butylbenzene	omitted		79	51	77	50	75	48	74	48	76	57.7	3.0
55		n-Propylbenzene	omitted		105	68	101	66	101	65	99	64	101	75.7	2.5
56		p-Isopropyltoluene	omitted		86	56	78	50	76	49	76	49	79	59.9	6.4
57		sec-Butylbenzene	omitted		117	76	115	74	115	75	111	72	114	86.0	2.4
58		tert-Butylbenzene	omitted		133	86	126	82	130	84	123	80	128	95.5	3.6
59		Tetrachloroethene	omitted		130	85	134	87	128	83	126	82	129	98.5	2.7
60		trans-1,2-Dichloroethene	omitted		122	79	127	82	127	82	117	76	123	92.9	3.7
61		Trichloroethene	omitted		129	84	133	86	124	81	131	85	129	89.4	3.0
62		Trichlorofluoromethane	omitted		108	70	123	80	117	76	114	74	115	94.4	5.6
63		Trichlorotrifluoroethane	omitted		100	65	109	71	104	68	101	65	103	90.0	4.2

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 19

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 153.8 UG/KG / 3.08 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	10 Day Absol.	10 Day Rec. %	Absolute AVG.	AVG. % REC of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	129	84	129	84	125	81	131	85	131	85	129	96.0	2.0
2	*	1,2,4-Trimethylbenzene	110	71	110	71	103	67	111	72	110	71	109	82.9	2.9
3	*	1,3,5-Trimethylbenzene	123	80	125	81	119	77	125	81	128	83	124	92.4	2.6
4	*	Benzene	123	80	122	79	114	74	117	76	122	79	119	87.5	3.3
5	*	Bromodichloromethane	119	77	121	78	113	73	115	75	119	77	117	94.8	2.8
6	*	Bromoform	69	45	70	46	71	46	69	45	66	43	69	63.2	2.8
7	*	Carbon Tetrachloride	123	80	121	79	111	72	112	72	117	76	117	95.4	4.7
8	*	Chloroform	136	88	136	88	133	86	130	84	138	89	134	100.6	2.3
9	*	cis - 1,3 - Dichloropropene	4	2.6	2	1	3	2	2	1.3	2	1	2	1.9	45.2
10	*	EDB (1,2-Dibromoethane)	85	55	83	54	82	53	79	51	81	52	82	62.7	3.0
11	*	Ethylbenzene	107	69	104	67	101	65	103	67	107	69	104	78.1	2.5
12	*	Methylene Chloride	141	92	129	84	114	74	120	78	126	82	126	93.5	8.1
13	*	MTBE	133	86	134	87	129	84	132	86	136	88	132	96.3	2.1
14	*	m&p-Xylene	218	71	215	140	214	139	222	144	217	141	217	80.7	1.4
15	*	Naphthalene	93	60	87	56	90	58	99	64	91	59	92	85.9	5.1
16	*	o-Xylene	124	80	118	77	113	73	125	81	125	81	121	91.2	4.4
17	*	Styrene	29	19	29	19	25	16	26	17	27	18	27	21.7	7.5
18	*	Toluene	112	73	113	73	108	70	108	70	111	72	110	82.0	2.1
19	*	trans - 1,3 - Dichloropropene	24	15	18	12	21	13	19	12	20	13	20	15.8	10.9
20	*	Vinyl Chloride	88	57	86	56	64	42	63	41	77	50	75	64.4	15.7
21		1,1 - Dichloropropene	108	70	107	69	102	66	102	66	106	69	105	79.5	2.6
22		1,1-Dichloroethane	131	85	132	86	118	77	120	78	129	84	126	93.1	5.2
23		1,1-Dichloroethene	114	74	116	75	92	59	94	61	100	65	103	80.4	10.7
24		1,1,1-Trichloroethane	139	90	134	87	122	79	121	79	135	88	130	99.3	6.2
25		1,1,1,2 - Tetrachloroethane	122	79	126	82	123	80	122	79	123	80	123	99.4	1.4
26		1,1,2,2-Tetrachloroethane	129	84	129	84	132	86	133	86	134	87	131	107.1	1.9
27		1,2-Dibromo-3-Chloropropane	113	73	109	71	115	74	108	70	112	72	111	87.2	2.6
28		1,2-Dichlorobenzene	128	83	125	81	125	81	129	84	129	84	127	96.7	1.6
29		1,2-Dichloroethane	129	84	128	83	129	84	130	84	130	84	129	97.0	0.5
30		1,2-Dichloropropane	139	90	130	84	125	81	125	81	131	85	130	97.7	4.4
31		1,2,3 - Trichloropropane	135	87	132	86	135	88	136	88	134	87	134	99.9	1.0
32		1,2,3-Trichlorobenzene	114	74	113	73	112	72	117	76	114	74	114	96.2	1.8
33		1,2,4-Trichlorobenzene	104	68	100	65	95	61	109	71	99	64	101	87.8	5.5
34		1,3-Dichlorobenzene	127	82	127	82	120	78	124	81	127	83	125	95.5	2.5
35		1,3-Dichloropropane	126	82	122	79	129	84	126	82	127	83	126	94.7	2.0
36		1,4-Dichlorobenzene	122	79	122	79	115	75	123	80	124	81	121	94.4	2.9
37		2-Chlorotoluene	121	79	124	81	122	79	129	84	127	82	124	94.7	2.6
38		2,2-Dichloropropane	121	79	119	77	100	65	100	65	104	67	109	93.1	9.8
39		4-Chlorotoluene	113	73	109	71	112	73	116	75	115	75	113	85.0	2.5
40		Allyl Chloride	56	36	63	41	62	40	50	33	61	40	58	44.5	9.1
41		Bromobenzene	125	81	122	79	128	83	128	83	126	82	126	97.9	2.0
42		Bromochloromethane	135	88	127	83	127	83	123	80	134	87	129	99.2	4.0
43		Chlorobenzene	126	82	124	80	120	78	127	83	126	82	124	95.2	2.2
44		Chloroethane	123	80	118	76	101	65	93	60	108	70	108	82.9	11.3
45		Chloromethane	27	18	29	19	20	13	21	14	24	15	24	21.3	15.4
46		cis-1,2-Dichloroethene	126	82	128	83	117	76	119	77	123	80	122	90.0	3.8
47		Dibromochloromethane	100	65	105	68	97	63	98	64	96	62	99	88.1	3.5
48		Dibromomethane	163	106	159	103	158	102	157	102	166	108	160	122.0	2.4
49		Dichlorofluoromethane	122	79	121	78	94	61	102	66	108	70	109	87.0	10.9
50		Di-isopropyl Ether	132	86	132	86	127	82	128	83	130	85	130	94.0	1.9
51		Ethyl Ether	123	80	121	79	119	77	118	77	124	81	121	87.7	2.0
52		Hexachlorobutadiene	122	79	129	84	126	82	125	81	123	80	125	94.3	2.2
53		Isopropylbenzene	121	78	119	77	119	77	123	80	124	80	121	89.3	1.9
54		n-Butylbenzene	70	46	67	44	65	42	69	45	68	44	68	51.5	2.8
55		n-Propylbenzene	93	60	94	61	92	59	95	62	95	61	94	70.0	1.6
56		p-Isopropyltoluene	66	43	67	43	65	42	71	46	63	41	66	50.4	4.3
57		sec-Butylbenzene	110	71	110	71	108	70	112	72	110	71	110	82.4	1.3
58		tert-Butylbenzene	124	81	124	80	120	78	125	81	126	82	124	92.5	1.7
59		Tetrachloroethene	127	82	127	83	138	89	130	85	123	80	129	98.1	4.2
60		trans-1,2-Dichloroethene	126	82	132	86	119	77	112	73	113	73	120	90.9	7.1
61		Trichloroethene	136	88	135	87	123	80	132	86	130	84	131	90.4	4.0
62		Trichlorofluoromethane	119	77	115	75	91	59	98	63	103	67	105	86.1	11.2
63		Trichlorotrifluoroethane	104	68	101	66	74	48	84	54	83	54	89	77.5	14.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 20

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	0 Hour Absol.	0 Hour Rec. %	Absolute AVG.	Average % REC. **	% RSD.
1	*	1,1,2-Trichloroethane	645	84	678	88	669	87	623	81	674	88	658	107.0	3.5
2	*	1,2,4-Trimethylbenzene	672	87	676	88	697	91	640	83	713	93	679	110.5	4.1
3	*	1,3,5-Trimethylbenzene	664	86	671	87	680	88	624	81	695	90	667	108.4	4.0
4	*	Benzene	655	85	673	87	671	87	618	80	682	89	660	107.3	3.9
5	*	Bromodichloromethane	655	85	667	87	672	87	614	80	690	90	659	107.2	4.3
6	*	Bromoform	580	75	625	81	622	81	556	72	645	84	605	98.5	6.0
7	*	Carbon Tetrachloride	678	88	680	88	684	89	637	83	710	92	678	110.2	3.9
8	*	Chloroform	699	91	705	92	700	91	655	85	717	93	695	113.0	3.4
9	*	cis - 1,3 - Dichloropropene	624	81	637	83	639	83	591	77	647	84	627	102.0	3.5
10	*	EDB (1,2-Dibromoethane)	646	84	665	86	672	87	631	82	684	89	659	107.3	3.2
11	*	Ethylbenzene	661	86	658	86	671	87	617	80	686	89	658	107.1	3.9
12	*	Methylene Chloride	650	84	654	85	658	85	616	80	678	88	651	105.9	3.4
13	*	MTBE	660	86	696	90	684	89	632	82	696	90	673	109.5	4.1
14	*	m&p-Xylene	1318	171	1316	171	1344	175	1222	159	1370	178	1314	106.8	4.2
15	*	Naphthalene	557	72	616	80	602	78	564	73	626	81	593	96.4	5.2
16	*	o-Xylene	653	85	657	85	666	87	610	79	677	88	652	106.1	3.9
17	*	Styrene	609	79	625	81	633	82	585	76	643	83	619	100.7	3.6
18	*	Toluene	663	86	661	86	676	88	618	80	683	89	660	107.3	3.9
19	*	trans - 1,3 - Dichloropropene	648	84	655	85	661	86	606	79	672	87	648	105.4	3.9
20	*	Vinyl Chloride	600	78	597	78	585	76	555	72	614	80	590	96.0	3.8
21		1,1 - Dichloropropene	668	87	670	87	670	87	620	81	698	91	665	108.2	4.2
22		1,1-Dichloroethane	680	88	696	90	687	89	638	83	712	92	682	111.0	4.0
23		1,1-Dichloroethene	689	90	676	88	687	89	642	83	692	90	677	110.1	3.0
24		1,1,1-Trichloroethane	700	91	701	91	703	91	652	85	721	94	695	113.1	3.7
25		1,1,1,2 - Tetrachloroethane	658	86	659	86	660	86	630	82	672	87	656	106.6	2.4
26		1,1,2,2-Tetrachloroethane	517	67	585	76	519	67	503	65	552	72	535	87.0	6.2
27		1,2-Dibromo-3-Chloropropane	612	79	691	90	649	84	655	85	704	91	662	107.7	5.5
28		1,2-Dichlorobenzene	617	80	623	81	629	82	594	77	640	83	620	100.9	2.8
29		1,2-Dichloroethane	670	87	682	89	679	88	631	82	696	90	671	109.2	3.7
30		1,2-Dichloropropane	675	88	671	87	681	88	619	80	684	89	666	108.3	4.0
31		1,2,3 - Trichloropropane	597	78	641	83	609	79	598	78	627	81	614	99.9	3.1
32		1,2,3-Trichlorobenzene	534	69	565	73	572	74	526	68	584	76	556	90.4	4.5
33		1,2,4-Trichlorobenzene	639	83	663	86	675	88	599	78	716	93	658	107.1	6.6
34		1,3-Dichlorobenzene	606	79	609	79	616	80	578	75	620	81	606	98.5	2.7
35		1,3-Dichloropropane	656	85	664	86	666	86	624	81	683	89	658	107.1	3.3
36		1,4-Dichlorobenzene	593	77	597	78	601	78	564	73	610	79	593	96.4	2.9
37		2-Chlorotoluene	610	79	610	79	612	79	578	75	622	81	606	98.6	2.7
38		2,2-Dichloropropane	583	76	566	74	563	73	509	66	558	73	556	90.4	5.0
39		4-Chlorotoluene	614	80	617	80	632	82	586	76	637	83	617	100.3	3.2
40		Allyl Chloride	579	75	591	77	571	74	532	69	593	77	573	93.2	4.3
41		Bromobenzene	610	79	597	78	603	78	576	75	614	80	600	97.6	2.5
42		Bromochloromethane	673	87	683	89	669	87	620	81	683	89	665	108.2	3.9
43		Chlorobenzene	639	83	643	83	654	85	607	79	660	86	640	104.1	3.2
44		Chloroethane	701	91	710	92	709	92	641	83	732	95	698	113.5	4.9
45		Chloromethane	543	71	553	72	549	71	516	67	565	73	545	88.6	3.3
46		cis-1,2-Dichloroethene	669	87	690	90	703	91	642	83	706	92	682	110.9	3.9
47		Dibromochloromethane	617	80	626	81	640	83	580	75	649	84	622	101.2	4.3
48		Dibromomethane	676	88	692	90	701	91	643	84	704	91	683	111.1	3.6
49		Dichlorofluoromethane	655	85	652	85	636	83	618	80	671	87	646	105.1	3.1
50		Di-isopropyl Ether	665	86	679	88	681	88	630	82	691	90	669	108.8	3.5
51		Ethyl Ether	705	92	721	94	707	92	666	87	723	94	704	114.5	3.2
52		Hexachlorobutadiene	583	76	589	76	594	77	565	73	619	80	590	95.9	3.3
53		Isopropylbenzene	649	84	650	84	647	84	612	79	665	86	644	104.8	3.0
54		n-Butylbenzene	590	77	612	79	631	82	570	74	657	85	612	99.5	5.6
55		n-Propylbenzene	650	84	653	85	662	86	621	81	683	89	654	106.3	3.4
56		p-Isopropyltoluene	671	87	698	91	720	94	653	85	742	96	697	113.3	5.2
57		sec-Butylbenzene	677	88	682	89	701	91	638	83	720	94	683	111.1	4.5
58		tert-Butylbenzene	673	87	679	88	693	90	635	82	709	92	678	110.2	4.1
59		Tetrachloroethene	648	84	643	84	652	85	600	78	667	87	642	104.4	3.9
60		trans-1,2-Dichloroethene	665	86	674	88	686	89	631	82	715	93	674	109.6	4.6
61		Trichloroethene	752	98	743	96	797	104	711	92	774	101	755	122.8	4.3
62		Trichlorofluoromethane	668	87	627	81	645	84	609	79	630	82	636	103.4	3.5
63		Trichlorotrifluoroethane	575	75	521	68	529	69	512	67	523	68	532	86.5	4.6

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 21

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	24 Hour Absol.	24 Hour Rec. %	Absolute AVG.	AVG. % REC. of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	658	85	676	88	681	88	665	86	668	87	669	101.8	1.4
2	*	1,2,4-Trimethylbenzene	662	86	679	88	671	87	704	91	661	86	675	99.4	2.6
3	*	1,3,5-Trimethylbenzene	655	85	677	88	660	86	685	89	655	85	666	99.9	2.1
4	*	Benzene	637	83	652	85	642	83	653	85	638	83	644	97.7	1.2
5	*	Bromodichloromethane	640	83	660	86	659	86	669	87	653	85	656	99.5	1.6
6	*	Bromoform	554	72	587	76	613	80	594	77	596	77	589	97.3	3.7
7	*	Carbon Tetrachloride	630	82	678	88	643	84	665	86	626	81	648	95.6	3.5
8	*	Chloroform	689	90	697	91	700	91	705	92	686	89	695	100.0	1.1
9	*	cis - 1,3 - Dichloropropene	458	60	492	64	495	64	466	60	478	62	478	76.1	3.4
10	*	EDB (1,2-Dibromoethane)	623	81	643	83	665	86	649	84	655	85	647	98.1	2.5
11	*	Ethylbenzene	628	82	646	84	646	84	647	84	633	82	640	97.1	1.4
12	*	Methylene chloride	640	83	642	83	640	83	632	82	627	81	636	97.7	1.0
13	*	MTBE	674	88	672	87	692	90	671	87	690	90	680	100.9	1.5
14	*	m&p-Xylene	1282	83	1304	85	1298	84	1308	85	1270	82	1292	98.4	1.2
15	*	Naphthalene	565	73	600	78	606	79	623	81	625	81	604	101.9	4.0
16	*	o-Xylene	641	83	652	85	660	86	654	85	635	83	648	99.3	1.6
17	*	Styrene	537	70	555	72	557	72	567	74	557	72	554	89.6	2.0
18	*	Toluene	634	82	643	84	637	83	652	85	630	82	639	96.8	1.4
19	*	trans - 1,3 - Dichloropropene	549	71	570	74	578	75	564	73	564	73	565	87.1	1.9
20	*	Vinyl Chloride	539	70	563	73	553	72	564	73	538	70	551	93.4	2.3
21		1,1 - Dichloropropene	632	82	637	83	638	83	654	85	626	81	637	95.8	1.6
22		1,1-Dichloroethane	684	89	683	89	677	88	681	88	675	88	680	99.6	0.6
23		1,1-Dichloroethene	628	82	671	87	644	84	656	85	629	82	645	95.3	2.8
24		1,1,1-Trichloroethane	667	87	704	91	677	88	687	89	673	87	681	98.0	2.2
25		1,1,1,2 - Tetrachloroethane	637	83	649	84	640	83	666	86	649	84	648	98.8	1.7
26		1,1,2,2-Tetrachloroethane	538	70	537	70	579	75	582	76	609	79	569	106.3	5.5
27		1,2-Dibromo-3-Chloropropane	613	80	636	83	670	87	606	79	705	92	646	97.6	6.4
28		1,2-Dichlorobenzene	619	80	627	81	630	82	638	83	629	82	628	101.3	1.1
29		1,2-Dichloroethane	657	85	663	86	675	88	659	86	658	85	662	98.6	1.1
30		1,2-Dichloropropane	667	87	679	88	677	88	665	86	661	86	669	100.5	1.2
31		1,2,3 - Trichloropropane	613	80	618	80	624	81	585	76	637	83	615	100.2	3.1
32		1,2,3-Trichlorobenzene	551	72	563	73	570	74	601	78	560	73	569	102.3	3.3
33		1,2,4-Trichlorobenzene	645	84	658	85	672	87	722	94	680	88	675	102.6	4.3
34		1,3-Dichlorobenzene	600	78	613	80	607	79	616	80	611	79	609	100.6	1.0
35		1,3-Dichloropropane	641	83	659	86	674	88	667	87	673	87	663	100.7	2.1
36		1,4-Dichlorobenzene	594	77	598	78	602	78	608	79	599	78	600	101.2	0.8
37		2-Chlorotoluene	595	77	615	80	602	78	611	79	593	77	603	99.5	1.6
38		2,2-Dichloropropane	564	73	571	74	547	71	548	71	522	68	550	99.1	3.4
39		4-Chlorotoluene	605	79	615	80	611	79	624	81	603	78	611	99.1	1.4
40		Allyl Chloride	517	67	526	68	526	68	529	69	510	66	522	91.0	1.5
41		Bromobenzene	592	77	596	77	601	78	609	79	602	78	600	100.0	1.1
42		Bromochloromethane	641	83	666	86	663	86	663	86	652	85	657	98.7	1.6
43		Chlorobenzene	630	82	643	83	634	82	640	83	626	81	634	99.1	1.1
44		Chloroethane	648	84	654	85	650	84	653	85	628	82	646	92.6	1.7
45		Chloromethane	494	64	489	63	488	63	498	65	489	63	491	90.1	0.9
46		cis-1,2-Dichloroethene	663	86	680	88	680	88	686	89	643	84	670	98.3	2.6
47		Dibromochloromethane	588	76	612	79	608	79	613	80	599	78	604	97.0	1.7
48		Dibromomethane	672	87	669	87	713	93	681	88	690	90	685	100.3	2.6
49		Dichlorofluoromethane	594	77	620	81	616	80	625	81	606	79	612	94.7	2.0
50		Di-Isopropyl ether	675	88	683	89	680	88	687	89	674	88	680	101.6	0.8
51		Ethyl Ether	686	89	694	90	688	89	688	89	699	91	691	98.1	0.8
52		Hexachlorobutadiene	580	75	612	79	606	79	633	82	624	81	611	103.6	3.3
53		Isopropylbenzene	624	81	650	84	634	82	644	84	624	81	635	98.6	1.8
54		n-Butylbenzene	570	74	603	78	585	76	637	83	579	75	595	97.2	4.5
55		n-Propylbenzene	623	81	640	83	636	83	654	85	622	81	635	97.1	2.1
56		p-Isopropyltoluene	662	86	685	89	677	88	721	94	670	87	683	98.0	3.4
57		sec-Butylbenzene	658	86	693	90	674	88	716	93	657	85	679	99.4	3.7
58		tert-Butylbenzene	655	85	678	88	674	88	693	90	660	86	672	99.1	2.3
59		Tetrachloroethene	620	81	643	83	627	81	647	84	610	79	629	98.0	2.5
60		trans-1,2-Dichloroethene	643	84	643	84	647	84	654	85	633	82	644	95.5	1.2
61		Trichloroethene	737	96	746	97	745	97	698	91	698	91	725	96.0	3.4
62		Trichlorofluoromethane	567	74	651	85	582	76	637	83	562	73	600	94.3	6.9
63		Trichlorotrifluoroethane	476	62	582	76	507	66	529	69	493	64	517	97.2	8.0

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 22

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	48 Hour Absol.	48 Hour Rec. %	Absolute AVG.	AVG. % REC. of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	650	84	651	85	678	88	641	83	661	86	656	99.7	2.2
2	*	1,2,4-Trimethylbenzene	688	89	677	88	690	90	678	88	667	87	680	100.1	1.4
3	*	1,3,5-Trimethylbenzene	664	86	666	86	686	89	667	87	661	86	669	100.3	1.5
4	*	Benzene	637	83	635	83	664	86	640	83	645	84	644	97.6	1.8
5	*	Bromodichloromethane	646	84	655	85	674	88	647	84	646	84	653	99.1	1.9
6	*	Bromoform	587	76	568	74	609	79	569	74	604	78	587	97.0	3.2
7	*	Carbon Tetrachloride	663	86	644	84	664	86	654	85	654	85	656	96.7	1.3
8	*	Chloroform	674	88	691	90	712	93	686	89	679	88	688	99.0	2.1
9	*	cis - 1,3 - Dichloropropene	413	54	435	57	442	57	402	52	413	54	421	67.1	4.0
10	*	EDB (1,2-Dibromoethane)	636	83	632	82	662	86	621	81	649	84	640	97.0	2.5
11	*	Ethylbenzene	634	82	623	81	660	86	626	81	634	82	635	96.5	2.3
12	*	Methylene chloride	628	82	627	81	651	85	624	81	624	81	631	96.9	1.8
13	*	MTBE	667	87	676	88	705	92	660	86	690	90	679	100.9	2.6
14	*	m&p-Xylene	1280	166	1244	162	1323	172	1265	164	1285	167	1279	97.4	2.3
15	*	Naphthalene	620	81	599	78	638	83	610	79	626	81	618	104.3	2.4
16	*	o-Xylene	643	84	640	83	664	86	644	84	652	85	648	99.4	1.5
17	*	Styrene	516	67	495	64	535	70	515	67	520	68	516	83.4	2.8
18	*	Toluene	636	83	623	81	659	86	630	82	634	82	636	96.4	2.1
19	*	trans - 1,3 - Dichloropropene	528	69	535	69	546	71	522	68	539	70	534	82.4	1.7
20	*	Vinyl Chloride	556	72	529	69	555	72	561	73	549	71	550	93.2	2.2
21		1,1 - Dichloropropene	639	83	628	82	666	87	640	83	642	83	643	96.7	2.2
22		1,1-Dichloroethane	656	85	661	86	693	90	669	87	669	87	669	98.1	2.1
23		1,1-Dichloroethene	642	83	632	82	644	84	651	85	644	84	642	94.9	1.1
24		1,1,1-Trichloroethane	669	87	672	87	699	91	681	88	684	89	681	98.0	1.7
25		1,1,1,2 - Tetrachloroethane	656	85	651	85	675	88	644	84	651	85	655	99.9	1.8
26		1,1,2,2-Tetrachloroethane	591	77	640	83	639	83	553	72	594	77	603	112.7	6.1
27		1,2-Dibromo-3-Chloropropane	639	83	636	83	675	88	632	82	677	88	652	98.5	3.4
28		1,2-Dichlorobenzene	634	82	626	81	653	85	621	81	631	82	633	102.0	2.0
29		1,2-Dichloroethane	649	84	652	85	679	88	649	84	665	86	659	98.1	2.0
30		1,2-Dichloropropane	659	86	654	85	686	89	666	86	667	87	666	100.0	1.8
31		1,2,3 - Trichloropropane	617	80	593	77	628	82	603	78	630	82	614	100.0	2.6
32		1,2,3-Trichlorobenzene	595	77	585	76	617	80	584	76	575	75	591	106.3	2.7
33		1,2,4-Trichlorobenzene	703	91	681	88	704	91	692	90	685	89	693	105.2	1.5
34		1,3-Dichlorobenzene	609	79	600	78	627	81	613	80	607	79	611	100.9	1.6
35		1,3-Dichloropropane	653	85	642	83	683	89	646	84	666	87	658	99.9	2.5
36		1,4-Dichlorobenzene	596	77	580	75	615	80	600	78	592	77	596	100.6	2.2
37		2-Chlorotoluene	602	78	605	79	621	81	597	78	605	79	606	100.0	1.5
38		2,2-Dichloropropane	523	68	502	65	528	69	501	65	494	64	510	91.7	3.0
39		4-Chlorotoluene	607	79	604	78	628	82	604	78	613	80	611	99.1	1.6
40		Allyl Chloride	504	65	504	65	525	68	510	66	503	65	509	88.8	1.8
41		Bromobenzene	594	77	592	77	612	80	591	77	603	78	598	99.7	1.5
42		Bromochloromethane	647	84	648	84	665	86	645	84	637	83	648	97.4	1.6
43		Chlorobenzene	631	82	612	79	656	85	628	82	633	82	632	98.7	2.5
44		Chloroethane	624	81	650	84	655	85	652	85	645	84	645	92.4	1.9
45		Chloromethane	487	63	481	62	493	64	492	64	482	63	487	89.3	1.1
46		cis-1,2-Dichloroethene	655	85	661	86	686	89	671	87	665	86	667	97.9	1.8
47		Dibromochloromethane	598	78	604	78	628	82	600	78	606	79	607	97.6	2.0
48		Dibromomethane	673	87	671	87	719	93	669	87	683	89	683	100.0	3.1
49		Dichlorofluoromethane	600	78	619	80	637	83	613	80	609	79	615	95.2	2.2
50		Di-Isopropyl ether	665	86	673	87	698	91	665	86	671	87	674	100.8	2.0
51		Ethyl Ether	675	88	690	90	703	91	675	88	682	89	685	97.2	1.7
52		Hexachlorobutadiene	637	83	622	81	626	81	608	79	627	81	624	105.7	1.7
53		Isopropylbenzene	632	82	633	82	654	85	628	82	627	81	635	98.5	1.7
54		n-Butylbenzene	604	78	583	76	614	80	598	78	572	74	594	97.1	2.8
55		n-Propylbenzene	634	82	621	81	643	83	632	82	616	80	629	96.2	1.7
56		p-Isopropyltoluene	699	91	683	89	703	91	687	89	674	88	689	98.9	1.7
57		sec-Butylbenzene	691	90	682	89	700	91	685	89	663	86	684	100.1	2.0
58		tert-Butylbenzene	671	87	671	87	693	90	671	87	661	86	673	99.3	1.7
59		Tetrachloroethene	629	82	615	80	640	83	624	81	637	83	629	98.0	1.6
60		trans-1,2-Dichloroethene	650	84	617	80	654	85	655	85	646	84	644	95.6	2.5
61		Trichloroethene	708	92	656	85	706	92	710	92	724	94	701	92.8	3.7
62		Trichlorofluoromethane	627	81	587	76	594	77	597	78	607	79	602	94.7	2.6
63		Trichlorotrifluoroethane	545	71	505	66	528	69	503	65	553	72	527	99.0	4.3

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 23

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	72 Hour Absol.	Rec. %	Absolute AVG.	AVG. % REC. of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	651	85	659	86	694	90	658	86	672	87	667	101.4	2.5
2	*	1,2,4-Trimethylbenzene	660	86	666	87	702	91	677	88	677	88	676	99.6	2.4
3	*	1,3,5-Trimethylbenzene	652	85	667	87	700	91	672	87	676	88	673	101.0	2.6
4	*	Benzene	622	81	629	82	680	88	637	83	656	85	645	97.7	3.6
5	*	Bromodichloromethane	645	84	659	86	692	90	651	85	664	86	662	100.4	2.7
6	*	Bromoform	563	73	572	74	589	76	583	76	580	75	577	95.4	1.7
7	*	Carbon Tetrachloride	628	82	666	87	679	88	651	85	678	88	660	97.4	3.2
8	*	Chloroform	679	88	684	89	720	94	690	90	697	91	694	99.9	2.3
9	*	cis - 1,3 - Dichloropropene	389	51	388	50	444	58	407	53	427	55	411	65.5	5.9
10	*	EDB (1,2-Dibromoethane)	626	81	631	82	665	86	623	81	643	83	637	96.6	2.7
11	*	Ethylbenzene	619	80	627	81	672	87	631	82	644	84	639	97.0	3.3
12	*	Methylene chloride	596	77	626	81	654	85	624	81	634	82	627	96.3	3.3
13	*	MTBE	661	86	666	87	684	89	668	87	669	87	669	99.4	1.3
14	*	m&p-Xylene	1224	80	1270	83	1335	87	1266	82	1292	84	1277	97.2	3.2
15	*	Naphthalene	574	75	575	75	579	75	599	78	578	75	581	98.0	1.8
16	*	o-Xylene	633	82	651	85	686	89	643	84	650	84	652	100.0	3.0
17	*	Styrene	477	62	492	64	515	67	476	62	495	64	491	79.3	3.2
18	*	Toluene	608	79	628	82	669	87	630	82	647	84	636	96.4	3.6
19	*	trans - 1,3 - Dichloropropene	505	66	493	64	564	73	521	68	536	70	524	80.8	5.3
20	*	Vinyl Chloride	492	64	538	70	566	73	541	70	558	73	539	91.3	5.3
21		1,1 - Dichloropropene	602	78	633	82	679	88	627	81	663	86	641	96.3	4.7
22		1,1-Dichloroethane	652	85	666	87	701	91	667	87	678	88	673	98.6	2.7
23		1,1-Dichloroethene	582	76	633	82	666	87	650	84	669	87	640	94.5	5.5
24		1,1,1-Trichloroethane	655	85	686	89	710	92	676	88	717	93	689	99.1	3.7
25		1,1,1,2 - Tetrachloroethane	639	83	665	86	692	90	659	86	661	86	663	101.1	2.9
26		1,1,2,2-Tetrachloroethane	568	74	606	79	671	87	658	86	663	86	633	118.3	7.1
27		1,2-Dibromo-3-Chloropropane	635	82	663	86	630	82	640	83	623	81	638	96.4	2.4
28		1,2-Dichlorobenzene	620	81	632	82	653	85	629	82	635	83	634	102.2	1.9
29		1,2-Dichloroethane	641	83	649	84	678	88	651	85	671	87	658	98.0	2.4
30		1,2-Dichloropropane	651	85	667	87	705	92	680	88	659	86	672	100.9	3.2
31		1,2,3 - Trichloropropane	609	79	617	80	607	79	617	80	625	81	615	100.1	1.2
32		1,2,3-Trichlorobenzene	554	72	541	70	576	75	575	75	566	73	562	101.1	2.6
33		1,2,4-Trichlorobenzene	651	85	666	86	709	92	681	88	668	87	675	102.5	3.2
34		1,3-Dichlorobenzene	593	77	610	79	637	83	614	80	619	80	614	101.5	2.6
35		1,3-Dichloropropane	635	82	645	84	682	89	656	85	647	84	653	99.2	2.8
36		1,4-Dichlorobenzene	577	75	602	78	621	81	608	79	605	79	602	101.6	2.7
37		2-Chlorotoluene	605	79	616	80	630	82	611	79	628	82	618	101.9	1.7
38		2,2-Dichloropropane	460	60	490	64	736	96	694	90	702	91	616	110.9	21.2
39		4-Chlorotoluene	594	77	615	80	641	83	625	81	626	81	620	100.5	2.8
40		Allyl Chloride	472	61	480	62	548	71	509	66	534	69	508	88.7	6.5
41		Bromobenzene	584	76	605	79	621	81	611	79	615	80	607	101.2	2.3
42		Bromochloromethane	620	81	652	85	675	88	656	85	670	87	654	98.3	3.3
43		Chlorobenzene	620	81	626	81	659	86	626	81	637	83	633	98.9	2.4
44		Chloroethane	605	79	650	84	656	85	658	85	657	85	645	92.4	3.5
45		Chloromethane	447	58	456	59	507	66	474	62	480	62	473	86.7	4.9
46		cis-1,2-Dichloroethene	632	82	670	87	706	92	654	85	682	89	669	98.1	4.2
47		Dibromochloromethane	590	77	620	81	638	83	595	77	616	80	612	98.3	3.2
48		Dibromomethane	649	84	680	88	708	92	669	87	696	90	680	99.6	3.4
49		Dichlorofluoromethane	587	76	626	81	646	84	613	80	629	82	620	95.9	3.5
50		Di-Isopropyl ether	655	85	674	88	703	91	670	87	680	88	676	101.1	2.6
51		Ethyl Ether	673	87	681	88	706	92	677	88	684	89	684	97.1	1.9
52		Hexachlorobutadiene	588	76	590	77	615	80	595	77	623	81	602	102.1	2.6
53		Isopropylbenzene	621	81	641	83	666	87	641	83	656	85	645	100.1	2.6
54		n-Butylbenzene	544	71	561	73	602	78	577	75	577	75	572	93.5	3.8
55		n-Propylbenzene	605	79	629	82	670	87	632	82	640	83	635	97.2	3.7
56		p-Isopropyltoluene	651	85	669	87	716	93	676	88	680	88	678	97.4	3.5
57		sec-Butylbenzene	657	85	676	88	713	93	683	89	685	89	683	99.9	2.9
58		tert-Butylbenzene	652	85	668	87	700	91	680	88	682	89	676	99.8	2.6
59		Tetrachloroethene	599	78	635	82	667	87	631	82	651	85	636	99.2	4.0
60		trans-1,2-Dichloroethene	593	77	639	83	667	87	643	83	645	84	637	94.6	4.2
61		Trichloroethene	695	90	690	90	690	90	646	84	659	86	676	89.5	3.3
62		Trichlorofluoromethane	512	67	601	78	604	78	608	79	658	86	597	93.8	8.8
63		Trichlorotrifluoroethane	425	55	543	71	529	69	547	71	568	74	522	98.2	10.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 24

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	7 Day Absol.	7 Day Rec. %	Absolute AVG.	AVG. % REC. of 0 Hour	% RSD.
1	*	1,1,2-Trichloroethane	675	88	662	86	685	89	667	87	671	87	672	102.2	1.3
2	*	1,2,4-Trimethylbenzene	664	86	669	87	684	89	665	86	677	88	672	98.9	1.3
3	*	1,3,5-Trimethylbenzene	673	87	666	86	684	89	665	86	677	88	673	100.9	1.2
4	*	Benzene	653	85	638	83	667	87	553	72	652	85	633	95.9	7.3
5	*	Bromodichloromethane	666	86	645	84	680	88	635	83	650	84	655	99.4	2.7
6	*	Bromoform	581	75	557	72	603	78	574	75	575	75	578	95.5	2.9
7	*	Carbon Tetrachloride	658	86	677	88	671	87	517	67	674	88	639	94.3	10.8
8	*	Chloroform	697	91	689	90	715	93	609	79	688	89	680	97.8	6.0
9	*	cis - 1,3 - Dichloropropene	285	37	288	37	263	34	267	35	308	40	282	44.9	6.4
10	*	EDB (1,2-Dibromoethane)	635	82	622	81	638	83	613	80	619	80	625	94.8	1.7
11	*	Ethylbenzene	631	82	621	81	636	83	604	78	628	82	624	94.7	2.0
12	*	Methylene chloride	634	82	632	82	641	83	529	69	615	80	610	93.7	7.6
13	*	MTBE	697	91	661	86	693	90	641	83	676	88	674	100.0	3.4
14	*	m&p-Xylene	1280	83	1266	82	1291	84	1252	81	1272	83	1272	96.8	1.1
15	*	Naphthalene	607	79	585	76	598	78	591	77	611	79	598	100.9	1.8
16	*	o-Xylene	658	85	648	84	660	86	647	84	649	84	652	100.0	0.9
17	*	Styrene	384	50	400	52	400	52	389	51	394	51	393	63.5	1.7
18	*	Toluene	641	83	629	82	651	85	593	77	638	83	630	95.5	3.6
19	*	trans - 1,3 - Dichloropropene	431	56	445	58	434	56	423	55	438	57	434	66.9	1.8
20	*	Vinyl Chloride	508	66	542	70	551	72	271	35	545	71	483	81.9	24.8
21		1,1 - Dichloropropene	630	82	634	82	644	84	501	65	632	82	608	91.4	9.9
22		1,1-Dichloroethane	680	88	676	88	699	91	542	70	685	89	656	96.2	9.8
23		1,1-Dichloroethene	629	82	662	86	663	86	414	54	656	85	605	89.3	17.8
24		1,1,1-Trichloroethane	686	89	690	90	698	91	533	69	686	89	659	94.7	10.7
25		1,1,1,2 - Tetrachloroethane	660	86	652	85	675	88	652	85	662	86	660	100.7	1.4
26		1,1,2,2-Tetrachloroethane	708	92	669	87	694	90	680	88	697	91	689	128.9	2.2
27		1,2-Dibromo-3-Chloropropane	649	84	643	84	675	88	635	83	655	85	651	98.4	2.3
28		1,2-Dichlorobenzene	640	83	632	82	645	84	631	82	642	83	638	102.8	1.0
29		1,2-Dichloroethane	682	89	655	85	676	88	620	81	653	85	657	97.9	3.7
30		1,2-Dichloropropane	694	90	672	87	693	90	631	82	681	88	674	101.2	3.8
31		1,2,3 - Trichloropropane	645	84	605	79	653	85	602	78	632	82	532	69.1	4.6
32		1,2,3-Trichlorobenzene	569	74	562	73	574	75	564	73	574	75	568	102.2	1.0
33		1,2,4-Trichlorobenzene	679	88	672	87	686	89	686	89	680	88	680	103.4	0.9
34		1,3-Dichlorobenzene	629	82	602	78	624	81	611	79	621	81	617	101.9	1.8
35		1,3-Dichloropropane	667	87	653	85	674	88	650	84	656	85	660	100.2	1.6
36		1,4-Dichlorobenzene	609	79	589	76	619	80	602	78	607	79	605	102.0	1.8
37		2-Chlorotoluene	615	80	607	79	625	81	613	80	618	80	615	101.5	1.1
38		2,2-Dichloropropane	678	88	666	87	659	86	487	63	638	83	625	112.6	12.6
39		4-Chlorotoluene	618	80	600	78	622	81	604	78	625	81	614	99.5	1.8
40		Allyl Chloride	451	59	469	61	471	61	340	44	463	60	439	76.6	12.8
41		Bromobenzene	616	80	594	77	620	81	604	78	611	79	609	101.5	1.7
42		Bromochloromethane	657	85	638	83	668	87	599	78	658	85	644	96.7	4.3
43		Chlorobenzene	641	83	634	82	655	85	627	81	639	83	639	99.8	1.6
44		Chloroethane	624	81	657	85	652	85	391	51	645	84	594	85.0	19.2
45		Chloromethane	428	56	459	60	483	63	246	32	465	60	416	76.3	23.4
46		cis-1,2-Dichloroethene	677	88	662	86	696	90	581	75	673	87	658	96.4	6.8
47		Dibromochloromethane	601	78	607	79	618	80	596	77	612	79	607	97.5	1.4
48		Dibromomethane	696	90	692	90	710	92	674	88	697	91	694	101.6	1.8
49		Dichlorofluoromethane	608	79	615	80	631	82	416	54	620	81	578	89.5	15.7
50		Di-Isopropyl ether	687	89	669	87	695	90	631	82	673	87	671	100.3	3.7
51		Ethyl Ether	696	90	677	88	698	91	638	83	684	89	678	96.3	3.6
52		Hexachlorobutadiene	596	77	606	79	603	78	589	76	613	80	601	101.9	1.6
53		Isopropylbenzene	643	84	639	83	653	85	625	81	646	84	641	99.5	1.6
54		n-Butylbenzene	528	69	548	71	544	71	530	69	544	71	539	88.0	1.6
55		n-Propylbenzene	618	80	613	80	632	82	608	79	625	81	619	94.7	1.6
56		p-Isopropyltoluene	649	84	658	86	666	86	649	84	669	87	658	94.5	1.4
57		sec-Butylbenzene	666	86	680	88	685	89	662	86	685	89	675	98.8	1.6
58		tert-Butylbenzene	663	86	673	87	683	89	666	87	676	88	672	99.2	1.2
59		Tetrachloroethene	642	83	633	82	649	84	602	78	643	83	634	98.7	2.9
60		trans-1,2-Dichloroethene	625	81	636	83	663	86	487	63	620	81	606	89.9	11.3
61		Trichloroethene	652	85	667	87	665	86	583	76	641	83	642	85.0	5.4
62		Trichlorofluoromethane	563	73	625	81	599	78	347	45	621	81	551	86.7	21.2
63		Trichlorotrifluoroethane	492	64	583	76	541	70	322	42	569	74	501	94.3	21.2

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

VOC STUDY RESULTS

Table 25

Matrix - Biologically Active Garden Soil

VOC METHOD 8260 STANDARD 769.5 UG/KG / 15.38 UG/L

			Rep. #1		Rep. #2		Rep. #3		Rep. #4		Rep. #5				
		ANALYTE	10 Day		10 Day		10 Day		10 Day		10 Day		Absolute AVG.	AVG. % REC. of 0 Hour	% RSD.
			Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %	Absol.	Rec. %			
1	*	1,1,2-Trichloroethane	680	88	651	85	670	87	693	90	666	86	672	102.1	2.3
2	*	1,2,4-Trimethylbenzene	677	88	655	85	667	87	701	91	659	86	671	98.9	2.7
3	*	1,3,5-Trimethylbenzene	667	87	665	86	674	88	690	90	667	87	672	100.9	1.5
4	*	Benzene	643	83	641	83	650	84	670	87	653	85	651	98.7	1.8
5	*	Bromodichloromethane	660	86	656	85	642	83	687	89	660	86	661	100.2	2.4
6	*	Bromoform	573	74	529	69	575	75	589	77	579	75	569	94.0	4.1
7	*	Carbon Tetrachloride	655	85	681	88	676	88	669	87	673	87	671	99.0	1.5
8	*	Chloroform	688	89	687	89	697	91	712	93	693	90	695	100.1	1.5
9	*	cis - 1,3 - Dichloropropene	268	35	227	29	233	30	226	29	233	30	237	37.8	7.3
10	*	EDB (1,2-Dibromoethane)	616	80	598	78	607	79	643	84	608	79	614	93.2	2.8
11	*	Ethylbenzene	621	81	610	79	620	81	635	83	628	82	623	94.6	1.5
12	*	Methylene chloride	628	82	631	82	650	84	662	86	642	83	642	98.7	2.2
13	*	MTBE	674	88	643	84	678	88	696	90	668	87	672	99.7	2.9
14	*	m&p-Xylene	1268	82	1246	81	1258	82	1308	85	1265	82	1269	96.6	1.8
15	*	Naphthalene	586	76	551	72	582	76	612	79	569	74	580	97.8	3.9
16	*	o-Xylene	646	84	633	82	646	84	678	88	645	84	649	99.5	2.6
17	*	Styrene	343	45	324	42	328	43	350	45	340	44	337	54.4	3.2
18	*	Toluene	633	82	616	80	631	82	656	85	643	84	636	96.3	2.3
19	*	trans - 1,3 - Dichloropropene	398	52	365	47	382	50	391	51	380	49	383	59.1	3.3
20	*	Vinyl Chloride	515	67	554	72	543	71	509	66	531	69	530	89.8	3.5
21		1,1 - Dichloropropene	631	82	645	84	621	81	629	82	630	82	631	94.9	4.6
22		1,1-Dichloroethane	672	87	673	87	688	89	696	90	686	89	683	100.0	1.5
23		1,1-Dichloroethene	629	82	658	86	651	85	630	82	641	83	642	94.8	2.0
24		1,1,1-Trichloroethane	678	88	691	90	701	91	703	91	690	90	692	99.6	1.4
25		1,1,1,2 - Tetrachloroethane	652	85	651	85	654	85	678	88	662	86	659	100.5	1.7
26		1,1,2,2-Tetrachloroethane	671	87	651	85	697	91	691	90	663	86	674	126.0	2.8
27		1,2-Dibromo-3-Chloropropane	638	83	606	79	681	88	673	87	635	82	646	97.7	4.7
28		1,2-Dichlorobenzene	645	84	624	81	639	83	661	86	637	83	641	103.3	2.1
29		1,2-Dichloroethane	659	86	645	84	661	86	685	89	656	85	661	98.5	2.2
30		1,2-Dichloropropane	686	89	656	85	661	86	706	92	680	88	678	101.8	3.0
31		1,2,3 - Trichloropropane	633	82	591	77	622	81	657	85	612	79	532	69.1	4.6
32		1,2,3-Trichlorobenzene	560	73	543	71	553	72	583	76	534	69	554	99.7	3.4
33		1,2,4-Trichlorobenzene	685	89	645	84	664	86	696	90	635	82	665	101.0	3.9
34		1,3-Dichlorobenzene	623	81	608	79	623	81	641	83	619	80	623	102.8	1.9
35		1,3-Dichloropropane	655	85	638	83	663	86	688	89	662	86	661	100.4	2.7
36		1,4-Dichlorobenzene	602	78	598	78	606	79	633	82	607	79	609	102.7	2.3
37		2-Chlorotoluene	608	79	616	80	624	81	638	83	613	80	620	102.3	1.9
38		2,2-Dichloropropane	615	80	607	79	602	78	601	78	584	76	602	108.3	1.9
39		4-Chlorotoluene	609	79	605	79	604	78	635	83	610	79	612	99.3	2.1
40		Allyl Chloride	434	56	433	56	438	57	434	56	433	56	434	75.8	0.5
41		Bromobenzene	610	79	610	79	614	80	627	81	616	80	615	102.5	1.1
42		Bromochloromethane	655	85	646	84	659	86	674	88	645	84	656	98.5	1.8
43		Chlorobenzene	632	82	625	81	635	83	650	84	641	83	637	99.4	1.5
44		Chloroethane	634	82	658	86	638	83	621	81	632	82	636	91.2	2.1
45		Chloromethane	436	57	468	61	446	58	455	59	444	58	450	82.5	2.7
46		cis-1,2-Dichloroethene	668	87	660	86	671	87	695	90	680	88	675	98.9	2.0
47		Dibromochloromethane	604	78	595	77	612	79	630	82	616	80	611	98.2	2.2
48		Dibromomethane	688	89	684	89	688	89	739	96	698	91	699	102.3	3.3
49		Dichlorofluoromethane	604	78	611	79	608	79	609	79	613	80	609	94.2	0.5
50		Di-Isopropyl ether	679	88	667	87	681	88	707	92	678	88	682	102.0	2.2
51		Ethyl Ether	676	88	655	85	681	88	713	93	683	89	681	96.7	3.0
52		Hexachlorobutadiene	588	76	577	75	600	78	620	81	591	77	532	69.1	3.1
53		Isopropylbenzene	644	84	642	83	647	84	652	85	640	83	645	100.1	0.8
54		n-Butylbenzene	540	70	522	68	520	68	552	72	513	67	529	86.5	3.0
55		n-Propylbenzene	617	80	613	80	615	80	630	82	613	80	617	94.5	1.2
56		p-Isopropyltoluene	651	85	646	84	632	82	663	86	638	83	646	92.7	1.9
57		sec-Butylbenzene	674	88	666	87	669	87	690	90	661	86	672	98.3	1.6
58		tert-Butylbenzene	670	87	667	87	682	89	702	91	673	87	679	100.1	2.1
59		Tetrachloroethene	634	82	632	82	626	81	644	84	647	84	636	99.1	1.3
60		trans-1,2-Dichloroethene	634	82	627	81	625	81	642	83	632	82	632	93.8	1.1
61		Trichloroethene	647	84	640	83	639	83	668	87	664	86	651	86.3	2.1
62		Trichlorofluoromethane	597	78	636	83	604	78	572	74	596	77	601	94.5	3.9
63		Trichlorotrifluoroethane	537	70	569	74	548	71	514	67	538	70	541	101.7	3.7

* Denotes analyte required to be added to this study by the WDNR and which must pass the imposed criteria to gain acceptance for this method in Wisconsin.

Table 26

Biological Degradation in Soils Using an Aqueous Spiking Solution

Ottawa Sand

	spike level ug/kg	% rec. 1 Day	% rec. 2 Day	% rec. 3 Day	% rec. 4 Day	% rec. 7 Day
Benzene	372	99.1	114	74.6	70.8	72.4
Toluene	329	98.2	112	76.3	68.5	71.2
Ethylbenzene	197	98.6	112	83.7	71.0	78.4
M-P Xylene	384	97.1	107	81.3	66.4	70.8
O- Xylene	219	97.1	104	78.3	68.6	75.1

Ust Contaminated Soil

	spike level ug/kg	% rec. 1 Day	% rec. 2 Day	% rec. 3 Day	% rec. 4 Day	% rec. 7 Day
Benzene	354	66.4	108.6	53.8	45.2	13.7
Toluene	329	73.8	99.8	49.9	34.9	10.0
Ethylbenzene	201	81.3	99.1	83.6	64.7	42.0
M-P Xylene	404	80.6	89.4	55.3	34.4	15.7
O- Xylene	210	78.5	94.8	104.1	86.9	84.0

Biologically Active Garden Soil

	spike level ug/kg	% rec. 1 Day	% rec. 2 Day	% rec. 3 Day	% rec. 4 Day	% rec. 7 Day
Benzene	292	91.4	75.8	75.3	54.2	33.2
Toluene	269	95.4	73.1	77.5	56.7	35.4
Ethylbenzene	167	122.8	104.4	97.6	85.6	82.0
M-P Xylene	319	132.7	106.2	100.5	88.7	92.9
O- Xylene	188	130.9	119.5	100.5	92.3	106.2

RECOVERY OF VOCS FROM SOILS WITH AND WITHOUT METHANOL PRESERVATION

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ABSTRACT

Four sterilized reference soils were fortified with nine Volatile Organic Compounds (VOCs), then aged from three to nineteen months in sealed glass ampoules. Prior to analysis ampoules were placed in sealed vials with water or methanol and then shattered, to allow the solvent to contact the soil. Samples were then analyzed in triplicate by dynamic headspace equilibrium (purge and trap) or static headspace equilibrium. Non preserved soil recoveries are compared to soil preserved with methanol for up to 32 days. Recovery of VOCs from soil were found to be dependent upon both the physiochemical properties of the VOC and the soil. Fortification technique and time had a significant impact on recovery of VOCs from soil, indicating that the mechanism and duration of soil contamination is a key factor in VOC recovery. Increasing contact time of the soil with methanol resulted in a corresponding increase in VOC recovery. Sonication and temperature effects were minor in comparison to solvent contact time. We strongly recommend that if the high level (methanol preservation) option of Method 5035 is selected the methanol/soil contact time be held constant and all sample vials be prepared in the same manor. The fugacity model generally over predicted the concentration of VOCs in the soil phase when evaluating soil/vapor equilibrium. The fugacity model generally over predicted the concentration VOCs in the aqueous phase when evaluating soil/water equilibrium. There were exceptions to both of these trends depending upon soil type and analyte. The fugacity model commonly employed for risk assessment is a poor predictor of VOC phase distributions for any soil type other than sand.

INTRODUCTION

Methanol preservation of soil samples has gained considerable interest with the promulgation of EPA SW-846 method 5035.[1] Methanol is a preservative which both eliminates biodegradation and substantially reduces the volatilization of VOCs during sample transport, handling and storage.[2] Many states are in the process of reevaluating their policy on VOC sample handling, and methanol field preservation is one of the techniques under consideration. Numerous researchers have shown higher recoveries of VOCs, when soil samples are either preserved or extracted with methanol.[3,4] The scientific literature has also sighted that slow sorption/desorption mechanisms play a significant role in the aging of soils, which impacts the recoverability of VOCs.[5,6]

By eliminating both biodegradation and volatilization of VOCs from the equation, one can evaluate the impact of methanol preservation on the recovery of VOCs from soil. The mechanisms of VOC partitioning can then be accessed with fugacity models which are commonly used in risk assessment. Analytical techniques can also be compared on an unbiased basis. A critical question to be answered is whether or not methanol preservation/ extraction will lead to an overestimation of groundwater concentrations when employing standard risk assessment techniques.

EXPERIMENTAL

Four soils, Ottawa Sand, Yokene Clay, Ft. Edwards Clay and CRREL Silt/Sand were dried, passed through a 30 mesh sieve then sent for physical characterization (Table 1). Each soil was then submitted to the Phoenix Memorial Laboratory at the University of Michigan for sterilization by gamma irradiated in the Ford nuclear reactor. It should be noted that PCE was a background contaminate in the CRREL soil.

Two sets of quadruplicate ampoules were prepared of each soil type, for the aqueous fortification study. One gram dry weight was transferred to one milliliter ampoules for direct vapor partitioning analysis and three grams were transferred to two milliliter ampoules for methanol preservation. The ampoules were then spiked with trans-1,2-dichloroethylene (TDCE), cis-1,2-dichloroethylene (CDCE), trichloroethylene (TCE), tetrachloroethylene (PCE), benzene, toluene, ethylbenzene and p-xylene, and treated with distilled VOC free water to create samples of identical analyte concentrations and moisture contents. The target concentration for each analyte was 0.2 mg/Kg. The ampoules were then flame sealed in a laminar flow hood. All ampoules were subjected to three freeze/thaw cycles over a 98 day period prior to analysis.

Twenty-two vials containing two grams of CRREL silt/sand were allowed to vapor fortify at 20ºC in a 5.6 L desiccator for 593 days. The fortification solution contained 170-320 ug each; TDCE, CDCE, TCE, PCE, benzene, toluene, ethylbenzene, o-xylene and p-xylene, in one milliliter of tetraglyme plus 40 mg of methanol. The expected analyte concentration from the vapor fortification process was between two and five mg/Kg. As with the aqueous fortified samples the ampoules were then flame sealed after the treatment period.

Samples were analyzed at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) by headspace gas chromatography with photo ionization detection (HS/GC/PID) and at TriMatrix Laboratory in Grand Rapids, Michigan by purge and trap gas chromatography with mass spectrometry (PT/GC/MS). Samples were analyzed in triplicate by both direct vapor equilibrium and methanol extraction techniques. The one milliliter ampoule was placed inside the headspace or purge and trap vessel along with the appropriate volumes of water and internal standards. The vessels were then shaken by hand until the ampoules fragmented completely. In the case of methanol extraction the three milliliter ampoule was placed in a vessel containing three ml of VOC free methanol. The vessel was then hand shaken until the vial fragmented, exposing the soil to the methanol. Approximately 100-200 µL of methanol was then removed from the soil and injected in a prepared vapor equilibrium vial for analysis by either the headspace or purge and trap technique.

Samples were analyzed on day zero by both soil/aqueous vapor equilibrium techniques and by methanol extraction. A series of predefined methanol contact times ranging from 30 minutes to 30 days were established at the onset of the study. All vials for methanol extraction/preservation were prepared on day zero, but methanol was not withdrawn for analysis until their scheduled analysis time. Several of the vials were sonicated for 30 minutes at 40ºC prior to analysis at pre-selected time periods.

MODELING

An inter-phase partitioning model was evaluated against experimental results to determine how accurately standard fugacity models predict phase partitioning. Inter-phase fugacity models are the basis for fate, transport and risk assessment predictions and form the foundation from which regulatory decisions are made. Modeling was completed by Tim Mayotte with Golder Associates in Lansing, Michigan.[7]

RESULTS

Results from the aqueous fortification study and vapor fortification study are summarized in tables two and three respectively. Results from the PT/GC/MS and HS/GC/PID vapor partitioning techniques correlated very closely. Values derived from the two techniques were nearly always within the standard deviation of the analysis technique. The average aqueous, low level purge and trap results were slightly greater than those for headspace, indicating that dynamic vapor partitioning may be causing a slight shift in the soil/water equilibrium.

DICUSSION

Fugacity modeling was used to predict the phase distribution of VOCs in the sealed aqueous spiked ampoules. Results indicated that for Ottawa sand 50% to 80% of the VOCs would volatilize to the headspace of the vial, 15% to 30% of the VOCs would partition into the aqueous phase and 1% to 20% would remain on the soil. Compounds with higher vapor pressures partitioned more readily into the vapor phase. This model simulation shows how easily VOCs can be lost to the atmosphere if great care in not taken during sample collection and handling. For all other soil types the fugacity model predicted from 40% to 98% of the VOC would be associated with the soil phase. This shows the significant impact of organic matter (%carbon) on the fugacity models. Compounds with greater octanol/water partition coefficients (K_{OW}) such as PCE and benzene, toluene, ethylbenzene and xylene (BTEX) are predicted to partition greater than 80% into the soil phase. The predominate factors influencing fugacity models commonly used for transport, fate and risk assessment are the VOC's vapor pressure, the VOC's K_{OW} and the percent carbon of the soil. Surface adsorption or other physio-chemical mechanisms which are know to occur on soil particle surfaces and in interstitial spaces have no influence on fugacity models commonly in use.

Aqueous fortification study results showed 100% recovery of VOCs from Ottawa sand. Recoveries decreased to the range of 15% to 50% for the CRREL silt/sand. The Ft. Edwards and Yokene clays showed VOC recoveries falling somewhere between those observed in the Ottawa sand and CRREL soil. Fugacity models predicted Ottawa sand recoveries within experimental error. Fugacity predictions generally followed the same compound to compound recovery trend for all other soil types, however model predictions generally varied from 10% to 100% of the experimental values. Prediction accuracy was dependent upon soil type and compound. The purgable fraction concentration for TDCE and CDCE was over predicted by 8 fold and 4 fold respectively for the CRREL soil.

A previous 14 day aqueous fortification of BTEX compounds on CRREL silt/sand yielded recoveries of 50% to 60% for all compounds. The current 98 day aqueous fortification study showed recoveries decreasing with compound hydrophobicity ranging from 50% for benzene down to only 30% for xylene. This indicates that VOC/soil contact time, often referred to as "aging", retards the movement of VOCs from the soil phase to the aqueous and vapor phases.

A preliminary 7 day vapor fortification study with benzene, toluene, TCE and TDCE on CRREL silt/sand showed an uptake of only about 10 µg of VOC per gram of soil. The 593 day vapor fortification study showed soil uptakes increasing with VOC hydrophobicity and ranging from 120 µg/g for TDCE to 300 µg/g for toluene. This data once again indicates that VOC/soil contact time or "aging" plays an important role in VOC uptake and release for certain soil types, due to the slow sorption/desorption mechanism.

Samples which were preserved with methanol and then analyzed within 1-2 hours showed recoveries equivalent to direct aqueous vapor equilibrium for aqueous fortified samples aging 98 days. Near 100% recovery was observed for all VOCs in Ottawa sand with recoveries gradually decreasing by soil type (Ottawa sand > Ft. Edwards Clay > Yokene clay > CRREL silt/sand). The CRREL silt/sand showed VOC recoveries ranging from 25% to 50%.

Methanol contact time ranging from 30 minutes to 30 days was evaluated with vapor fortified CRREL soil after aging 593 days. All VOC recoveries steadily increased with methanol contact time, in some cases more than an order of magnitude. The rate of increase decreased with compound hydrophobicity. These results are in agreement with previous research on less volatile organic compounds. The data demonstrates that the transport of VOCs from certain soil matrices can be extremely slow and is very much dependent upon contamination age.

Sonication is sometimes recommended in conjunction with method 5035 to reduce the variability in results due to methanol contact time. Sonication imparts both mechanical and thermal energy into the sample which should have a significant impact on the thermodynamics of the system. We performed a series of parallel studies where both sonicated (30 minutes at 40ºC) and static samples were extracted and analyzed at the same methanol contact times. Contact times ranged from 3.5 hours to 101 days. Some improvement was noted in extraction efficiency at the 3.5 hour equilibration period, however any added benefits of sonication were lost after only 24 hours of equilibration. No statistical difference could be detected between samples that were and were not sonicated when methanol contact times were 24 hours or greater.

Standard inter-phase model techniques were used to predict partitioning of VOCs from CRREL silt/sand into the aqueous and gas phases. Experimental aqueous vapor equilibrium results for the 593 day vapor fortified samples were compared to fugacity calculations. An initial soil VOC mass as determined by the 30 day methanol contact time was used, since the true soil concentration is not known. We recognize that the 30 day methanol contact time result will be conservative, therefore this is the minimum mass of VOC present in the soil. We do not believe that the total mass of VOCs on the soil is dramatically greater than the 30 day result, as the rate of VOC increase had decreased substantially by 30 days. The fugacity model was found to dramatically over predict the mass of VOCs expected to partition into the aqueous and gas phases (Figure 1). The over prediction ranged from 100% to more than 23 fold depending upon the compound. The over prediction is conservative since more VOC may actually be present in the soil.

Since standard fugacity calculations failed significantly using a three compartment model we took a step back and used a two compartment inter-phase model to predict the vapor fortification process. The model predicted fairly closely the gas/soil partitioning of benzene and TCE, but under estimated the movement of TDCE and CDCE from the gas phase to the soil (Figure 2). Toluene, ethylbenzene, p-xylene and PCE movement from the gas phase to the soil phase was either consistently overestimated or we only achieved 50% recovery of VOCs from the CRREL silt/sand even after a 30 day methanol contact period.

CONCLUSIONS

We highly recommend that a fixed methanol soil contact time be established for method 5035 and that the methanol be decanted from the soil after the established contact period. If this is not done test results will simply not be comparable! We also question the use of methanol preservation/extraction for applications other than identifying contamination locations. The common practice of assuming infinite depletion for contamination sources in risk assessment and setting cleanup limits is even less appropriate when using methanol extraction data. Methanol

extraction data should never be used for transport, fate or risk assessment, since in the real world we are dealing with groundwater and not "ground-methanol". If equilibrium can not be reached after 30 days of contact with an organic solvent, how long will it take to reach equilibrium between groundwater and soil? The extremely slow release of organic constituents form aged soil may allow time for biota to acclimate and degrade many organic contaminates. The could this be why natural attenuation is showing so much promise.

We have demonstrated that standard fugacity based inter-phase partitioning models do a good job of predicting the movement of VOCs between air, water and soil, when the soil is sand and the contamination is recent. Unfortunately for the majority of sites this is not the case. The CRREL silt/sand was found to have greater retention of VOCs than Yokene clay, which had three times more organic mater, surface area and cation exchange capacity. This shows that these properties are not the only factors effecting gas/soil and water/soil partitioning. Yet, existing fugacity based inter-phase partitioning models place nearly 100% of the soil sorption capacity on the percent organic matter it contains. The CRREL silt/sand retained VOCs to a much greater extent than predicted by the fugacity model, which indicates that other significant factors must be included in our models to get accurate estimates of VOC fate and transport in the environment. Additional research is needed in this area. Silicate, aluminum and clay mineral surface adsorption along with the nature of organic mater present in the soil must be taken into consideration at a minimum. How can we make risk assessment and regulatory policy decisions related to VOC contamination and exposure when our basic assumptions are flawed?

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REFERENCES

1. *Test Methods for Evaluating Solid Waste;* U.S. Environmental Protection Agency, National Technical Information Service: Washington, DC, 1996
2. Hewitt, A.D. "Evaluation of Methanol and $NaHSO_4$ for Preservation of Volatile Organic Compounds in Soil Samples", *American Environmental Laboratory,* 8: pp. 16-18, 1995
3. Minnich, M.M.; Schumacher, B.A. "Comparison of soil Gas, Heated Headspace, and Methanol Extraction Techniques for Soil Volatile Organic Compound Quantification", *12th Annual Waste Testing & Quality Assurance Symposium,* July, 1996
4. Minnich, M.M., "Behavior and Determination of Volatile Organic Compounds in Soil - A Literature Review", *EPA 600/R-93/140*, 1993
5. Pignatello, J.; Xing, B. "Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles", *Environmental Science & Technology,* Vol. 30 No. 1, 1996
6. Ball, W.P. et al. "Hot Methanol Extraction for the Analysis of Volatile Organic Chemicals in Subsurface Core Samples from Dover Air Force Base, Delaware", *Water Monitoring & Remediation,* Vol. 17, No. 1, 1997
7. Mayotte, T.J. "Observations from Theoretical Interphase Mass Partitioning Modeling and Comparisons with Analytical Data", *Golder Associates Report 993-8491,* 26 March, 1999.

Table 1. Soil Physical/Chemical Properties

	pH	CEC	BET	C	OM	Ca	Mg
Units	**s.u.**	**me100g**	**m2/g**	**%**	**%**	**ppm**	**ppm**
Ottawa Sand	7.7	0.1	0.09	<0.1	<0.1	150	7
Ft Edwards Clay	8.3	13	43.7	0.8	1.4	4350	797
Yokene Clay	7.2	35	14.9	2.3	3.9	2705	841
CRREL Silt/Sand	7.5	10	5.2	0.7	1.2	1000	20

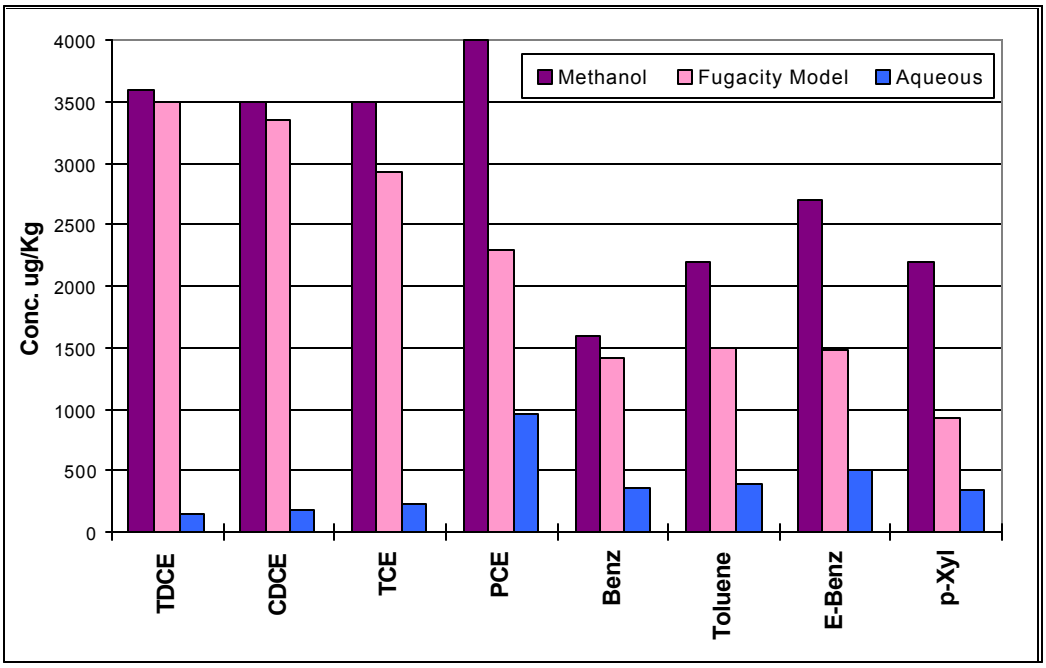

Figure 1

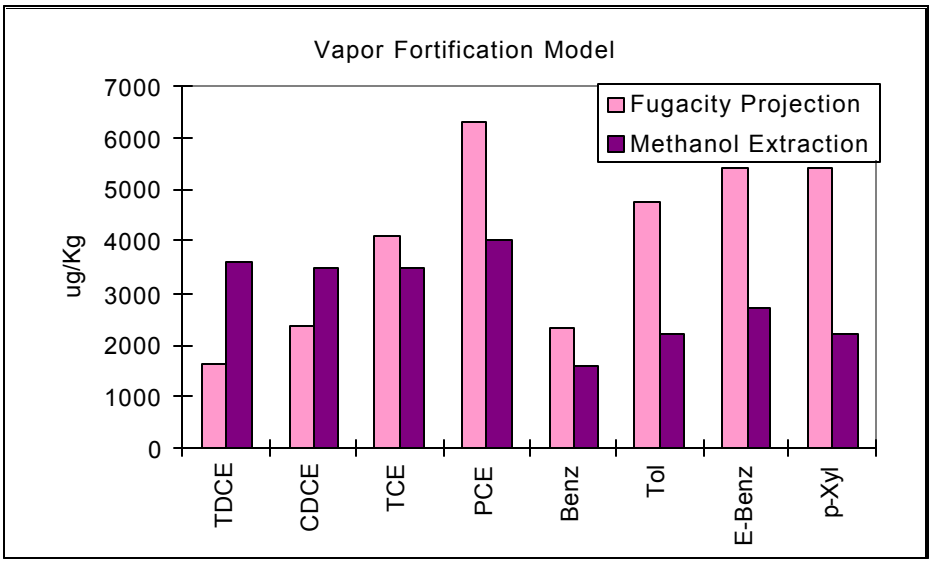

Figure 2

Table 2. Three Month Aqueous Fortification of soils (ng/g)

Soil Type		Day 0	Day 0	Day 0	Day 2	Day 1	Day 2
cis-1,2-DCE	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	28.5	18.8	53.2	71.0	114.0	130.0	159.0
Yokene	102.5	104.5	116.0	132.0	137.0	137.0	
Ft. Edw.	139.5	113.0	137.0	176.0	176.0	176.0	
Ottawa	163.0	163.8	179.0	185.0	174.0	181.0	181.0
trans-1,2-DCE	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	57.3	21.8	24.3	71.1	118.0	131.0	136.0
Yokene	144.3	135.0	87.8	109.0	115.0		
Ft. Edw.	191.8	141.0	113.0	165.0	171.0		
Ottawa	214.3	201.5	145.0	162.0	157.0	157.0	159.0
Benzene	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	108.0	92.5	92.0	96.4	120.0	127.0	148.0
Yokene	145.0	133.5	122.0	130.0	134.0		
Ft. Edw.	188.3	145.5	153.0	174.0	175.0		
Ottawa	209.0	202.5	174.0	175.0	171.0	172.0	176.0
TCE	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	520.3	436.3	379.0	460.0	735.0	897.0	1350.0
Yokene	153.5	139.8	140.0	161.0	166.0		
Ft. Edw.	209.5	153.0	179.0	215.0	216.0		
Ottawa	224.3	216.5	219.0	224.0	213.0	213.0	213.0
Toluene	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	84.5	90.5	67.8	85.5	118.0	127.0	153.0
Yokene	147.3	162.3	128.0	144.0	145.0		
Ft. Edw.	204.3	179.0	175.0	189.0	186.0		
Ottawa	218.7	215.5	202.0	196.0	191.0	189.0	193.0
PCE	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	104.8	97.8	102.0	124.0	139.0	143.0	162.0
Yokene	114.0	139.3	109.0	131.0	133.0		
Ft. Edw.	119.6	116.0	154.0	185.0	188.0		
Ottawa	173.7	170.3	184.0	172.0	173.0	167.0	172.0
Ethylbenzene	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CRREL	78.0	90.0	63.8	84.1	106.0	112.0	124.0
Yokene	110.3	127.5	92.3	118.0	117.0		
Ft. Edw.	160.3	123.0	148.0	145.0	141.0		
Ottawa	200.7	176.0	184.0	159.0	157.0	156.0	162.0
m+p-Xylene	**P&T Low**	**P&T High**	**HS Low**	**HS High**	**HS Sonc**	**HS Sonc**	**HS Sonc**
CIRREL	57.5	74.5	44.2	67.6	98.5	110.0	122.0
Yokene	101.5	131.8	89.0	113.0	118.0		
Ft. Edw.	154.8	129.5	155.0	158.0	151.0		
Ottawa	191.3	185.8	188.0	160.0	158.0	159.0	162.0

539 DAY VAPOR FORTIFIED CRREL SOIL STUDY

3/5/1999 Revision - Corrected for Standard Differences but not Methanol Loss (ug/kg)

	TDCE	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
	123	151	266	197	301	736	433	286	672
HS	5.13	4.04	11.24	8.39	30.37	5.00	1.15	2.31	5.00
	a	a	a	a	a,b	a,b	a,b	a	a,b
	141	192	350	221	399	954	563	370	910
PT	44.30	30.92	30.37	37.16	58.00	121.66	63.85	60.62	101.80
	a	a	b	a	a,b,c	a,b	a,b,c	a	a,b
	285	253	316	336	440	1213	675	539	1134
HS 30 min	38.68	35.57	28.75	27.02	35.85	104.08	35.13	46.50	55.68
	a	a	a,b	a	a,b,c	c	b,c	b	c
	290	246	336	264	465	1152	730	572	1118
PT 30 min	28.38	23.71	14.93	32.53	36.47	132.56	97.89	109.89	171.64
	a	a	b	a	b,c	b,c	c	b	b,c
	864	655	468	647	646	1681	1006	822	1445
HS 4 hour	130.50	143.26	38.18	62.27	70.50	100.66	93.09	93.74	105.83
	b	b	c	c	d	d,e	d	c	d
	779	486	447	481	632	1492	962	835	1480
PT 4 hour	62.39	24.95	10.79	54.64	60.34	180.30	147.73	269.37	293.79
	b	b	c	b	d	d	d	c	d
	1940	1424	763	1322	1005	2501	1435	1250	1857
HS 1 day	234.59	137.48	43.10	83.27	47.26	140.12	40.00	25.17	55.68
	c	c,d	d,e,f	d,e	e,f	g,h	e	d	e
	2402	1567	820	1329	1235	2528	1762	1495	2489
PT 1 day	205.37	126.26	20.79	128.78	106.51	116.94	211.09	83.65	277.16
	d,e	c,d,e	d,e,f,g	d,e,f	f,g,h	g,h	f	e,f	g
	1940	1453	776	1368	1028	2546	1457	1269	1880
HS 1 sonc	215.48	106.93	31.34	60.00	65.06	95.39	49.33	70.24	76.38
	c	c,d	d,e,f	d,e,f	e,f	g,h	e	d	e
	2450	1506	813	1244	1137	2390	1506	1456	2142
PT 1 sonc	273.01	119.78	26.39	44.64	60.67	50.47	63.11	29.67	102.21
	d,e	c,d,e	d,e,f,g	d,e	e,f,g	g	e	e,f	f,h
	2233	1657	827	1541	1159	2611	1544	1364	2108
HS 4 day	155.88	109.70	22.74	51.96	55.08	50.33	75.06	36.06	112.69
	d,e	d,e,f	d,e,f,g	f,g	f,g	f,g,h	e	d,e	f,h
	2885	1777	875	1458	1264	2434	1563	1495	2166
PT 4 day	157.09	132.02	16.65	46.78	17.16	98.40	57.01	83.65	60.35
	f	f	g	e,f	f,g,h	g	e	e,f	f,h
	2273	1813	849	1671	1213	2649	1573	1383	2158
HS 7 day	145.72	131.15	26.10	98.49	62.45	51.32	41.63	45.83	55.68
	d,e	e,f	f,g	g	f,g,h	g,h	e	d,e,f	f,h
	2951	2001	871	1517	1335	2373	1567	1456	2162
PT 7 day	213.56	30.62	24.66	81.01	26.31	116.50	24.03	29.67	12.34
	f	g	f,g	f	g,h,j	g	e	e,f	f,h
	2627	2240	1003	2021	1410	2856	1746	1555	2345
HS 15 day	17.32	119.30	0.00	102.14	52.92	69.28	64.29	75.06	76.38
	e,f	h	h	h	h,j	j	f	e,f	f,g,h
	2642	1999	813	1501	1383	1962	1432	1353	1974
PT 14 day	190.55	146.69	39.17	88.37	270.08	104.43	33.95	39.32	62.63
	e,f	g	f,g	f	h,j	f	e	d,e	e,f,h
	3263	3257	1383	3037	1959	3546	2176	2095	2713
HS 28 day	276.10	177.86	64.29	156.31	90.74	125.03	98.49	86.22	160.73
	g	i	i	i	k	k	g	g	h,j
	1725	2536	971	2198	1781	1830	1544	1515	2183
PT 28 day	230.12	185.75	104.43	168.82	77.69	255.59	137.89	97.09	130.09
	c	h	h	h	k	e,f	e	e,f	g,h
	3520	3478	1517	3314	2105	3824	2266	2120	2730
HS 32 day	351.06	126.62	65.57	112.40	40.41	34.64	115.47	121.24	117.90
	g	i	i	i	k	k	g	g	i
	3617	4432	1905	4278	2807	4789	3072	2927	3609
PT 32 day	1264.56	123.31	96.23	156.98	163.76	493.28	435.92	458.00	407.78
	g	k	k	k	l	l	g	g	j

Values with common letter are not significantly different at the 95% confidence interval (ANOVA and fishers protected LSD)

PAH SEPARATION AND DETECTION BY GC/FID. BRINGING METHOD 8100 INTO THE 90'S.

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Method 8100 Revision 0 (the original version) was promulgated in September of 1986. This method was based upon a packed column GC method that did not have the capability of adequately resolving 4 critical pairs of PAHs. We will describe part of a two-year study, which has resulted in a revised capillary GC method. We will describe the multilab validation, which was carried out on an optimized PAH, GC capillary column method. The result was 12 methods which provided adequate resolution of PAHs regulated by the US EPA, including the four pairs of compounds not resolved in the original Method 8100. Further, 4 of the methods will yield results adequate for the EPA method 8270 (semi-volatiles) where a GC/MS is used. Using arbitrarily defined as the best set of conditions (best method) in one of the 12 methods, we placed 10 columns in three different laboratories and carried out a round robin study. The results of this round robin will be presented.

Column#	Retention time Peak 1	Retention Time Peak 16	Resolution Factor 11-12	Resolution Factor 14-15
1-gr3	4.273	42.143	1.58	3.47
2-gr4	5.148	45.138	1.65	3.29
3-gr1	4.311	42.143	1.59	3.50
4-gr2	4.342	42.343	1.62	3.54
5-lg2	4.306	42.143	1.58	3.54
6-lg1	4.273	42.143	1.58	3.53
7-dg1	4.417	42.663	1.60	3.46
8-dg2	4.340	42.229	1.56	3.41
9-dg3	4.379	42.430	1.61	3.36
10-lg3	4.311	42.143	1.61	3.48
Mean	4.410	42.625	1.60	3.46
Standard Deviation	0.342	1.487	0.033	0.090
% RSD	7.7	3.5	2.0	2.6

The table shows only a brief amount of the data acquired in the different labs. We will describe the features and benefits of this revision of Method 8100 in detail, including some comparisons between the HPLC method and the GC (GC/MS) methods with detection limits and other data.

EXTRACTION OF DIESEL RANGE ORGANICS (DRO) AND WASTE OIL ORGANICS (WOO) FROM SOILS AND SEDIMENTS: EXPANDING METHOD 3545A (PRESSURIZED FLUID EXTRACTION)

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Method 3545A specifies the use of Pressurized Fluid Extraction (PFE) for the extraction of organic compounds from soils and other solid wastes. This technique uses conventional liquid solvents at elevated pressures and temperatures to obtain rapid and complete extractions. PFE has been compared to Soxhlet and ultrasonic

extraction for the extraction of compounds covered by RCRA, and in all cases, PFE gives equivalent or superior results. Currently, Method 3545A covers the following compounds: bases/neutrals and acids (BNAs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), organophosphorus pesticides (OPPs), chlorinated phenoxy herbicides, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from soils, clays, sediments, sludges, and solid wastes. However, validation data for the extraction of hydrocarbons have not been submitted for inclusion in Method 3545A. The purpose of this presentation is to discuss the method development results and validation data for the extension of Method 3545A to diesel range organics (DRO) and waste oil organics (WOO).

Prior to this work, data had been reported[1] showing that two or more complete extractions with PFE were needed to get quantitative recovery of TPH from wet clay samples when using IR-transparent solvents such as perchloroethylene (PERC). For the validation data set, we did not want to use two or more extractions, and we wanted to use a GC method for the determinative step. This necessitated the use of other solvents and operating conditions. As part of the method development, six different solvents were investigated: hexane, heptane, methylene chloride, and 1:1 mixtures of each of these solvents with acetone. Temperatures ranging from 100 ºC to 200 ºC were investigated. Wet as well as dry samples were investigated. The conditions that were identified from the method development phase are methylene chloride/acetone (1:1), 175 ºC with 15 mL total solvent and 15 minutes total time for 10-g samples. The recovery from certified soils using these conditions averaged 116% with 3.6% RSD (relative standard deviation).

After the method development phase, we conducted a validation phase. This consisted of two parts. First, we determined the bias and precision of the method using three different matrices (clay, loam, and sand) and at two different concentrations (5 and 2000 mg/kg). These samples were spiked with both #2 diesel and 30w motor oil. GC was the determinative step in all cases. Sample extracts were treated with standard clean up procedures using silica gel and Na_2SO_4 and concentrated to 1 mL. Second, portions of real-world samples were extracted using PFE, automated Soxhlet, and ultrasonic extraction. In all cases, the bias and precision using PFE were comparable or superior to the results obtained using the other techniques. The complete data set will be discussed in this presentation.

These data have been submitted for consideration to be included in Update IVb of the SW-846 Methods Manual so that Method 3545A can be extended to include DRO and WOO.

Reference

1. M.L. Bruce, *Proceedings of the Eleventh Annual Waste Testing and Quality Assurance Symposium*, American Chemical Society, 1995, 114-120.

THE ANALYSIS OF CARBAMATES USING LC/MS

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ABSTRACT

The analysis of carbamates has received renewed interest recently in light of their implication as potential endocrine disrupters, and their use as common pesticides for food products. Before their use, carbamates must be manufactured from various raw materials that are themselves potential endocrine disrupters, and the manufacturing waste must be characterized prior to disposal. All total, carbamates and related products are entering into eco-system with potential adverse effects.

The EPA Office of Solid Waste has recently published a final rule covering the analysis of 40 carbamate waste constituents.[1] To monitor all these currently requires 6 different analytical methods from GC to LC. Several of the listed carbamate methods utilize mass spectrometry detection.

This presentation will discuss the analysis of several commonly used carbamates using HPLC-Positive Electrospray Mass Spectrometry, a preliminary new method similar to Method 8321A using thermospray mass spec detection. Linearity will be demonstrated from 5 to 1000 ppb which covers the general calibration range, with an LOD of 1 to 2 ppb and with %RSD of response of less than 10%. Supporting the utility of the LC/MS method is the analysis of drinking water, including spiked carbamate recovery, and a vegetable matrix.

This work will shed insight into how new mass spectrometry technology can be applied to enhance the monitoring of environmental carbamate pollutants as well as other organics.

INTRODUCTION

Carbamates are commercially available pesticides derived from carbamic acid. Highly effective and having a broad spectrum of activity, carbamates are used worldwide to protect crops and other vegetation from the ravages of insect pests.

Carbamates, their intermediaries, their degradation products, and their metabolites are of great concern to members of the regulatory and scientific communities as more and more drinking water sources are testing positive for the presence of carbamates. They find their way into the aquifers and surface water through agriculture runoff after being directly applied to food crops such as grains, fruits, and vegetables. If food crops are harvested too soon after application, residues and their byproducts may remain on the produce. Additionally buyers of grain, fruits, and vegetables are becoming increasingly vigilant for pesticide residues due to their toxic nature.

In an effort to protect drinking water resources, the US Environmental Protection Agency and other international governing bodies now regulate pesticide use and require routine monitoring of drinking and raw source water. This effort has been extended to solid waste products such as soil and hazardous waste disposal, all of which could potentially comtaminate the drinking water supply.

EXPERIMENTAL

In this study, various instrumental conditions were examined and optimized for the analysis of a 10 carbamate component standard mixture without the use of pre or post column derivatization.

System:	Waters Alliance® LC/MS with MassLynx™ system control & data processing
Mass Spec:	Waters ZMD Detector (4000 amu mass range)
MS Interface:	Positive Electrospray (ESI+)
Column:	Waters Symmetry® C_{18}, 1 mm x 150 mm
Temperature:	35° C
Mobile Phase:	Linear Gradient from 10%-80% MeOH in 10 mM NH_4OAc
Flow Rate:	75 µL/min
Injection Vol:	10 µL/min
Analysis Time:	18 minutes

For comparison purposes, a similar carbamate standard mixture and samples were analyzed using post column derivatization, the accepted method of analysis.

System:	Waters Alliance® System for Carbamate Analysis and Millennium^{32} system control & data processing
Column:	Waters Carbamate Column, 3.9 mm x 150 mm
Temperature:	30° C
Mobile Phase:	Multistep Gradient using MeOH / AcCN / Water
Flow Rate:	1.5 mL/min
Injection Vol:	400 µL/min
Post Column:	Dual post column reaction with NaOH and OPA @ 0.5 mL/min
Detection:	Fluorscence, 339 nm excitation, 445 nm emission
Analysis Time:	30 minutes

The 10 carbamates plus beta Naphthol working standards were prepared from an AccuStandard (New Haven, Conn.), M531 Carbamate Mixture, 0.1 mg/mL concentration in AcCN. Dilutions were made with 1 mM HCl (pH 3) for the post column method, and 100% MeOH for the mass spec method.

DISCUSSION

Figure 1 shows the total ion chromatogram from the full scan analysis of 20 ng (10 µL of 2 µg/L) of each of the 10 component carbamate mixture. Another carbamate standard at 10 µg on column was analyzed using the post column fluorescence method is shown in Figure 2. Note that using the MS separation conditions, the first 4 carbamates coelute, but are fully resolved with the post column method. For conventional carbamate identification and quantitation, carbamate resolution is critical. However, for mass spectrometry, resolution is not critical.

By extracting from the full scan, the $[M+H]^+$ or $[M + NH_4]^+$ ions specific to each coeluting compound, individual chromatograms can be resolved by the mass spectrometer, as shown in the insert of figure 1. This allows for other unknown carbamates or organics in a complex matrix, such as wastewater or solid waste, to be selectively detected, identified, and quantitated without the need for chromatographic resolution using complex gradient methods.

Figures 3 and 4 show the full scan mass spectra of aldicarb sulfoxide and aldicarb sulfone. Note that although similar in structure and in retention characteristics, they give unique mass spectra. The mass spectrometer was optimized using the cone voltage programmability capability of the Waters ZMD for response of the carbamate $[M+H]^+$ ion, except for oxamyl and aldicarb where the carbamate $[M + NH_4]^+$ ion was used. This feature allows the operator to change ionization cone voltage to maximize the response, and to switch between positive and negative electrospray within the same run, although negative electrospray$^-$ was not used for this study.

The carbamate mixture was re-analyzed and acquired in the SIR (single ion recording) mode, where the MS detector was set to detect only a single $[M+H]^+$ ion value. Each chromatogram only shows the single, individual carbamate in the mixture, and demonstrates the selectivity of mass spec detection. Concurrently, acquisition in the SIR mode also enhances sensitivity. This is a primary benefit of mass spec detection, which is shown in figure 5.

A series of 6 carbamate working calibration standards between 5 and 1000 ng/mL (ppb), representing between 50 and 10,000 pg on column, were analyzed in triplicate, and calibration curves generated using SIR response and a 1/x weighting. The 1/x weighting was used to minimize the statistical effect of the higher concentrations on the linear regression. Figure 6 shows the calibration curve for Carbofuran, a carbamate that coelutes with propoxur. Again, this demonstrates that resolution is not as important with MS detection as it is with conventional detection. The coefficient of determination for the weighted regressions is given in Table 1.

Table 1. Coefficient of Determination (r^2) Linearity

Carbamate	Coeff. Of Determination	Carbamate	Coeff. Of Determination
Aldicarb Sulfoxide	0.9969	Aldicarb	0.9963
Aldicarb Sulfoxide	0.9982	Propoxur	0.9963
Oxamyl	0.9990	Carbofuran	0.9981
Methomyl	0.9959	Carbaryl	0.9994
3-OH Carbofuran	0.9970	Methiocarb	0.9995

The lowest carbamate calibration standard, 5 ng/mL (ppb) or 50 pg on column, was analyzed 5 times to calculate the limit of detection, defined as 3 times the standard deviation, the limit of quantitation, defined as 10 times the standard deviation, and the precision, defined as %RSD = (mean)(100)/std dev). This data is tabulated in Table 2.

In real samples such as drinking water and vegetables, carbamates are typically present at concentrations near the limit of detection described above. Solid waste and aqueous samples are typically extracted using a methylene chloride liquid-liquid partitioning, and the methyene chloride is taken to dryness and resolubilized with methanol.[2] An alternative sample prep enrichment, eliminating the use of methylene chloride, was employed for a carbamate recovery from a typical drinking water sample.

Table 2. Mass Spec Carbamate Sensitivity and Precision

Carbamate	Limit of Detection ng/mL (ppb)	Limit of Quantitation ng/mL (ppb)	Response at 50 pg %RSD
Aldicarb Sulfoxide	0.8	2.6	3.5
Aldicarb Sulfone	1.8	6.1	9.6
Oxamyl	0.7	2.2	3.2
Methomyl	1.6	5.5	10.0
3-OH Carbofuran	0.4	1.4	2.1
Aldicarb	0.2	0.5	0.7
Propoxur	0.7	5.5	11.3
Carbofuran	0.9	3.0	7.5
Carbaryl	0.3	1.1	1.8
Methiocarb	0.4	1.4	2.0

Milford, Mass drinking water was spiked with 500 ng/L (500 ppt) of each carbamate. Two hundred and fifty (250) mLs was passed through a Waters Oasis® HLB Cartridge to retain the carbamates. The carbamates were eluted from the cartridge using 6 ml of 10% MeOH / MTBE. This solution was taken to dryness and resuspended in 1 mL of acetonitrile, which was used for MS analysis. This represents a 250-fold enrichment. The same sample was analyzed using the conventional post column fluorescence method. The recovery data and method comparison data are given in Table 3.

Table 3. Comparison of MS and Post Column (PCFD) Method Carbamate Recovery

Carbamate	Mass Spec %Recovery	Mass Spec %RSD	PCFD %Recovery	PCFD %RSD
Aldicarb Sulfoxide	74.8	19	54.7	0.5
Aldicarb Sulfone	88.7	16	98.7	4.0
Oxamyl	83.2	18	90.8	7.0
Methomyl	92.3	8.0	99.9	6.4
3-OH Carbofuran	101	8.6	98.7	2.3
Aldicarb	79.4	9.3	90.7	9.3
Propoxur	103	13	97.5	5.6
Carbofuran	95.6	7.5	97.2	4.7
Carbaryl	97.7	14	89.6	2.2
Methiocarb	81.2	14	91.6	2.2

The mass spec carbamate recoveries observed in this experiment are consistent with the recovery data using method 8231A published in SAIC Carbamate Method Evaluation Report.[3] Although the mass spec recoveries are lower than those determined by the conventional post column florescence method, this data indicates that both the mass spec method and the conventional post column fluorescence method yield acceptable results.

A solid vegetable sample, bell pepper, was prepared by an outside source using the State of Florida Modified–CDFA Multiresidue Method effective as of July 1998.[4] Fifty grams of vegetable is homogenized and extracted with acetonitrile. This extracted is passed over an aminopropyl solid phase extraction cartridge, the effluent taken to dryness and resolubilized in 1 mL of methanol.

The same extracted bell pepper sample was analyzed using both the LC/MS method and the PCFD method for comparison purposes. The PCFD method was performed several days after the LC/MS analysis. The results are summarized in Table 4, and the SIR chromatograms shown in figure 7 through 9.

These analyses indicated that the solid phase extraction procedure and both methods yield acceptable results.

Table 4. Analysis of Bell Pepper, data expressed as ppb

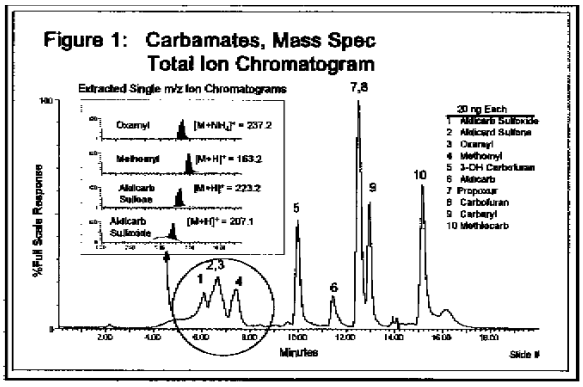
Methomyl		Oxamyl		Carbaryl		Propoxur	
PCFD	LC/MS	PCFD	LC/MS	PCFD	LC/MS	PCFD	LC/MS
46.0	46.5	ND	ND	ND	ND	293.8	276.5
411.5	342.5	ND	ND	ND	ND	319.7	323.5
32.5	40.5	ND	ND	ND	ND	298.6	241.0
ND	ND	32.4	48.0	14.2	13.5	280.6	263.5
ND	ND	54.1	76.0	136.7	154.5	290.5	341.5

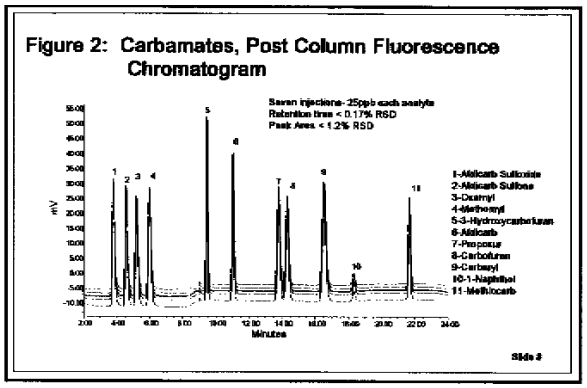
CONCLUSION

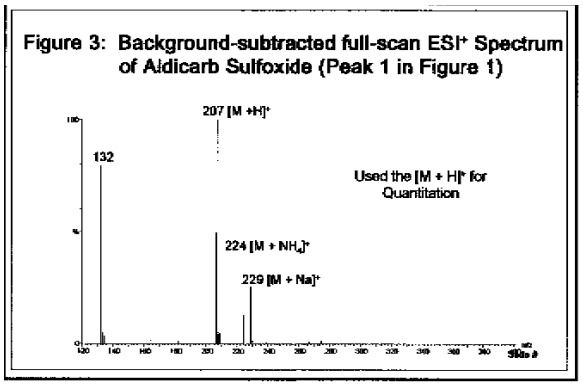
These data indicate that the use of positive electrospray mass spec detection is a viable technique for the analysis of carbamates in drinking water and on vegetables. The detection limit, precision, and %recovery show that this electrospray method gives equivalent results to the thermospray method described in 8321A. However, for best sensitivity, the conventional post column fluorescence method, providing detection below 0.5 µg/l (ppb), is the technique of choice.

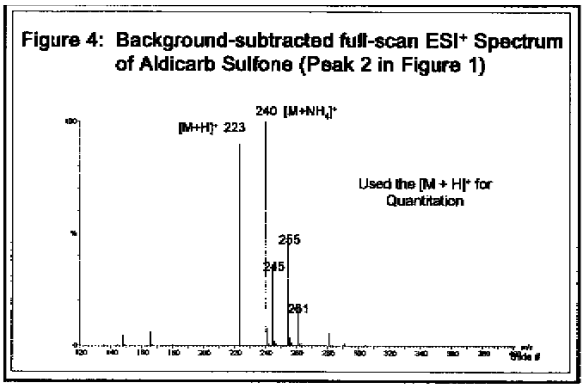
REFERENCES

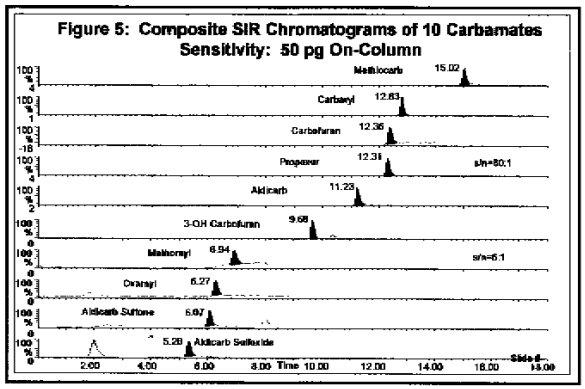
1. Emergency Revision of the Land Disposal Restrictions (LDR) Treatment Standards for Listed Hazardous Wastes from Carbamate Production, (63FR4740), Sept 4, 1998.
2. Method 8318, N-MethylCarbamates by High Performance Liquid Chromatography (HPLC), Rev 0, Sept 1994.
3. Carbamate Method Evaluation Report, prepared by SAIC, Dunn Loring VA, 22027, Aug 20, 1998, prepared for B. Lesnik, EPA Office of Solid Waste.
4. Chemical Residue Laboratory, Florida Dept of Agriculture & Cons Services, Florida Modified-CDFA Multiresidue Method, Rev 4, SOP# CR Method 42, July 1998.

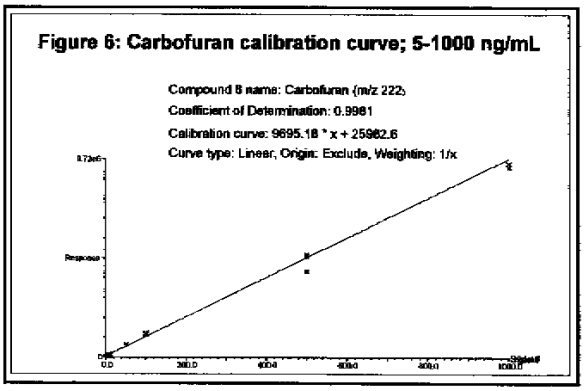


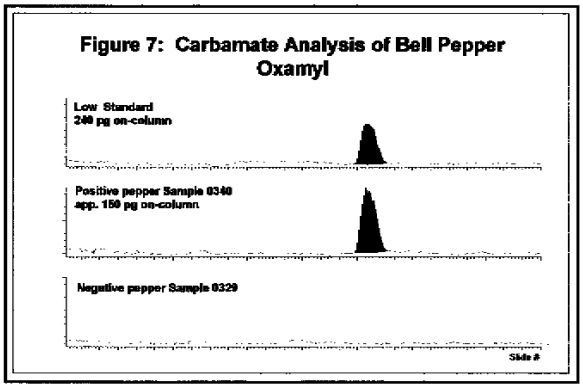


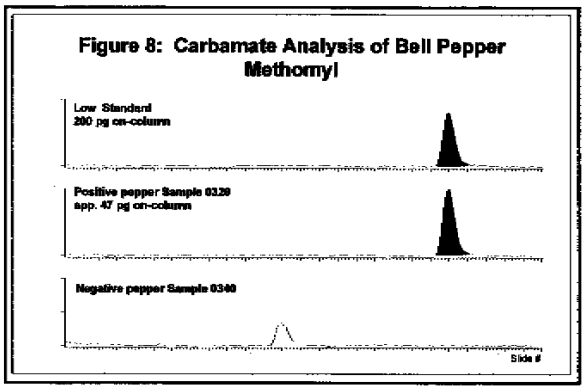


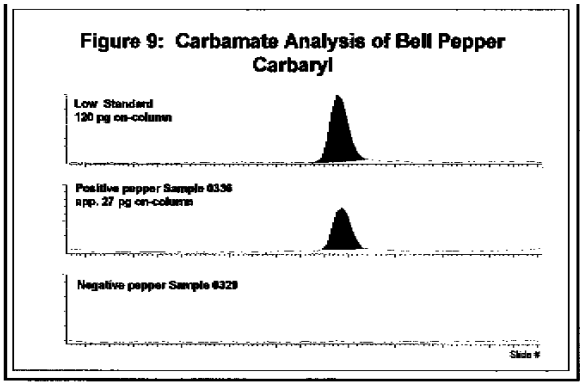












NOVEL BIOSENSORS FOR CHARACTERIZING ENVIRONMENTAL ENDOCRINE CHEMICALS

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Accumulating evidence strongly indicates that certain pesticides, environmental pollutants, industrial chemicals and naturally occurring phytoestrogens can dramatically alter normal physiological functioning of the endocrine system. Obtaining information on which chemicals in the environment should be labeled as EDCs is critical, requiring a significant amount of time and efforts. This poses a great challenge to current methodologies such as GC/MS due to their cost and long turn-around time.

Several factors have been identified for making the monitoring and surveillance studies of EDCs difficult. First, the cost and time involved in screening (or testing) a wide variety of synthetic EDCs and their metabolites. Secondly,

EDCs generally exhibit an unusual dose-response behavior unlike most toxic substances. The dose-response curves for most toxic substances usually increase with increasing levels of the chemical compound and eventually levels off. Whereas, the response curves for environmental estrogens exhibit an inverted U-shape and the greatest response is produced at extremely low doses. Thirdly, there are concerns that the effects of different EDCs are additive or even synergistic and hence regulations concerning individual compounds may not be adequate. Consequently, scientists and regulators are looking for very simple, fast and least costly screening methods that are capable of identifying and classifying all EDC as well as potentially contaminated sites within the environment. Once screening methods are developed, further laboratory re-analysis, confirmation and long-term studies would be necessary to identify endocrine disrupting characteristics among the population.

We have utilized the concept of renewable inummosensing and electrochemical microassembly technologies to analyze a range of suspected EDCs, including polychlorinated biphenyls (PCBs), chlorinated phenols, atrazines, and heavy metals. Experiments performed with PCB antibodies resulted in a detection limit of 0.1 ng/ml for selected Aroclors, for a total analysis time of about 20 minutes. This paper discusses the potential of affinity biosensors and immunocytochemistry for characterizing potential EDCs.

THE THEORY OF OPERATION AND APPLICATIONS OF THE PULSED FLAME PHOTOMETRIC DETECTOR (PFPD) FOR GAS CHROMATOGRAPHY

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Introduction

The Pulsed Flame Photometric Detector (PFPD) was developed in the early 1990's by Dr. Aviv Amirav.[1-3] Unlike the traditional flame photometric detector which has a continuous flame, the PFPD is based on a pulsed flame for the generation of flame chemiluminescence. The detector operates with a fuel rich mixture of hydrogen and air. This mixture is ignited and then propagates into a combustion chamber three to four times per second where the flame front extinguishes. Carbon light emissions and the emissions from the hydrogen/oxygen combustion flame are complete in two to three milliseconds, after which a number of heteroatomic species give delayed emissions which can last from four to 20 milliseconds. These delayed emissions are filtered with a wide band pass filter, detected by an appropriate photomultiplier tube, and electronically gated to eliminate background carbon emission. Twenty-eight elements can be detected with the PFPD, thirteen of which give delayed emissions, and therefore infinite selectivity. These latter elements include environmentally and industrially important S, P, As, Sn, and N.

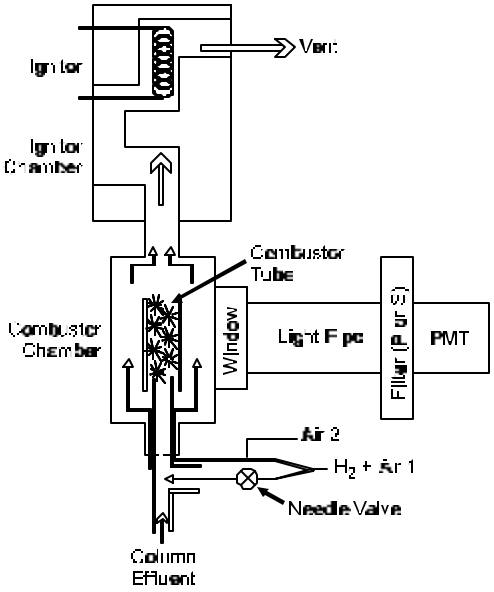
Applications of the PFPD in the Sulfur mode for the analysis of sulfur compounds in petrochemical products as well as in beverages are shown. Several petrochemical applications of interest are follows: 1) thiophene in benzene, 2) sulfur gases in natural gas, and 3) COS in propylene. The Phosphorus mode of operation is very sensitive and is applicable to the detection of organophosphorus pesticides. The use of the PFPD as an elemental specific detector used in concert with a mass spectral detector is shown to be very helpful in providing additional information to more easily identify target pesticides.

High speed data acquisition firmware and software enables one to easily set up the PFPD and to review the pulsed emission data emanating from each chromatogram. This allows the qualitative confirmation of target compounds. Dual channel data processing also provides the ability to qualitatively analyze two elemental modes simultaneously.

Experimental

In a conventional flame photometric detector (FPD), a sample containing heteroatoms of interest is burned in a hydrogen-rich flame to produce molecular products that emit light (i.e., chemiluminescent chemical reactions). The emitted light is isolated from background emissions by narrow bandpass wavelength-selective filters and is detected by a photomultiplier and then amplified. The detectivity of the FPD is limited by light emissions of the continuous flame combustion products including CH*, C2*, and OH*. Narrow bandpass filters limit the fraction of the element-specific light which reaches the PMT and are not completely effective in eliminating flame background and hydrocarbon interferences. The solution to this problem, conceived by Professor Amirav of Tel Aviv University was to set the fuel gas (H_2) flow into the FPD so low that a continuous flame could not be sustained. But by inserting a constant ignition source into the gas flow, the fuel gas would ignite, propagate back through a quartz combustor tube to a

constriction in the flow path, extinguish, then refill the detector, ignite and repeat the cycle. The result was a pulsed flame photometric detector (PFPD) shown in figure 1.



The background emissions from the hydrogen-rich air:hydrogen flame (approximately 10 mL/min H_2 and 40mL/min Air) is a broad band chemiluminescence. The combustion of hydrocarbons is highly exothermic, rapid and irreversible, producing a light emission by the hydrocarbon products equal to the time for the flame to propagate through the combustor or 2 to 3 milliseconds. Many of the chemiluminescent reactions of other elements such as S (S2*), P (HPO*), N (HNO*) etc., are less energetic and more reversible, and proceed after the temperature behind the propagating flame has dropped. These heteroatom emissions are therefore delayed from the background emissions. By using the leading edge of the flame background emission to trigger a gated amplifier with an adjustable delay time, heteroatomic emissions can be amplified to the virtual exclusion of the hydrocarbon background emission. The selective amplification of the element-specific emissions is the basis of the PFPD's unique sensitivity and selectivity (see figure 2).

Figure 1. Schematic Cross Section of the PFPD

The PFPD pulses approximately 3 times per second so that in a period of about 330 milliseconds the detector fills with the mixture of fuel gases and column effluent. When the flame propagates through this mixture, all the light emission from a given flux of some element, sulfur, for example, is concentrated into a period of only 20 milliseconds following each flame pulse. This light intensity is approximately 16 times brighter than the steady state emission from a conventional FPD where the emission would be spread over a period of 330 milliseconds. This effect plus the fact that the gated amplifier is only active during a 20 millisecond period for sulfur combines to greatly improve the signal to noise ratio in the PFPD.

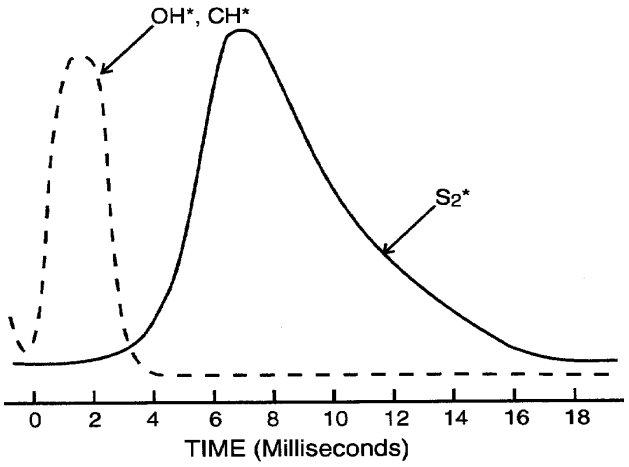
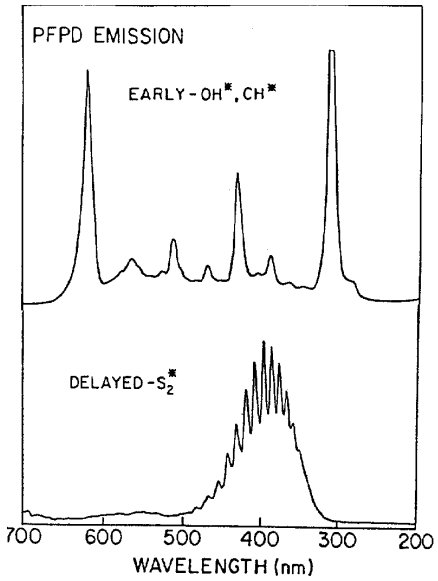


Figure 2. Flame Background and Sulfur Emission Time Profiles



Of equal importance is the ability to resolve the emissions of the heteroatoms from the flame background. The delayed sulfur or phosphorus emissions are integrated after the flame background has dropped to a negligible level. This delay permits the use of much wider bandpass optical filters that no longer must filter the background but can be selected to target the wavelength range of the desired element specific emissions. The result is lower overall noise levels and therefore greater detectivity.

PFPD Specifications

The PFPD detects 28 elements:

S, P, N, As, Sn, Se, Mn, B, Br, Ga, Ge, Pb, Si, Te, V, Al, Bi, Cr, Cu, Eu, Fe, Ni, Rh, Ru, W, In, Sb

Figure 3. Hydrocarbon and Sulfur Emission Profiles as a function of Wavelength. Filter used for S is the BG-12.

Thirteen of these elements have delayed emissions from the background Carbon emission and therefore exhibit infinite selectivity:

S, P, N, As, Se, Sn, Ge, Ga, Sb, Te, Br, Cu, In

Detectivities and selectivities are shown in Figure 4.

Control of the PFPD parameters is either from the GC or workstation (Figure 5).

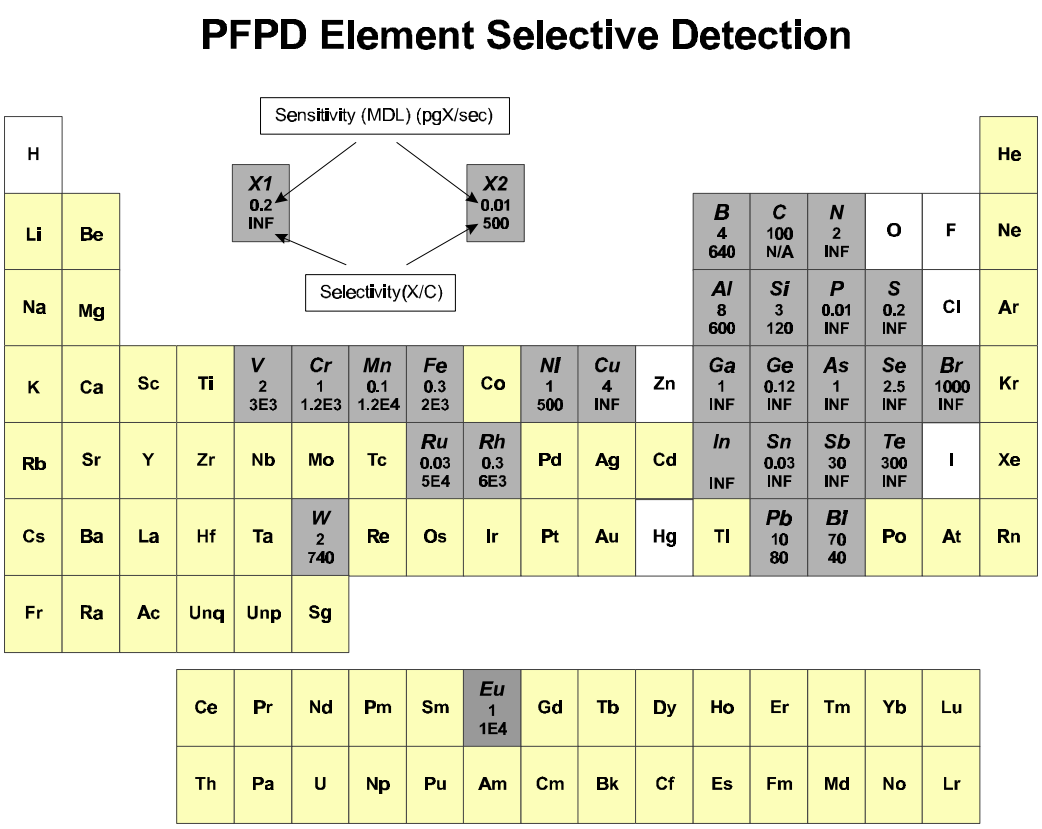


Figure 4. The PFPD periodic chart: Detectivities and Selectivities of Elements

Application areas of particular interest with the PFPD would include petrochemical, industrial, and environmental with some interest in food. Figure 6 shows the separation of three sulfur gases, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan at 1 ppm each from Natural gas using a Supelco 60 M x 0.53mm x 5 µ SPB-1 capillary column. This analysis is important since these compounds possess unpleasant odors, are unstable and corrosive and poisonous to industrial catalysts. Figure 7 shows the separation of COS in propylene, a problem for both the column and detector, run on a J&W GSQ PLOT column.

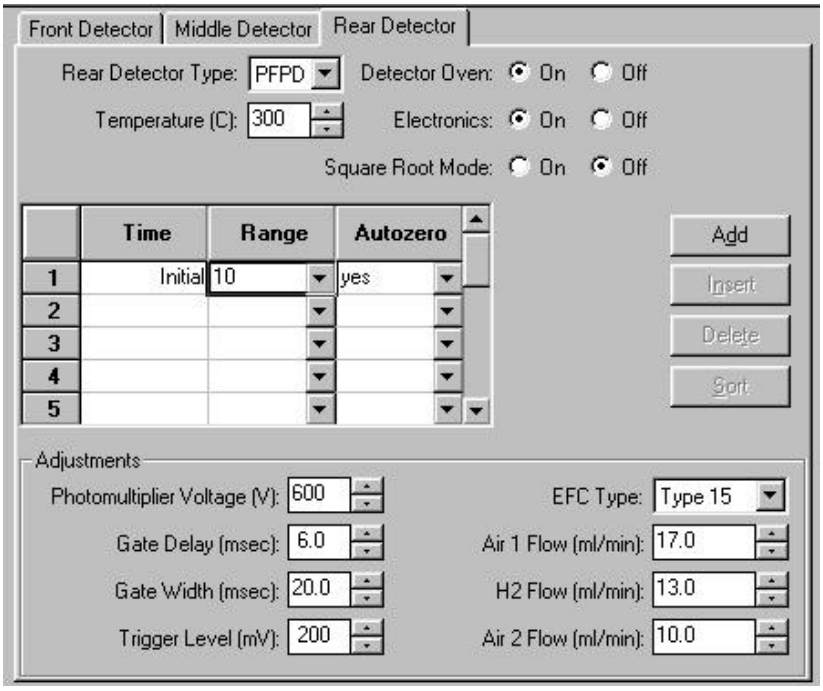


Figure 5. Workstation Control of PFPD

Applications

Headspace Solid phase microextraction (SPME) is used to extract sulfur compounds in Beer with a Carboxen™/PDMS fiber and PFPD detection in Figure 8.

Phosphorous detectivity on the PFPD is 0.1 pg/sec or the same as the TSD or NPD detectors but without the peak tailing and with better selectivity toward hydrocarbons and nitrogen compounds. Its application for the determination of phosphorus pesticides in a vegetable extract is shown in Figure 9.

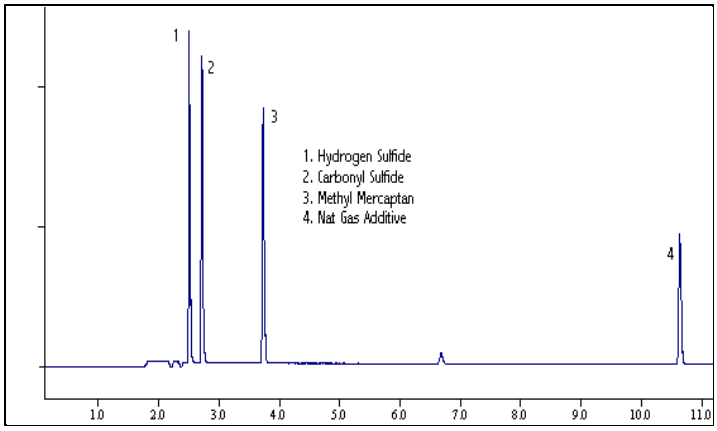


Figure 6. 1 ppm ea. Suflur Gases in Natural Gas

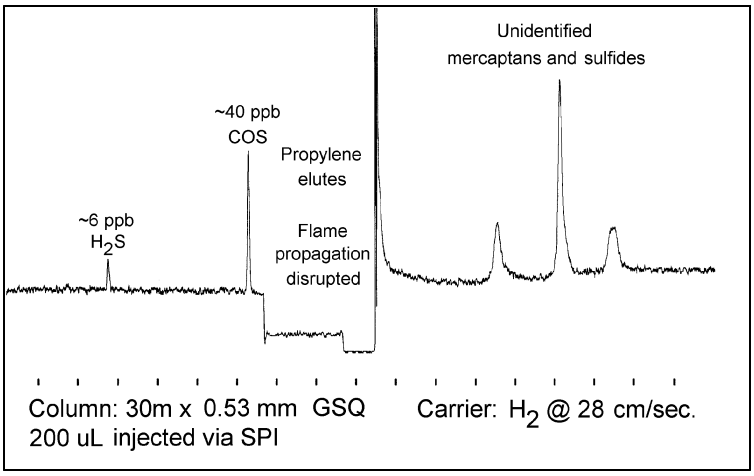
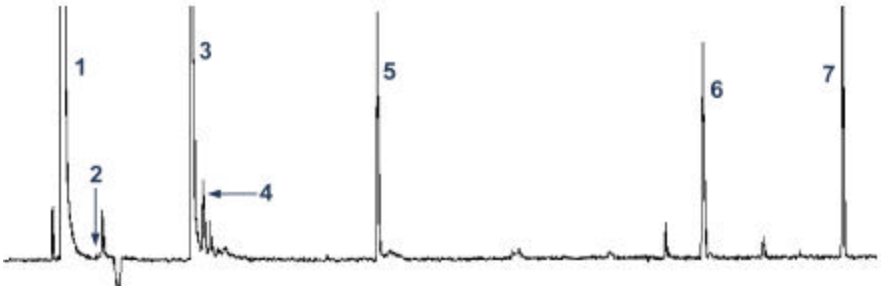


Figure 7. COS in Propylene



1. Dimethyl Sulfide
2. Diethyl Sulfide
3. ?
4. Dipropyl Sulfide
5. ?
6. ?
7. 3-methylthio-1-propanol

Figure 8. Sulfur Compounds in Beer by SPME

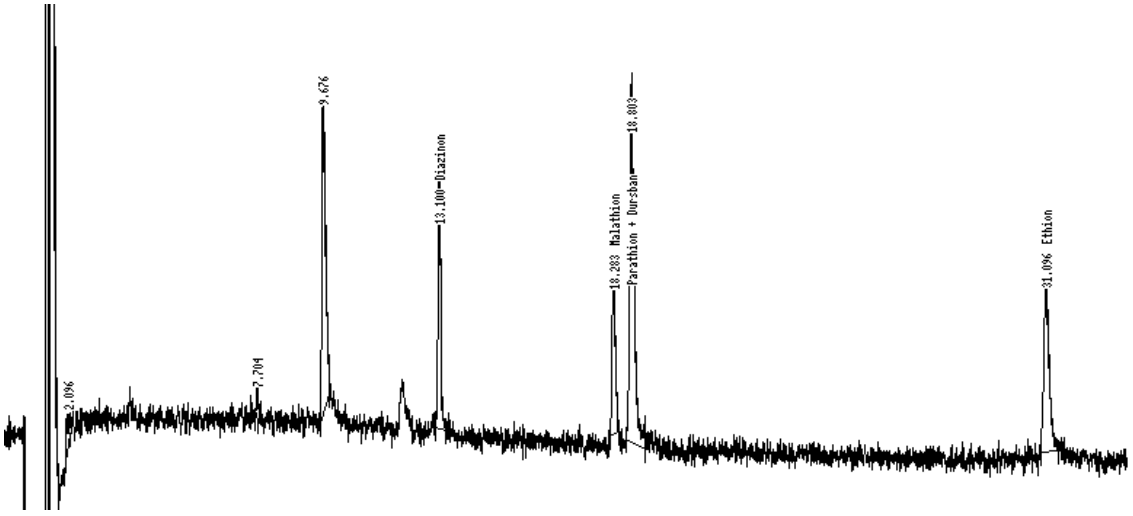


Figure 9. Phosphorus Pesticides in a Lettuce Extract Matrix at 10 ppb

The PFPD has good arsenic selectivity and detectivity that allows it to be used for the monitoring of catalyst poisoning gases such as arsine. The PFPD can also simultaneously detect AsH3 and PH3 as shown in Figure 10 where propylene is the major component.

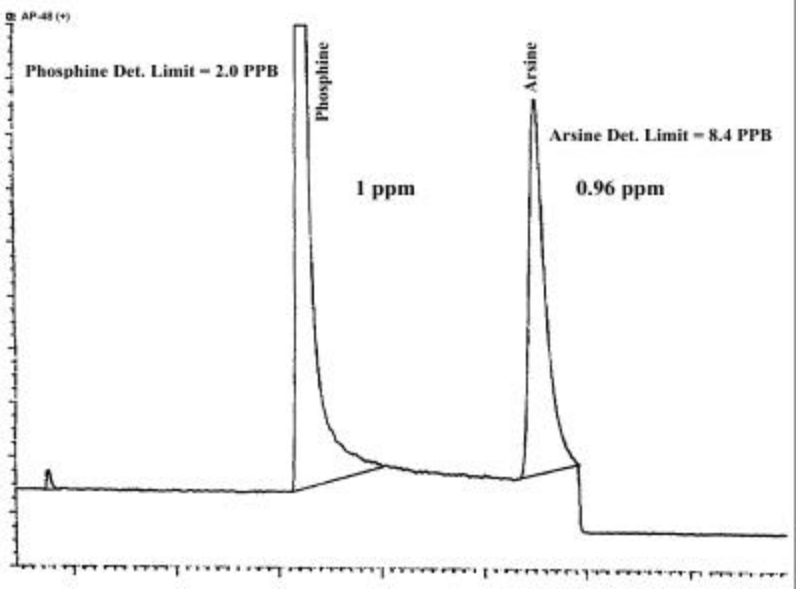


Figure 10. Simultaneous Determination of PH3 and AsH3 in Propylene

Analytical Software

Analytical software available for the PFPD permits one to view the emissions of the PFPD on a scope like window (Figure 11). This allows for quick set up and optimization of the detector flows. It also allows the user to view the emission profile of the background and eluting peak for qualitative information. Finally, the emission data from the complete chromatogram can be saved as a data file and viewed (Figure 12). The resulting data may also be manipulated to provide dual elemental chromatograms.

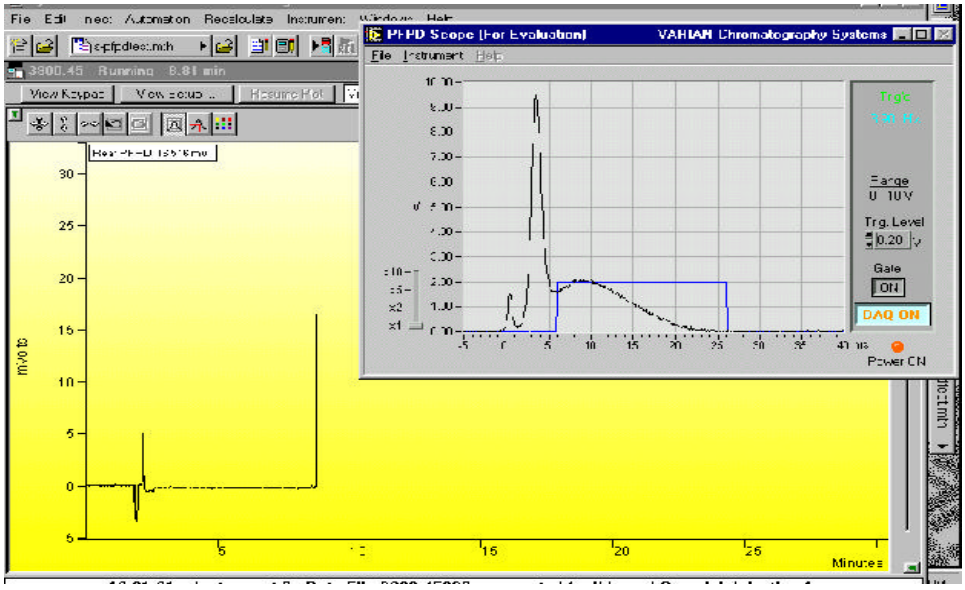


Figure 11.

Conclusions

The PFPD is a highly sensitive and selective flame photometric detector capable of detecting 28 elements, 13 of these with infinite selectivity. Analytical software is capable of providing elemental qualitative information from the pulse emission data for one or two channels. The detector has many applications is the petrochemical, industrial, environmental and food industries.

References

1. Amirav, "Pulsed Flame Detector Method and Apparatus". USA, Patent No. 5153673, Israel Patent No. 95617, European patents approved, Japan patent pending.
2. Atar, S. Cheskis and A. Amirav, "Pulsed Flame - A Novel Concept for Molecular Detection", Anal.Chem., **63**, 2061-2064 (1991).
3. Cheskis, E. Atar and A. Amirav, "Pulsed Flame Photometer - A Novel Gas Chromatography Detector", Anal. Chem., **65**, 539-555 (1993).

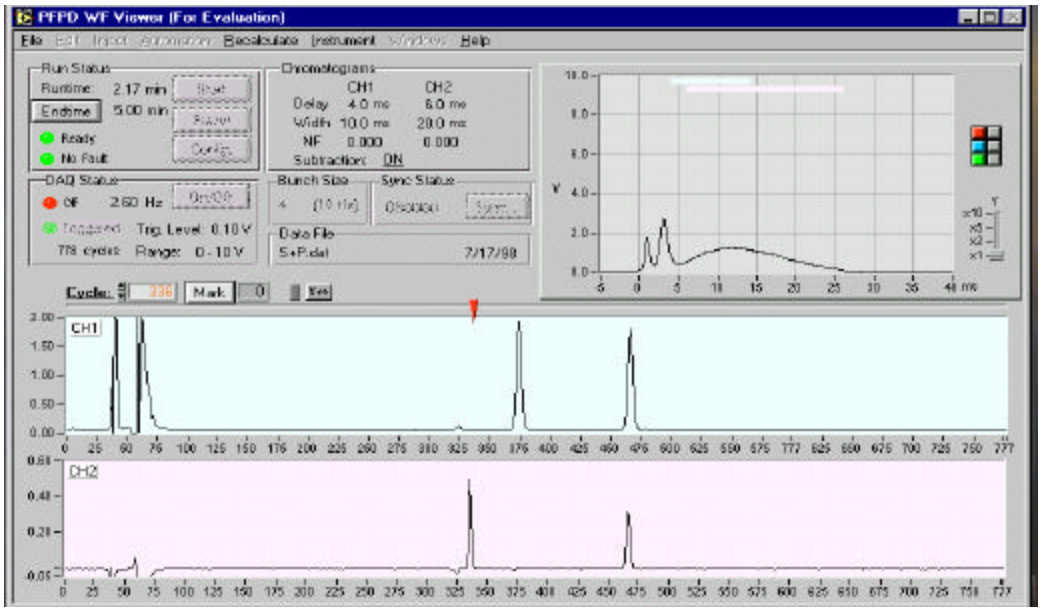


Figure 12. PFPD Data File Viewer Showing Phosphorus and Sulfur Chromatograms

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SIMULTANEOUS MEASUREMENT VOLATILE AND SEMIVOLATILE COMPOUNDS: INTRODUCING METHODS 3611 AND 3670

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The simultaneous measurement of volatile and semivolatile compounds will be embraced by the USEPA with the release of SW-846 later this year. Methods 3511 and 3570 provide protocols for the extraction of waters and soils, respectively, developed by the Electric Power Research Institute (EPRI) and used for a decade at former manufactured gas plant (MGP) sites around the country. With few exceptions, these methods simultaneously extract volatiles (8260), semivolatiles (8270), polycyclic aromatic hydrocarbons (8100), pesticides (8081), polychlorinated biphenyls (8082), chlorophenols, total petroleum hydrocarbons (8015B), volatile petroleum hydrocarbons (MADEP), extractable petroleum hydrocarbons (MADEP), and any other organic compound extractable by dichloromethane. These microextraction methods are fast, flexible, field compatible, inexpensive, sensitive, and suitable for GC/FID, GC/PID, GC/ECD, and GC/MS. These methods can be substituted for many sites requiring Method 5035 for methanol preserved volatiles in soil. The method description, validation data, and application history will be presented.

A COMPARISON OF STATIC HEADSPACE AND SOLID-PHASE MICROEXTRACTION FOR THE DETERMINATION OF VOLATILE ORGANICS IN WATER

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Introduction

EPA method 5021 is a static headspace (SHS) method for volatiles in soils. This method is part of the SW-846 manual and may be used with either GC or GC/MS. It covers a wide range of compounds over a concentration range of 20 to 200 parts per billion (PPB). The method lists 58 compounds from dichlorodifluromethane to naphthalene. Solid-Phase Microextraction (SPME) is a relatively simple technique where an adsorbent coated fused silica fiber may be exposed to the headspace above an aqueous sample for a fixed period of time. The fiber is then injected into and desorbed in the injection port of a GC or GC/MS. The objective of this initial study was to compare various quantitative parameters of these two techniques to determine the possible applicability of SPME for the determination of VOC's in soils. Soils were not used in these initial studies, only the matrix modifiers.

The behavior of organic standards extracted from a matrix modifier are compared for a set of model compounds using the headspace technique and three different SPME fibers. This study was performed with a CTC Combi PAL AutoSampler which is capable of headspace and SPME analysis. Headspace samples of 200 mL were extracted and injected after shaking a sample for 30 minutes at 60°C. SPME fibers were exposed to the sample headspace for 30 minutes with shaking at 40°C and then desorbed for 5 minutes. A Saturn ion-trap GC/MS was used for chromatographic analysis.

The following studies and results are shown: 1) a comparison of the absolute response to gaseous VOCs with SPME and SHS showing improved response with SPME, 2) a comparison of mid to late eluting VOCS showing variable response comparisons between SHS and the three SPME fibers, 3) linearity studies indicating that the SPME fiber can become overloaded if too many compounds are adsorbed simultaneously, 4) good area count precision exhibited for selected compounds for all SPME and SHS, and 5) calculations of minimum detectable quantities using SPME, SHS, and Purge and Trap proving that SPME has comparable detection limits for many analytes and may be an acceptable alternative for VOC's in soils or waste water.

Experimental

CTC Combi PAL AutoSampler equipped with 10 mL vial tray:

Headspace injection: Heated headspace gas tight syringe (1.0 mL)

- 5 mL sample equilibrated in 10 mL vial with shaking for 30 minutes at 60°C
- Injection volume: 200 mL

SPME injection: SPME fiber holder and fiber

- Headspace: 5 mL in 10 mL vial
- Adsorption: 30 minutes with shaking at 40°C, desorption 5 minutes
- Fibers: PDMS (100 mM); Carboxen™ 1006-PDMS; Carboxen™ 1006-DVB-PDMS

Varian Saturn 2000 GC/MS:

- Column: 60M x 0.32mm DB-624
- Injection: Splitless at 230°C
- Ion-trap: 150°C

In the EPA method 5021 static headspace method, a soil sample is added to a 22 mL vial containing 10 milliliters of matrix modifier. After this vial is sealed, internal and surrogate standards are injected. In the present study 10 mL vials were used with 5 mL of modifier. Standards were added to the vial via syringe injections through the septum cap prior to analysis. Vials were then loaded into the Combi PAL 10 mL vial tray. The autosampling procedure was then started. During the sampling process each sample is transferred to the incubator for heating and mixing (by shaking) for 30 minutes at 60°C (see figure 1 and 2). While the sample continues to be heated and mixed, a gas tight syringe withdraws 200 mL which is then injected into the GC/MS injector.

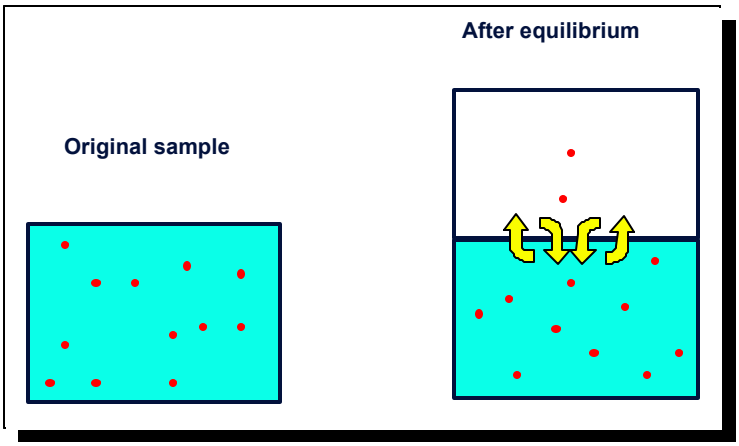


Figure 1. Conventional Static Headspace Sampling

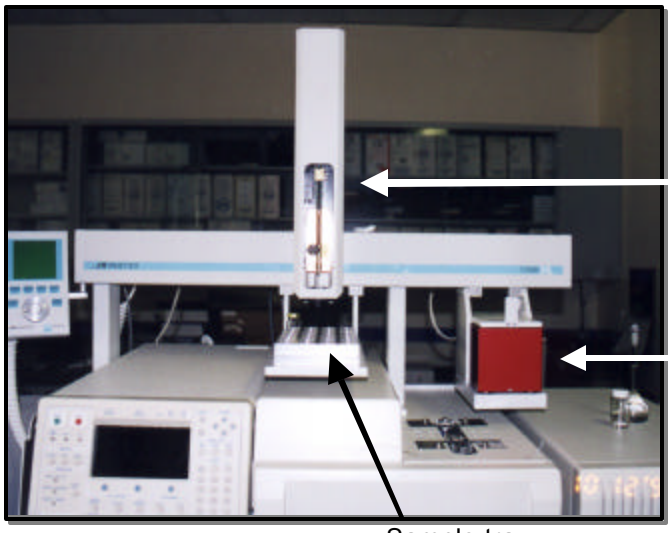


Figure 2. Combi PAL in SPME Mode

Solid phase microextraction is an equilibrium technique where analytes are not completely extracted from the headspace matrix. The recovery is dependent on the partitioning or equilibrium of analytes among the three phases present in the vial: the aqueous sample, the headspace, and the fiber coating on the fused silica needle. Adsorbent coatings can be films (30-100 µM) of polymer, copolymer, carbonaceous adsorbent, or a combination of these. The coated fused silica fiber is attached to a metal rod and the entire assembly comprises the SPME syringe assembly. The fiber is within a protective sheath in the standby mode. The sheath is pushed through the vial septum by the autosampler and lowered into the headspace. The fiber is then inserted into the headspace and adsorption is commenced. Following this step, the fiber is pulled back into the sheath, withdrawn from the autosampler vial and injected into the GC injector (see figures 3 and 4). In the present studies fibers were held in the 5 mL headspace for 30 minutes at 40°C.

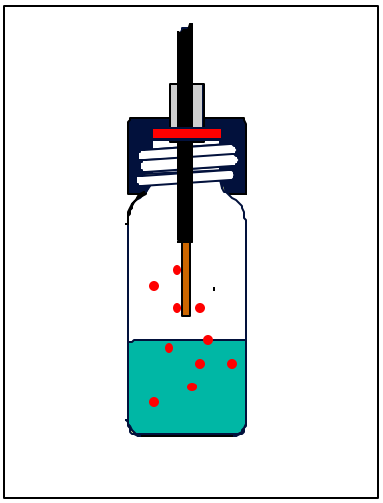


Figure 3. SPME Headspace Sampling

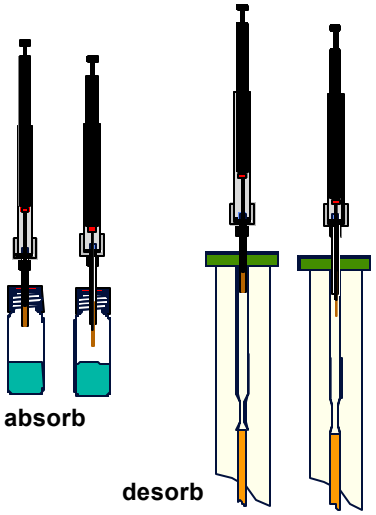


Figure 4. SPME Adsorb and Desorb Steps

Results and Discussion

Following the procedures outlined above, 200 µg/L solutions of three gaseous VOCs were prepared by spiking 5 mL of martrix modifier in each of several 10 mL septum capped vials. These analytes were then analyzed by both headspace and SPME. Three different fibers were used in the SPME experiments. The results are shown in Figure 5. The Carboxen SPME fiber gave the best response to the three VOC's followed by the headspace technique. The PDMS fiber is ineffective with the low boiling VOC's while the three-phase fiber, Carboxen-DVB-PDMS, falls in the middle.

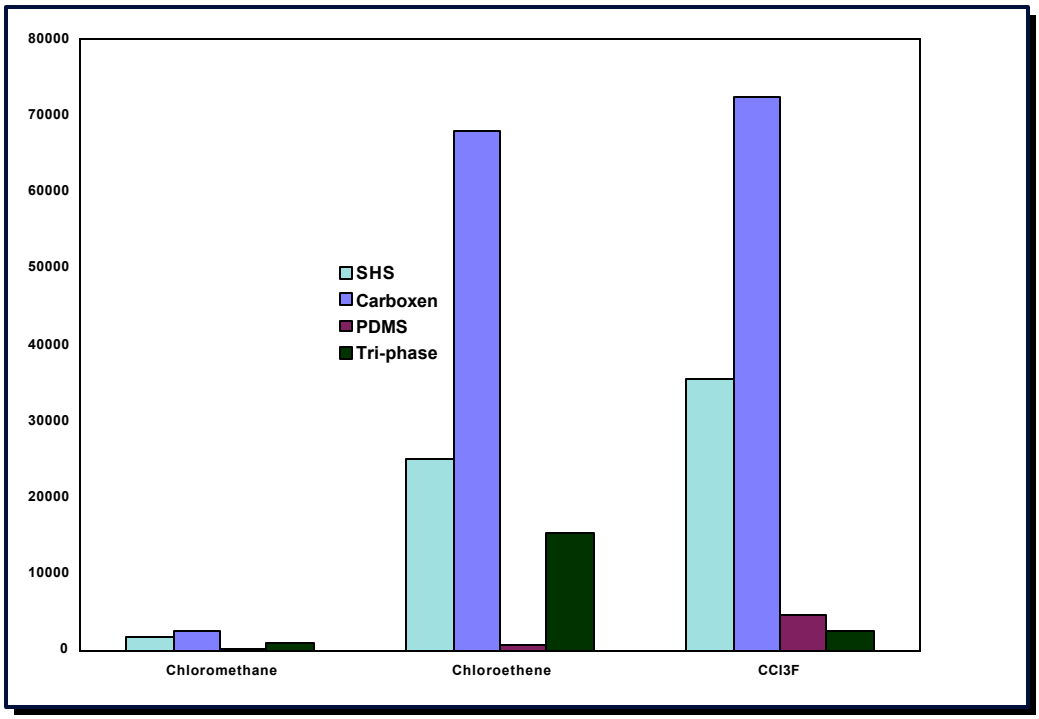


Figure 5. Absolute Response to Gaseous VOC's with Headspace and SPME

This same type of study was performed with higher boiling VOC's, the results shown in Figure 6. The Carboxen fiber is effective in adsorbing the higher boiling VOC's. The three-phase fiber also adsorbs the higher boiling analytes efficiently.

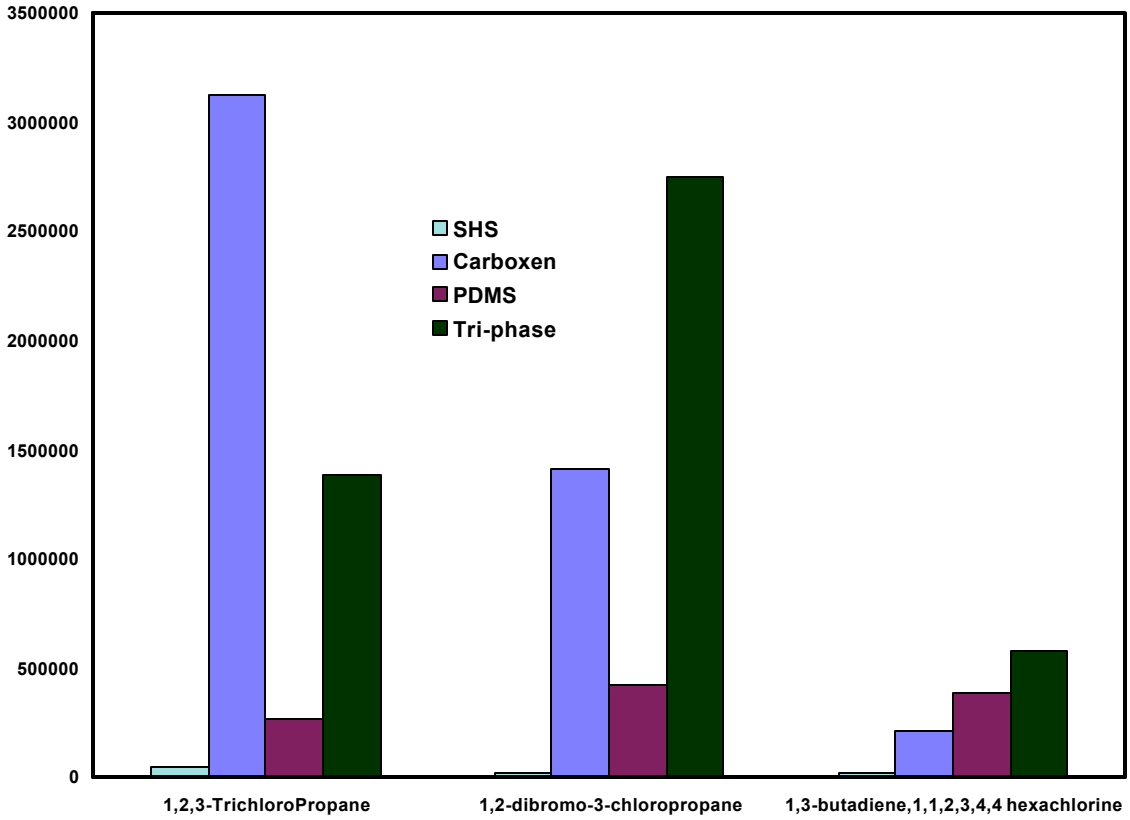
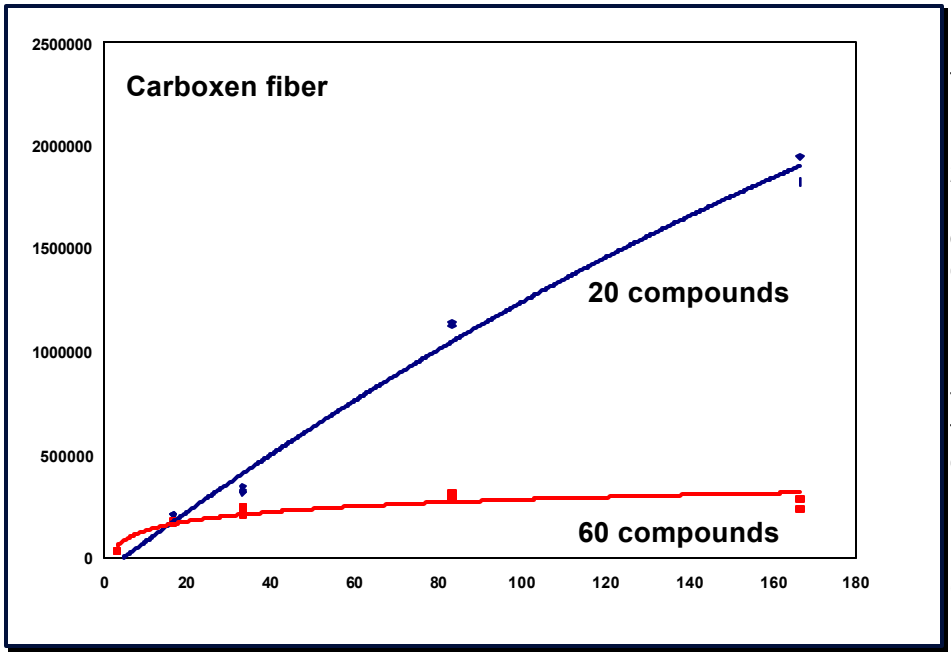


Figure 6. The absolute Response to Later Eluting VOC's with Headspace and SPME

Early SPME linearity studies with 60 target compounds of EPA method 5021 indicated that the fiber was being

saturated. When the number of compounds screened was reduced to 20, this observation was confirmed (see figures 7 and 8).



Linearity studies were conducted from 3.3 to 176 ppb with two test mixtures, one containing 60 compounds and the other containing 20 compounds. With the 60 compound standard, linearity flattens out as the concentrations increase. With the 20 component mixture, linearity is quite good for both compounds over the tested range. These results are consistent with the supposition that the fibers will saturate if too many components occur at these levels in the headspace.

Figure 7. SPME Calibration Curves for Trichlorofluoromethane

Statistical data was collected for a representative list of VOCs from the EPA method 5021 target com- pound list. The results for SPME (Carboxen) and static headspace are shown in Table 1.

Purge and trap studies for the same compound list were also performed on a separate system. The minimum detectable quantities of these compounds were determined using a S/N equal to five as an estimation. These results are shown in Table 2.

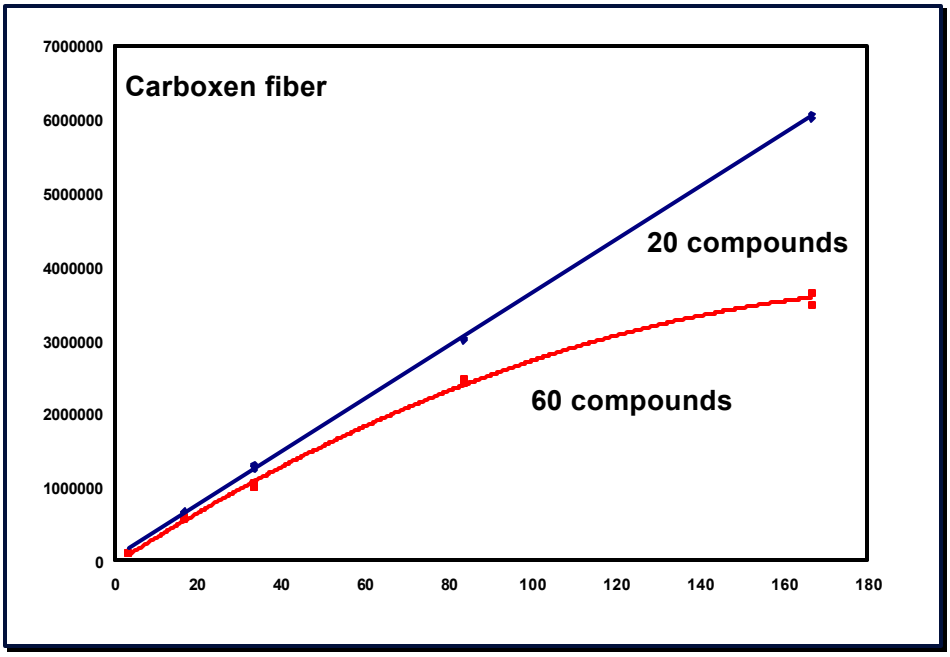


Figure 8. SPME Calibration Curves for 1,1,2-Trichloroethane

Table 1. Precision for Selected VOC's at 33 ppb, n=4

Compound	%RSD SPME	%RSD Headspace
Vinyl Chloride	4.3	5.4
CCl3F	3.4	8.0
TCE	1.5	2.4
1,1,2-TCA	2.0	2.4
1,2,3-TCP	2.2	6.2

Minimum detectable quantities obtained for SPME are comparable or lower than those obtained by static headspace.

Table 2. Minimum Detectable Quantities of Selected VOC's, S/N=5, Average of n=4

Compound	SPME-Car (ppb)	Headspace (ppb)	P and T (ppb)
Vinyl Chloride	0.2	4.5	0.06
CCl3F	0.1	0.8	0.02
TCE	0.01	0.5	0.02
1,1,1-TCA	0.1	2.8	0.2
1,2,3-TCP	0.03	3.3	0.09

Conclusions

The results of these preliminary studies comparing SPME to static headspace indicate that SPME could be a reasonable alternative for determining volatiles in water or soils. SPME could also make an excellent screening tool prior to Purge and Trap analyses.

Linearity experiments gave good results although it is possible to saturate the SPME fiber if too many compounds are being monitored simultaneously.

Precision was good and the detection limits of SPME are lower than headspace.

While these studies were carried out with a matrix modifier, the results would be expected to be similar to those obtained with soil samples.

EVALUATION OF A VACUUM DISTILLER FOR PERFORMING METHOD 8261 ANALYSES

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The Environmental Protection Agency's Office of Research and Development has developed a vacuum distillation method to determine volatile organic compounds in difficult matrices. The developed method is intended for use by both the Superfund and RCRA Programs and incorporates a novel approach to establish data quality. The resultant method (SW-846 Method 8261, Update IVB) uses surrogate compounds to measure matrix effects and to compensate for their biases.

This poster presents the results of an evaluation of the first commercial version of the ORD vacuum distillation apparatus, the VD1000 (produced by Cincinnati Analytical Instruments, Cincinnati OH under a license agreement with the Environmental Protection Agency). The vacuum distiller combined with an HP 5972 GC/MS is tested for compliance with calibration criteria identified within Method 8261. In addition, method detection limits for the vacuum distiller for water, soil, and fish tissue are presented. The potential for contamination of samples by a high-concentration sample (by each Method 8261 analyte) is also presented as the percent of a high concentration standard detected in a subsequent blank.

The review of Method 8261 analytical data is simplified by graphical presentation of method performance and the impact that a sample matrix imparts on analyte recoveries. The use of surrogates to monitor matrix effects on a given sample provides the means to determine analyte recovery as a function of critical chemical properties and to present the functions graphically. Additional check surrogates are monitored to quantify the accuracy of the recovery functions. Examples of data and graphic presentations for review are presented.

Sample throughput is evaluated on the basis of average Superfund sample sets. The comparison of analytical costs associated with Method 8261 and current Superfund requirements are presented. Estimates of how the use of Method 8261 could impact Superfund is presented.

METHOD 8261: USING SURROGATES TO MEASURE MATRIX EFFECTS AND CORRECT ANALYTICAL RESULTS

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The Environmental Protection Agency's Office of Research and Development has developed a vacuum distillation method to determine volatile organic compounds in difficult matrices. With the understanding that such a method would be intended for use by both the Superfund and RCRA Programs with a need to establish data quality, a novel approach to optimize QA requirements is incorporated. The resultant method (SW-846 Method 8261, Update IVB) uses surrogate compounds representing the range of chemical properties of the method's analytes in order to measure matrix effects and to compensate for their biases. Method 8261 eliminates the need for matrix spike/matrix spike duplicates as well as calibration of instrumentation by matrix type. This poster presents the theory behind the surrogate corrections incorporated within the method.

There are primarily three main chemical properties of volatile organic compounds that define their behavior and recovery during vacuum distillation. These properties are the compounds' vapor pressure (measured as boiling point, BP), partition coefficient between air and water (K_{aw}), and partition coefficient between an organic phase and air (K_{ao}). By adding surrogate compounds to measure recoveries as a function of these properties, the impact of any matrix (*e.g.*, biota) on recovery of analytes is predicted. The measurement of matrix effects by sample eliminates the need for matrix spike/matrix spike duplicates as well as the need to calibrate instrumentation by matrix (*i.e.*, Method 5030 for water and Method 5035 for soil).

The impact of Method 8261 corrections allows for an expanded list of analytes that include the volatile organic compounds (VOCs), polar compounds such as dioxane and pyridine, the nitrosamines and aniline, and compounds that are considered semi-volatile such as naphthalene. With the streamlining of analytical requirements and expanded analyte list, the productivity of using Method 8261 is greatly superior to alternative methods.

The measurement of matrix effects by sample simplifies the review of Method 8261 analytical data. The relationship of the chemical properties (BP, K_{aw}, and K_{ao}) to recovery are displayed graphically. The mysterious and dubious "matrix effects" disclaimer provided by other methods when an analysis does not perform as anticipated is not a hindrance to Method 8261. Extreme matrix effects are accurately compensated. Additional use of "check" surrogates allows the evaluation of matrix corrections effectiveness. Examples of data and graphic presentations for review are presented.

Notice
The U. S. Environmental Protection Agency (EPA) through its Office of Research and Development (ORD), funded this research and approved this abstract as a basis for a poster presentation. The actual presentation has not been peer reviewed by EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.

APPLICATION OF A DIOXIN/FURAN IMMUNOASSAY KIT TO FIELD SAMPLES

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Several immunoassay screening methods have been approved under the 4000 series of Field Screening Methods within SW-846 and are now widely used in the field. In less than a decade since their introduction, the commercial immunoassay kits behind these methods have significantly changed the process of assessment and remediation of hazardous waste sites. The major advantages include dramatically accelerated turnaround, decreased cost, and improved statistical reliability of site assessments because of the greater number of samples analyzed.

For the first time, these advantages are now also available to dioxin analysts. A previously described enzyme immunoassay (EIA) for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) has been applied to a variety of soil, sediment, and ash samples. Several simple sample preparation methods have been developed specifically for use with this immunoassay. The resulting protocols can be used in a simple field laboratory without extensive equipment. The methods are simple enough to be learned quickly without face-to-face training.

Sample throughput for a single analyst can be 15 or more samples per 8 to 10 hour day, which includes 4 hours for incubations during which no handling is needed. Use of an optional overnight incubation allows staggered processing of multiple batches. This approach can boost productivity to 30 or more samples per 12 to 14 hours over 2 days.

Results from several comparison studies will be described which demonstrate strong correlation between EIA results and TEQ, ranging from low ppt to high ppb levels. Special attention will be given to the data package for Method 4025 (Dioxin in Soil by Immunoassay). Issues relating to implementation of this technology in both fixed and field lab situations will be discussed, including QA requirements and limitations of the method. Selected customer experiences will be used to demonstrate related points, such as data interpretation and troubleshooting. The most recent results from an ongoing program of method improvement will be described.

VOLATILE AND EXTRACTABLE PETROLEUM HYDROCARBONS: A ROUND ROBIN ILLUSTRATES ESSENTIAL PBMS STANDARDS

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The Massachusetts Department of Environmental Protection (MADEP) formally released the Volatile Petroleum, Hydrocarbon (VPH) and Extractable Petroleum Hydrocarbon (EPH) methods in January, 1998. These methods offer toxicologically meaningful replacements for traditional measurements of Total Petroleum Hydrocarbons (TPH) which employ infrared (IR) or gas chromatography (GC) techniques. The VPH and EPH methods simultaneously measure two range aromatics, four range aliphatics, and twenty-three individual. aromatics including BTEX, MTBE, and PAHs. These methods are also two of the first finalized and widely employed "performance based" methods. Unlike traditional EPA protocols, analytical modifications are allowed, provided specific performance criteria are satisfied. Before releasing the VPH and EPH protocols for regulatory monitoring, the MADEP conducted a round robin in order to evaluate the effectiveness of unmodified and modified versions of the method.

The round robin results demonstrated a promising performance among participating laboratories, as well as several

potential problems for interlaboratory comparability. The MADEP used the results of the round robin to incorporate specific performance criteria for the final release of the methods. These included criteria for sample preparation procedures, alternative capillary columns and detectors, surrogates, chromatographic integrations, method proficiency standards, reporting limits, detection limits, report content, and self-certification statements. These performance criteria guard against analytical short-cuts which compromise the public health orientation of the VPH and EPH methods.

This presentation will describe the MADEP VPH and EPH methods, the round robin results, several common method modifications, the importance of reference materials, and the performance criteria necessary for assuring data accuracy and comparability.

FAST AND EFFICIENT VOLATILES ANALYSIS BY PURGE AND TRAP GC/MS

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ABSTRACT

Recent changes in environmental regulatory paradigms, such as EPA's performance-based measurement systems (PBMS), are lowering method compliance barriers for laboratories working under the Resource Conservation and Recovery Act (RCRA). One of the stated goals of PBMS is to educate the regulators and the regulated community on the inherent and intended flexibility of SW-846 methods. Operating under EPA's PBMS guidelines, laboratories could employ the flexibility of SW-846 methods to simplify and improve purge and trap GC/MS volatile organic analyses (P/T GC/MS VOAs). Laboratories performing Method 8260B for P/T GC/MS VOAs have two basic GC configuration options: wide bore columns connected to the mass spectrometer through a jet separator or narrow bore columns directly interfaced to the mass spectrometer.

SW-846 methodology recognizes both approaches as valid. The narrow bore column/direct interface approach is the better of the two techniques for most analyses when certain modifications are made. When newer purge and trap concentrator designs are employed and when several Method 8260B instrument parameters are modified dramatic performance benefits result. This "enhanced" narrow bore column/direct interface approach produces results such as reduced susceptibility to column contamination by high level samples, improved chromatographic behavior of early eluting and closely eluting compounds, analysis times under 20 minutes, and improved hardware ruggedness. The outcome is better quality data, higher sample throughput, and fewer instrument mechanical failures.

INTRODUCTION

Connecting the purge and trap concentrator to the GC inlet is one of the major challenges in P/T GC/MS VOAs. The challenge stems from vastly different flow rate requirements of the purge and trap concentrator, the capillary column, and the mass spectrometer. Method 8260B[1] describes GC/MS systems equipped with either cryogenic cooling devices attached to narrow bore (0.25 mm and 0.32 mm) capillary columns or wide bore (0.53 mm) capillary columns connected to enrichment devices such as jet separators. Many laboratories choose wide bore capillary columns with jet separators when running Method 8260B because they can easily accept the high flow rates required to efficiently desorb the trap. The jet separator provides the necessary decrease in carrier gas flow rate prior to entering the mass spectrometer. The wide bore column/jet separator approach has been the traditional approach to P/T GC/MS VOAs for some time. The wide bore column/jet separator approach has a host of problems. The problems include susceptibility to column contamination by high level samples, poor chromatographic behavior of early eluting and closing eluting compounds, long analysis times (run times approaching 40 minutes), and frailty of the jet separator. Narrow bore capillaries, which potentially offer better chromatography, have not been used as much for volatiles analysis primarily because they cannot easily handle the relatively high flow rates coming from the purge and trap concentrator. Method 8260B suggests cryofocusing the analytes on a capillary pre-column interface situated between the purge and trap concentrator and the GC capillary column. This device condenses the desorbed sample components and focuses them into a narrow band that can be transferred to the analytical capillary column.

However, this is an additional capital expense and it adds to the total analysis time. Newer purge and trap concentrator designs allow a much simpler interface. A conventional split/splitless injector usually already installed on the GC/MS system can be plumbed in series with the purge and trap concentrator. The operating principle is quite simple: the excess flow coming from the purge and trap is vented at the column inlet allowing a reduction in carrier gas flow rate to one more suitable for high resolution chromatography. Feyerherm and Neal[2,3] have described how this is done with a Hewlett Packard 5890 GC. Aside from this instrument modification, the concentrator desorb time and the GC oven temperature program should be optimized to improve the chromatographic behavior of method compounds and shorten analysis time. The concentrator desorb time may be as short as 30 seconds depending on the trap material. Shortening the desorb time reduces the amount of water transferred to the GC system and thus improves chromatography. The GC oven temperature program for P/T GC/MS VOAs must accommodate compounds with a relatively wide boiling point range. The initial oven temperature will determine how well-behaved the gases (Dichlorodifluoromethane, Chloromethane, Vinyl Chloride, Bromomethane, and Chloroethane) are. Once the compounds are on the GC column, the higher boilers are not difficult to resolve. Fast (50-60°C/min.) GC oven temperature ramps can be used to save time without any loss in resolution. This paper describes a series of modifications to Method 8260B for P/T GC/MS analysis of VOA samples. The method performance has been tested primarily with spiked water (Method 5030) in a single laboratory.

EXPERIMENTAL

Instrumentation and materials

All work was performed with an OI (College Station, TX) MPM-16 autosampler/4560 Purge and Trap concentrator. An OI tenax, silica gel, and charcoal trap (OI trap #10) was used as the sorbent trap. To connect the purge and trap, perform the following operations. Cut the total flow line to the split/splitless inlet about 3 - 4 cm from the septum nut. Using a 1/16" stainless steel union, connect the supply end to the "CARRIER IN" fitting on the purge and trap concentrator. Using another 1/16" stainless steel union, connect the transfer line from the purge and trap concentrator to the split/splitless GC inlet. These connections allow the use of the GC total flow controller to control the purge and trap desorb flow rate. All other connections are identical to other purge and trap installations. Figure 1 contains a plumbing diagram of the purge and trap concentrator-GC inlet connections. A Hewlett Packard (Palo Alto, CA) 5890 GC with EPC/Hewlett Packard 5971 MSD was employed as the GC/MS system. The analytical column used was a Restek (Bellefonte, PA) Rtx-5 (30m x 0.25mm x 1.0µm) with no guard column. Analytical standards were purchased from Ultra Scientific (N. Kingstown, RI) and were prepared by dilution with purge and trap grade methanol. All samples were 5 mL water samples prepared by spiking stock solutions into organic-free reagent water.

Operating Conditions

The purge and trap conditions and the GC/MS conditions are listed in Tables I and II respectively. After an 11 min. purge, the trap was heated to 180°C for 0.5 min. for sample desorption. Following the desorption step, the trap was baked at 200°C for 7.00 min. to complete the autosampler cycle. The injector was operated in the split mode with PURGE A (or B) ON all the time. A single taper 4 mm ID glass liner without glass wool was used in the GC inlet. An injector temperature of 200°C produced the best overall results. Liquid nitrogen was used to cool the oven to the initial temperature of 10°C. The GC temperature was ramped faster at the beginning and at the end of the GC oven program where the compounds exhibit a wide range of boiling points. The total carrier gas flow was 20 mL/min. and the split ratio was set at 40:1. The column flow was set at 0.5 mL/min (26.2 cm/sec.). We used a GC/MS interface temperature of 280°C.

RESULTS AND DISCUSSION

BFB may be directly injected to save time, but the injector should be operated in the splitless mode. BFB solutions are typically made up in methanol. Due to the solvent effect in splitless injections, standards made up in methanol do not give good peak shapes. Purging the BFB takes a little more time, but solves all of the above problems. We used a typically short GC oven temperature ramp for the BFB run.

Figure 2 is a total ion chromatogram of a 200 µg/L VOA standard on a narrow bore capillary column/direct interface GC/MS system. The chromatographic run time is 17 minutes with a total GC cycle time of 20 minutes. There are no noticeable water effects in the chromatogram. Notice the gaussian peak shapes of the five gases (DCDFM, Cloromethane, Vinyl Chloride, Bromomethane, and Chloroethane). The gases give an indication of the system's overall chromatographic performance. These compounds are usually difficult to separate and typically produce poor peak shapes on 0.53 mm column/jet separator systems. Ethyl Benzene and the *m,p*-Xylene pair which are typically unresolved on a 0.53 mm column. Styrene and *o*-Xylene usually coelute on a 0.53 mm column. We achieved baseline resolution on Ethyl Benzene and the *m,p*-Xylene pair and partial resolution on Styrene and *o*-Xylene.

Because of the large number of analytes, we do have several resolution challenges. Bromochloromethane and Chloroform coelute at 6.3 min. Bromoform elutes between Styrene and *o*-Xylene at 11.2 min. and is difficult to see on the total ion chromatogram. A similar close elution occurs with sec-Butylbenzene and 1,3- Dichlorobenzene at 13.93 and 13.94 min. None of the coeluting targets share common ions so their ion chromatograms are easily identified and quantified. For our system, a 0.5 min. desorb time dramatically reduced the amount of desorbed water while giving good chromatographic responses. With a tenax, silica gel, and charcoal trap, all compounds easily desorb at 180°C within 30 seconds with minimal carryover into subsequent blank water QC samples. For a tenax, silica gel, and charcoal trap, the purge flow rate didn't seem to affect chromatographic peak responses as much as other parameters. Purge and trap valve and transfer line temperatures around 100°C gave better results than hotter temperatures in the 180-200°C range. There was no apparent condensation of the higher boiling volatiles in the 100°C transfer line. The trap bake time was set so the purge and trap cycle time corresponded to the 20 minute GC cycle time.

The narrow bore capillary column system was calibrated by running a five-point curve with standards at 10, 20, 50, 100, and 200 µg/L (50, 100, 250, 500, and 1000 ng of standard injected). Table III is a summary of mean relative response factors (RRF), percent relative standard deviation (%RSD), method detection limits (MDLs), and estimated quantitation limits (EQLs) for selected compounds. Three of the four ketones (acetone, 2-butanone, and 4-methyl-2-pentanone) exhibit typically low RRFs, but the overall purging efficiencies are comparable to other methods. The linearity data of Table III suggest that a wider calibration range is possible for most of the VOA targets. The MDL and EQL data exhibit exceptional sensitivity for 5 mL samples. These data reflect a very simple and robust system that can generate accurate and reproducible results.

The one potential disadvantage to this approach is the requirement for sub-ambient GC oven cooling to reach the initial temperature of 10°C. This could be overcome by choosing a different GC column or a thicker film.

CONCLUSIONS

Performing split injections with P/T GC/MS VOAs allows a narrow bore column to handle the relatively high flow rates coming from the purge and trap concentrator. Narrow bore columns can be interfaced to purge and trap concentrators via split/splitless injectors by performing a relatively simple hardware modification. Combining this hardware modification with method optimizations in the concentrator desorb time and the GC oven temperature program produces dramatic performance improvements. This easy alternative to the more traditional wide bore column/jet separator approach to P/T GC/MS VOAs results in reduced susceptibility to column contamination by high level samples, improved chromatographic behavior of early eluting and closely eluting compounds, analysis times under 20 minutes, and improved hardware ruggedness.

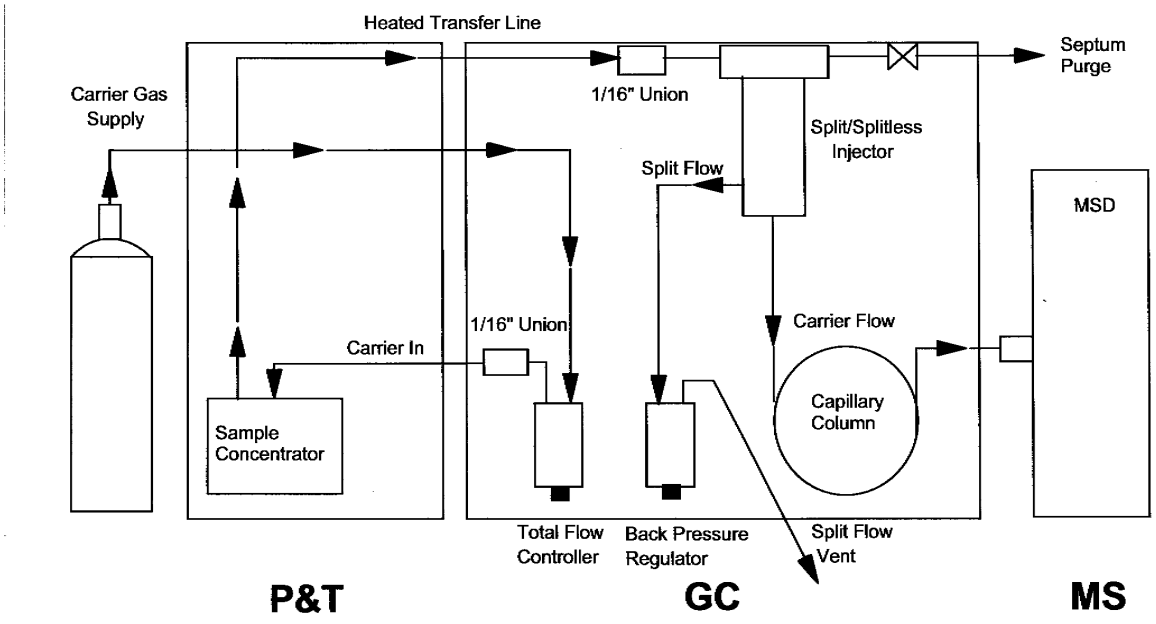

Figure 1. Basic plumbing diagram for a back pressure regulated split/splitless injector with a P/T autosampler.

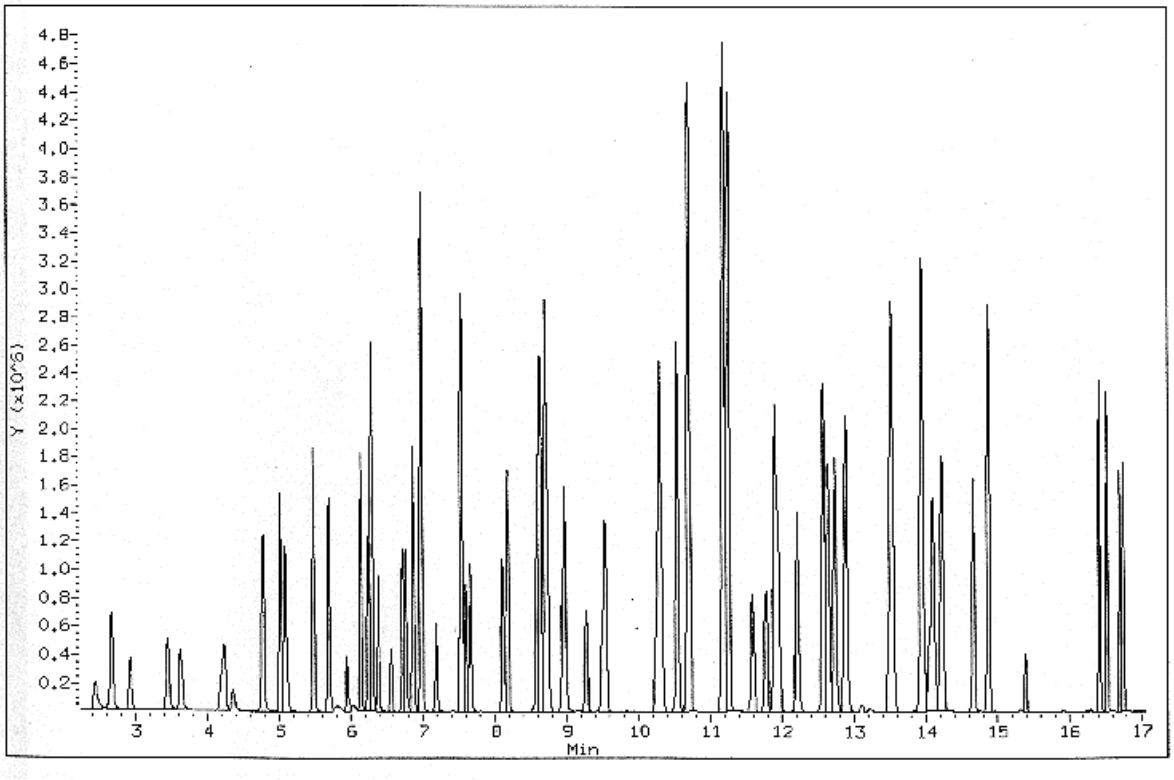

Figure 2. Total ion chromatogram of a 200 µg/L VOA calibration standard using a narrow bore capillary/direct interface system.

REFERENCES

1. USEPA SW-846 "Test Methods for Evaluating Solid Waste," Method 8260B *Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)*, December 1996.
2. Feyerherm, Fred; *Capillary Direct VOA's*, Hewlett Packard Company, Houston, TX, 1991.
3. Neal, Barney; *EPA Volatiles Analysis Using Narrow Bore Capillary Columns*, Hewlett Packard Company, Analytical Education Center, Atlanta, GA, 1992.

TABLE I. Purge and Trap Conditions.

Trap Material	Tenax, Silica Gel, and Charcoal (OI trap #10)
Sample Volume	5 mL
Purge Flow Rate	40 mL/min.
Purge Temperature	ambient
Purge Time	11 min.
Desorb Temperature	180 ºC
Desorb Time	0.5 min.
Bake Temperature	200 ºC
Bake Time	7 min.
Valve Temperature	100 ºC
Transfer Line Temperature	100 ºC

TABLE II. GC/MS Conditions.

Injector Mode	Split
GC Inlet Liner	Single taper, 4 mm ID, no glass wool
GC Inlet Temperature	200 ºC
Total Flow	20 mL/min.
Septum Purge	3 mL/min.
Column	Rtx-5, 30 m x 0.25 mm, 1 µm film
Column Linear Velocity	26.2 cm/sec. (0.5 mL/min.)
GC Oven Ramp	Hold 2.0 min. @ 10 ºC 10 - 90 ºC @ 20 ºC/min. 90 - 140 ºC @ 6 ºC/min. 140 - 240 ºC @ 60 ºC/min Hold 1.5 min. @ 240 ºC
GC-MS Interface temperature	280 ºC
Scan Range	35-300 amu
Solvent Delay	2 min.

TABLE III. Summary of mean RRFs, %RSDs, MDLs, and EQLS for selected compounds.

COMPOUND	MEAN RRF	%RSD	MDL (ppb)	EQL (ppb)
Chloromethane	1.09818	1.336	0.14	0.45
Bromomethane	0.48876	1.467	0.36	1.20
Acetone	0.07834	2.717	1.23	4.11
2-Butanone	0.09202	4.150	1.10	3.66
Chloroform	0.95677	2.073	0.18	0.60
Benzene	1.50253	3.086	0.05	0.18
Ethyl Benzene	1.71616	1.807	0.06	0.21
1,3-Dichlorobenzene	1.46463	2.014	0.12	0.40
Hexachlorobutadiene	0.41990	4.389	0.19	0.64
1,2,3-Trichlorobenzene	0.83833	4.532	0.35	1.17

A NEW APPROACH FOR HIGHLY COMPLEX ORGANIC ANALYSES USING SIMULTANEOUS SELECTED ION AND FULL ION SCANNING

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ABSTRACT

Regulated semivolatile organic compounds are present in our environment at widely diverse concentrations with an equally disparate range of sensitivity requirements. Nowhere is this more evident than in hazardous waste and site remediation samples. The number of target analytes in a Gas Chromatography/Mass Spectrometric (GC/MS) analysis is one of the most extensive. The ability to identify and quantify all of these compounds with one analysis pushes the method and technology to extremes. In most instances additional preparatory work and analyses are required to address the range of concentrations and the number of analytes.

Full scan ion monitoring is by far the most prevalent mode of operation for these types of samples. It covers the necessary mass range and provides classical spectra that can be library searched for positive identification. Selected Ion Recording (SIR also called SIM) is a GC/MS mode of operation where only the ions of interest are

monitored, independent from surrounding interferences and coelutions, providing dramatic increases in sensitivity. SIR has not been widely accepted in environmental testing labs. It requires prior knowledge of the sample matrix. Only targeted masses are detected and all others go unreported.

The combination of simultaneous Selected Ion and Full Ion (SIFI) scanning is a new approach providing the advantages of both techniques in a single chromatographic run. Using SIFI, samples comprised of analytes with wide response variations can be identified and quantified in the same chromatographic run. Analytical problems due to interferences can be greatly minimized. During a chromatographic analysis using the full scan mode, analytes requiring very low level detection in a complex matrix can be quantified using the added sensitivity of Selected Ion Recording (SIR) and still display library searchable spectra obtained from the full scan mode. Both the full scan and SIR scan functions are combined into one analysis providing low level detection in complex matrices while retaining all the functionality of full scan for the more responsive analytes.

This paper presents semivolatile organic data from analyses using a simultaneous Selected Ion and Full Ion (SIFI) scanning method. It also discusses some of the many productivity gains possible.

INTRODUCTION

There are well over 100 compounds that can be detected using EPA Method 8270[1]. Some compounds are particularly sensitive to these analytical conditions and respond with a strong signal while others are more difficult to detect, particularly at low levels. Calibration standards are generally at the same concentrations for the majority of target analytes. This often requires a system optimized for detection of the less sensitive compounds, while sacrificing signal at the higher concentrations for the more responsive ones. Consequently, compounds that don't have rigorous sensitivity requirements, are quantitated at unnecessarily low levels forfeiting quantitation in the more useful upper ranges.

By implementing selected ion recording only where the additional sensitivity is needed, the analytical range of the remaining analytes is not affected. Additionally, the compounds monitored utilizing selected ion recording can use the full ion scan if higher concentrations are encountered. This does not require an additional analysis, since both scan modes are implemented at the same time.

EXPERIMENT AND RESULTS

Six standards containing a number of semivolatile organic compounds listed in EPA method 8270 were analyzed using the GC/MS conditions listed in **Tables 1 & 2**. The selected compounds represent the various sensitivities encountered when analyzing for semivolatiles using GC/MS. Standards representing final concentrations of 1, 2, 5, 10, 20, and 40 ppb were selected as reasonable levels reflecting a range of sufficient sensitivities for soils and groundwater. Each contained internal standards at a constant concentration of 40 ppb.

Table 1. Chromatography Conditions.

Gas Chromatograph:	Perkin-Elmer AutoSystem XL
Column:	PE-5MS 30 m x 0.25 mm; 0.25 mm film thickness
Oven Temperature Program:	40 °C for 1 min; 45 °C/min. to 160 °C for 3 min; 6 °C/min to 320 °C for 2 min
Capillary Splitless Injection:	250 ºC
Programmable Pneumatic Control (PPC):	Helium @ 1.0 mL/min.
Split Vent:	Splitless -1.00 to 1.00 min; Split 20 mL @ 1.00 min.
Injection Volume:	1.0 µL

The specific analytes, Estimated Quantitation Levels (EQLs) as listed in EPA Method 8270, along with the regulated drinking water Maximum Contaminant Levels (MCLs) and the Maximum Contaminant Level Goals (MCLGs) are listed in **Table 3**. Method 8270 is obviously not intended to be sensitive enough for drinking water determinations, but appropriate for more complex matrices. We will demonstrate how compounds with widely varying sensitivity requirements can be combined into one analysis for project specific needs. This is in no way intended to recommend mixing drinking water samples with more highly contaminated samples, but sensitivity requirements can vary

from compound to compound for any particular project, requiring greater method flexibility. A method combining full ion and selected ion scanning provides this flexibility and is illustrated in **Figure 1**. Function 1 contains the full scan parameters. After a 4-minute filament delay, scanning of m/z 45 to m/z 450 proceeds for the duration of the chromatographic run. Function 2 contains selected ion recording (SIR) scanning parameters specific to 2-methyl-4,6-dinitrophenol. Mass 198 is monitored at this compound's expected retention time. Function 3 contains similar SIR information for pentachlorophenol using m/z 266 and function 4 at m/z 149 for bis-(ethylhexyl)phthalate. All four functions are executed during each analysis.

Table 2. Mass spectrometer method.

Perkin-Elmer TurboMass Mass Spectrometer				
	Full Scan Monitoring	Selected Ion Monitoring		
	Function 1	Function 2	Function 3	Function 4
Mass Scan Range:	45 – 450 m/z	198 m/z	266 m/z	149 m/z
Scan Time(sec):	0.30	0.02	0.02	0.02
Inter-scan Delay (sec):	0.20	0.02	0.02	0.02
Filament Delay:	4 min			
Ion Source Temperature:	175 ºC			
Transfer Line Temperature:	275 ºC			
Ionization Mode:	EI			

Table 3. Analytes, Method 8270 EQLs, drinking water MCLs and MCLGs.

Analytes	EPA Method 8270 EQLs (Ground water µg/L)	Drinking Water MCL (µg/L)	Drinking Water MCLG (mg/L)
2-Methyl-4,6-dinitrophenol	50		
Acenphthene-d10 (ISTD)			
Aminobiphenyl	20		
Anthracene	10		
Benz(a)anthracene	10		
Benzidine			
bis-(ethylhexyl)phthalate	10	6	zero
Bromophenyl phenyl ether	10		
Butyl benzyl phthalate	10		
Chrysene	10		
Chrysene-d12 (ISTD)			
Dibutyl phthalate	10		
Dichlorobenzidine	20		
Dimethylaminoazobenzene	10		
Fluoranthene	10		
Hexachlorobenzene	10	1	zero
Naphthalene-d8 (ISTD)			
Pentachlorophenol	50	1	zero
Perylene-d12 (ISTD)			
Phenanthrene	10		
Phenanthrene-d10 (ISTD)			
Pyrene	10		

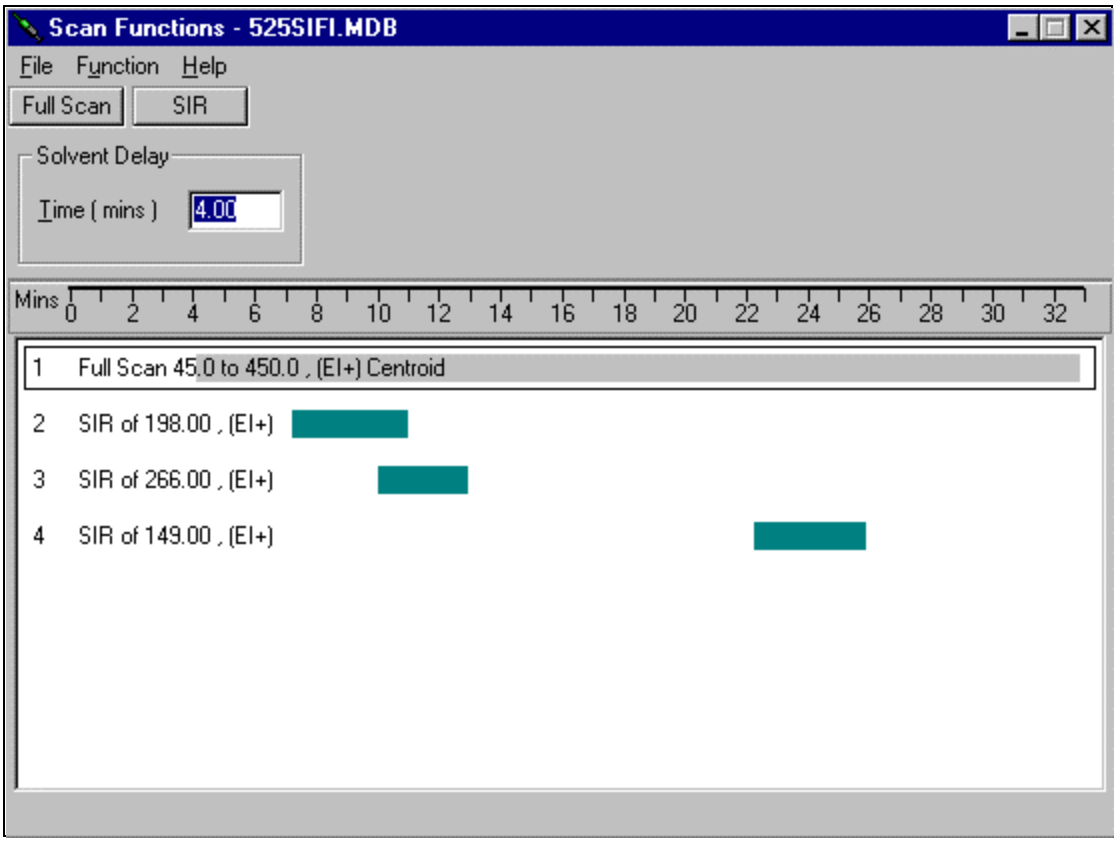

Figure 1. Simultaneous Selected Ion and Full Ion Scanning.

The percent Relative Standard Deviations (% RSDs) were calculated for every compound using all six calibration standards. This was demonstrated for one of the compounds for which full ion scanning and selected ion scanning was implemented, bis-(ethylhexyl) phthalate. **Table 4** lists the initial calibration results for this compound. Relative Response Factors (RRFs) and %RSDs are presented for both full ion and selected ion scanning. Each demonstrates compliance with the 30% RSD maxima method criteria. However, the selected ion mode of operation can be used to identify and quantify at much lower levels if and when necessary.

Table 4. Initial Calibration using full ion monitoring and selected ion recording.

Initial Calibration for bis-(ethylhexyl)phthalate		
Standards	**Full Ion Scanning (RRFs)**	**Selected Ion Scanning (RRFs)**
1 ppb	0.794	42.342
2 ppb	0.801	43.397
5 ppb	0.850	44.162
10 ppb	0.737	38.044
20 ppb	0.864	43.873
40 ppb	1.272	63.550
Average RRF	**0.886**	**45.895**
% RSD	19.987	17.775

Figure 2 shows the total ion chromatogram (TIC), the extracted ion current (EIC), and the selected ion recording (SIR) from one analysis. The signal produced in the SIR mode for bis-(ethylhexyl)phthalate at 1ppb is approximately four times that of the extracted ion in the full scan mode as measured by signal-to-noise.

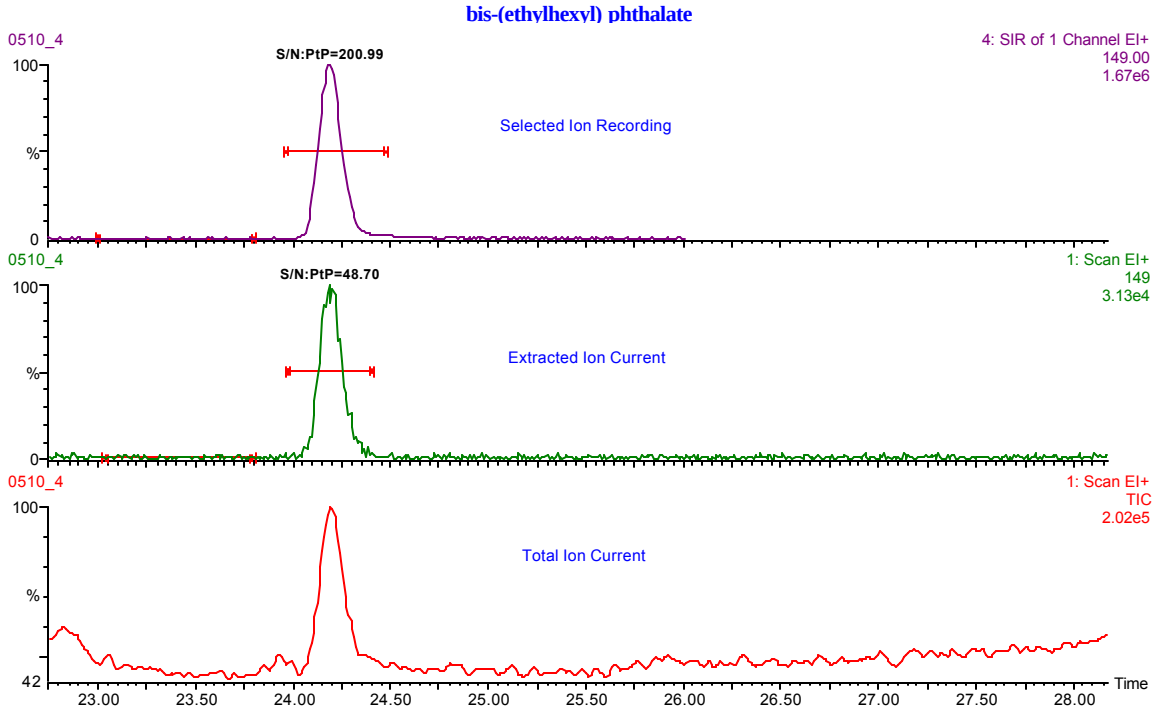

Figure 2. SIR and full scan signal-to-noise comparison.

The spectra obtained from these traces are displayed in **Figure 3**. The SIR mode provides increased sensitivity by scanning for longer periods of time on a few specific masses, in this case m/z 149, while the full scan mode produces a spectra which can be library searched for accurate identification.

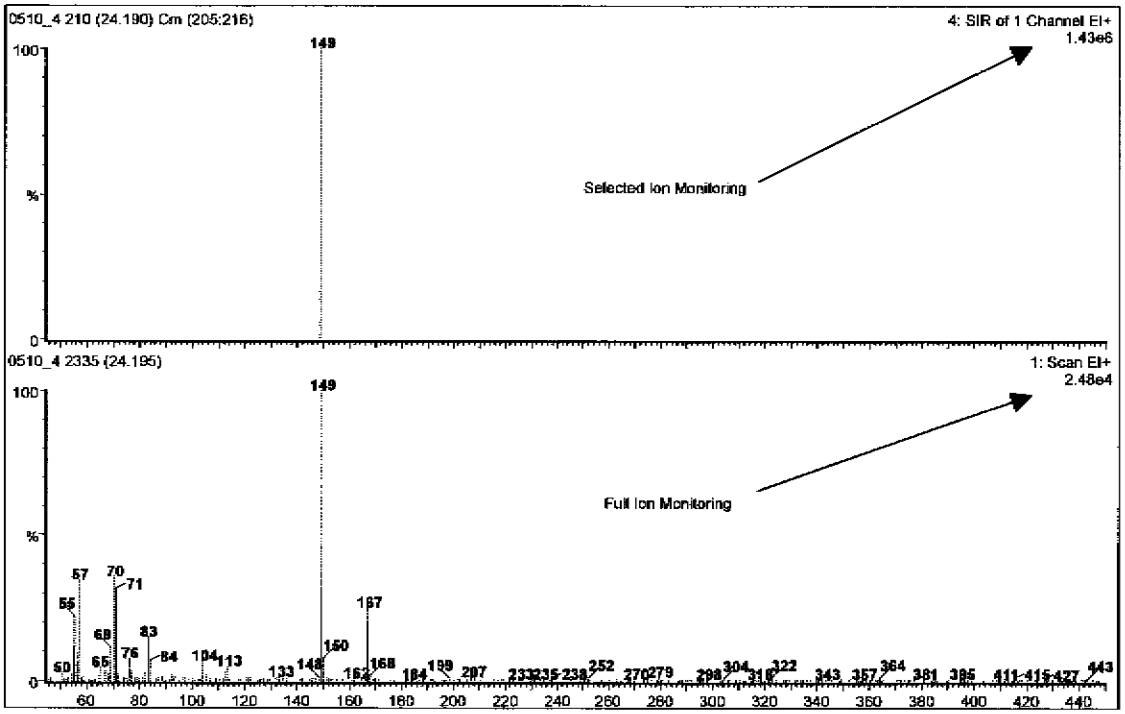

Figure 3. Spectra and signal intensity for bis-(ethylhexyl)phthalate using SIR and full scan mode.

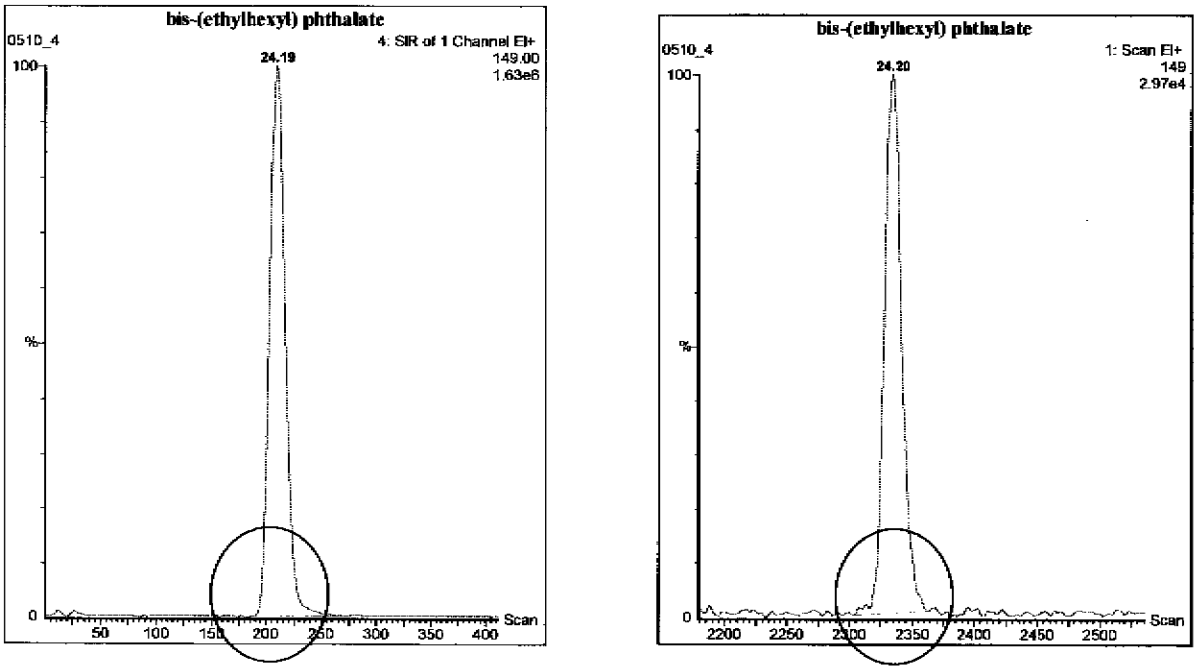

Figure 4. Both SIR and EIC yield a sufficient number of scans across the peak.

There must be a sufficient number of scans across each peak to ensure accurate integration. **Figure 4** displays the SIR and the EIC for bis-(ethylhexyl)phthalate from one analysis. The scan number can be read across the x-axis below each peak and clearly shows more than enough scans, assuring accurate integration.

SUMMARY

A GC/MS analysis can be optimized to take advantage of the highest concentrations necessary for all the analytes using the full scan mode, while at the same time increasing the sensitivity only where it is needed using selected ion recording. Compounds can be identified and quantified in either scan mode in the same analysis. This added flexibility can expand the overall analytical range across a widely disparate group of compounds by selectively choosing when and where increased sensitivity is needed.

REFERENCE

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3^{d} edition; Final Update III; Method 8082, rev 0, Dec 1996.

DOES CHEMICAL IONIZATION HAVE A FUTURE IN THE ENVIRONMENTAL LABORATORY?

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ABSTRACT

Electron Capture Negative Chemical Ionization Mass Spectrometry (EC NCI MS) is a technique which, for the most part, has been overlooked by the environmental testing community. It offers advantages in selectivity and sensitivity for a variety of environmental applications.

Pesticide and PCB analyses are routinely performed using an electron capture detector (ECD) or electron ionization mass spectrometer (EI MS), each of which offers unique advantages and disadvantages. ECDs afford greater selectivity for the identification of halogenated compounds along with increased sensitivity, although confirmatory analyses are required. While EI MS offers a higher confidence level for accurate compound identification, it is usually at the

expense of sensitivity. EC NCI MS combines many of the advantages from each of these techniques. As with ECD applications, chemical ionization offers a high degree of selectivity for specific classes of compounds while affording even greater sensitivity.

EI MS can produce highly fragmented spectra with a concomitant reduction of base peak intensity. Alternatively, EC NCI uses a moderator gas for low-energy electron capture as with an ECD. This leads to minimal fragmentation, maximizing signal intensity. Sensitivity gains can also be realized by scanning for longer periods of time on a few specific masses, using Selected Ion Recording (SIR also called SIM).

NCI using Full Ion scanning provides enhanced sensitivity and characteristic spectral patterns yielding valuable compound information. At the same time, Selected Ion scanning affords even further sensitivity gains. The acquisition of data using simultaneous Selected Ion and Full Ion (SIFI) scanning in the EI NCI mode combines the advantages of both techniques for a dramatic increase in sensitivity. **Figure 1** displays the chromatograms of an EI NCI simultaneous SIFI analysis.

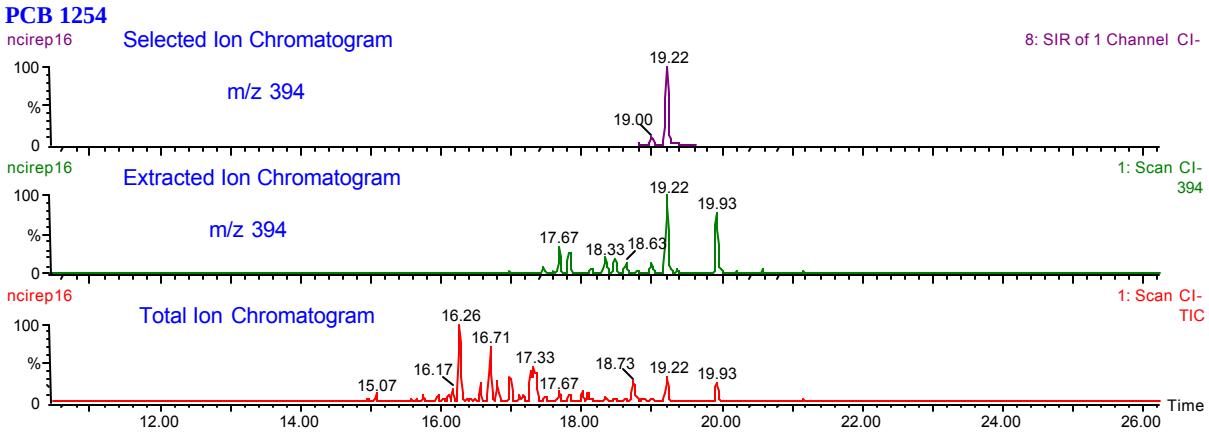

Figure 1. Aroclor 1254 acquired with NCI and simultaneous SIFI

The results of PCB analyses using NCI and simultaneous SIFI scanning will be shown. Sensitivity data is presented as well as a discussion on the merits of the use of this technique in the high throughput environmental laboratory.

INTRODUCTION

To date, most environmental labs have determined PCB concentrations by averaging the areas of a few selected characteristic peaks from a total ion chromatogram. It is generally recognized that the measurement of the PCB individual biphenyl congeners provides greater overall quantitative accuracy. It is preferable for determining PCB containing samples with unrecognizable chromatography patterns such as highly weathered samples and samples containing multiple Arochlors. SW-846 states "The PCB congener approach affords greater quantitative accuracy…the congener method is of particular value in determining weathered Arochlors." Pesticide and PCB analyses are routinely performed using an electron capture detector (ECD) or electron ionization mass spectrometer (EI MS), each of which offers unique advantages and disadvantages. ECDs afford greater selectivity for the identification of halogenated compounds along with increased sensitivity, although confirmatory analyses are required. While EI MS offers a higher confidence level for accurate compound identification, it is usually at the expense of sensitivity. Chemical Ionization Mass Spectrometry (CI MS) combines many of the advantages from each of these techniques. As with ECD applications, chemical ionization (CI) offers a high degree of selectivity for individual classes of compounds while affording even greater sensitivity. These features make chemical ionization an excellent candidate for low level biphenyl identification and quantification.

EXPERIMENT and RESULTS

The list of biphenyl congeners is quite extensive. For the purposes of this paper we will focus on ten congeners representing each successive level of halogenation. Standards containing the specific congeners listed in **Table 1** were analyzed using electron ionization and negative chemical ionization (NCI).

Table 1. Individual Biphenyls

•2-Chlorobiphenyl (Cl)	•'2,2',3,3',6,6'-Hexachlorobiphenyl (6 Cl)
•'3,3'-Dichlorobiphenyl (2 Cl)	•'2,2',3,4,5,5',6- Heptachlorobiphenyl (7 Cl)
•2,4,5-Trichlorobiphenyl (3 Cl)	•'2,2',3,3',4,4',5,5'-Octachlorobiphenyl (8 Cl)
•'2,2',4,4'-Tetrachlorobiphenyl (4 Cl)	•'2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (9 Cl)
•'2,3',4,5',6-Pentachlorobiphenyl (5 Cl)	•'2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl (10 Cl)

Table 2 lists the chromatographic conditions used for both ionization modes. **Table 3** lists the Perkin-Elmer TurboMass mass spectrometer parameters used for each ionization mode. Methane was selected as the reagent gas for NCI. None is used for EI. The electron energy was kept constant for both modes of operation. In NCI the injection of reagent gas increases the gas pressure in the ion source. The ion source temperature was kept constant while the electron multiplier was run at a slightly higher setting in NCI mode. The selected masses using NCI reflect the most abundant mass and are usually from the molecular ion cluster, while those for EI were the most abundant and do not necessarily reflect the molecular ion owing to greater fragmentation.

Table 2. Chromatography Conditions

GC:	Perkin-Elmer AutoSystem XL
Column:	PE-5MS 30 m x 0.25 mm; 0.25 mm film thickness
Oven Temperature Program:	55°C for 5 min., 45°C/min. to 160°C; 6°C/min to 320°C
Capillary Splitless Injection:	250°C
Programmable Pneumatic Control (PPC):	Helium @ 1.0 mL/min.
Split Vent:	Splitless -1.00 to 1.00 min; Split 50 mL @ 1.00 min.
Injection Volume:	1.0 µL

Table 3. EI and NCI Parameters

TurboMass Parameters	Electron Ionization	Negative Chemical Ionization
Reagent Gas:	None	Methane
Electron Energy:	70 eV	70 eV
Pressure:	6.9 x 10^{-6} Torr	1.5 x 10^{-4} Torr
Ion Source Temperature:	150°C	150°C
Electron Multiplier:	524 V	651 V
Full Scan:	m/z 160 to m/z 600	m/z 160 to m/z 600
Analytes:	10 individual biphenyls	10 individual biphenyls
Selected Ion Scans:	m/z 188, 222, 256, 292, 326, 360, 394, 430, 464, & 498	m/z 187, 221, 255, 292, 326, 360, 394, 430, 464, & 498

A mixed concentration standard containing the previously named 10 biphenyls was analyzed using electron ionization and negative chemical ionization. **Figure 2** shows an overlay offset of both total ion current chromatograms.

Specific analyte concentrations are annotated over the individual peaks. The EI chromatogram shows an inverse response to increasing levels of halogenation, with chlorobiphenyl the most responsive and decachlorobiphenyl the least. The overall response is much less than that of the same compounds using NCI. In the NCI mode of operation we see a general increase in response to increasing levels of halogenation with the exception of pentachlorobiphenyl and hexachlorobiphenyl.

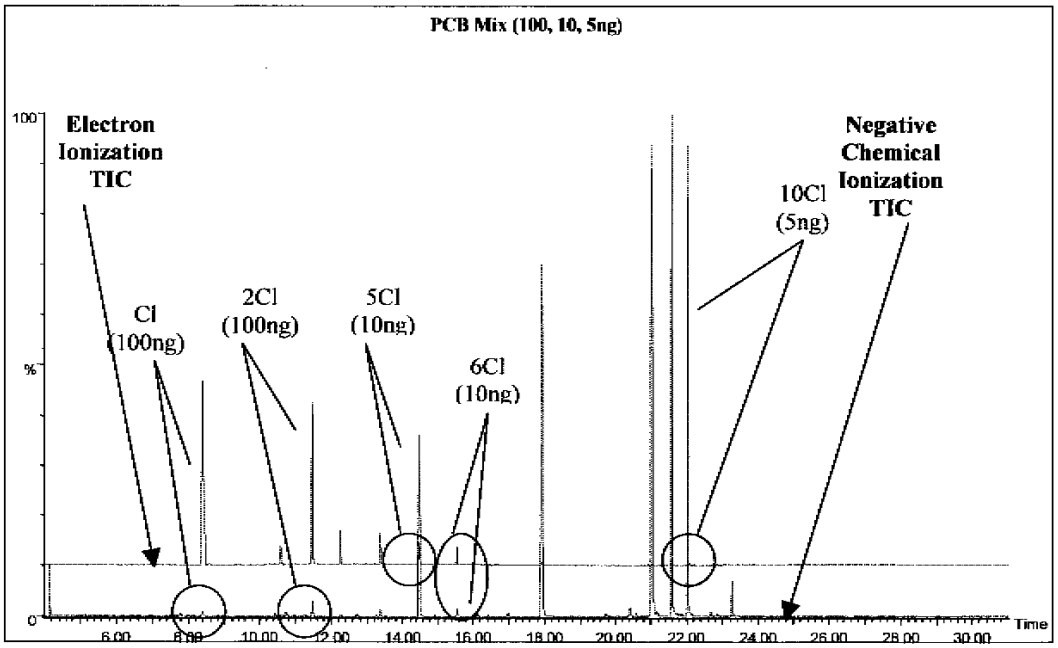

Figure 2. TICs of a Biphenyl Standard Mix using EI & NCI

Decachlorobiphenyl shows a dramatic increase in NCI response whereas chlorobiphenyl exhibits a reduced signal. It is believed that the inverse response of penta- and hexachlorobiphenyl is related to the isomeric structure. The 2,4,6 conjugation of the chlorines in the pentachlorobiphenyl may enable the ring to stabilize the negative charge better, reducing fragmentation and increasing signal. **Figure 3** shows chlorobiphenyl and decachlorobiphenyl comparing the integrated areas obtained using EI and NCI. EI shows greater sensitivity for the less halogenated compound, although the NCI signal is quantifiable. NCI shows even greater sensitivity gains with increasing halogenation while the decachlorobiphenyl peak using EI shows a barely discernible signal.

The optimal technique will depend on the particular biphenyls targeted and the sensitivity levels required. NCI offers greater sensitivity for a larger number of the biphenyls examined here than EI offers. The ability to change between modes of operation, i.e., NCI and EI is crucial for optimum versatility and instrument utilization. The combination of these two techniques can provide more information relative to sample content and realization of dramatic increases in sensitivity. Ion sources can be easily interchanged without disrupting the chromatography conditions or column retention times. The chromatogram shown previously in **Figure 2** exemplifies this. The TurboMass ion source can be changed in about 1 minute (exclusive of cool down and heat up times) allowing for confirmation using EI and the NIST library along with the sensitivity gains realized using NCI. The two modes of operation are complimentary.

If greater sensitivity is needed for less halogenated biphenyls using NCI, selected ion monitoring is an attractive alternative. The TurboMass mass spectrometer can perform Selected Ion Recording (SIR also called SIM) scanning while also acquiring in the Full Scan mode. A mass spectrometer data acquisition method was created combining both Full scan and SIR modes. The selected masses and retention time windows are listed in Figure 4. Full ion scanning is performed throughout the entire chromatographic run, while the individual biphenyl signature masses are scanned at the appropriate chromatographic elution times.

The SIR peak can then be used for quantification while the Full Scan provides spectra for accurate identification. In this manner biphenyls with varying responses can be combined in one analysis. Quantification can be performed using Full Scan or SIR on a compound-by-compound basis. Simultaneous Selected Ion & Full Ion (SIFI) Scanning combines all the benefits from both modes of operation into one chromatographic run.

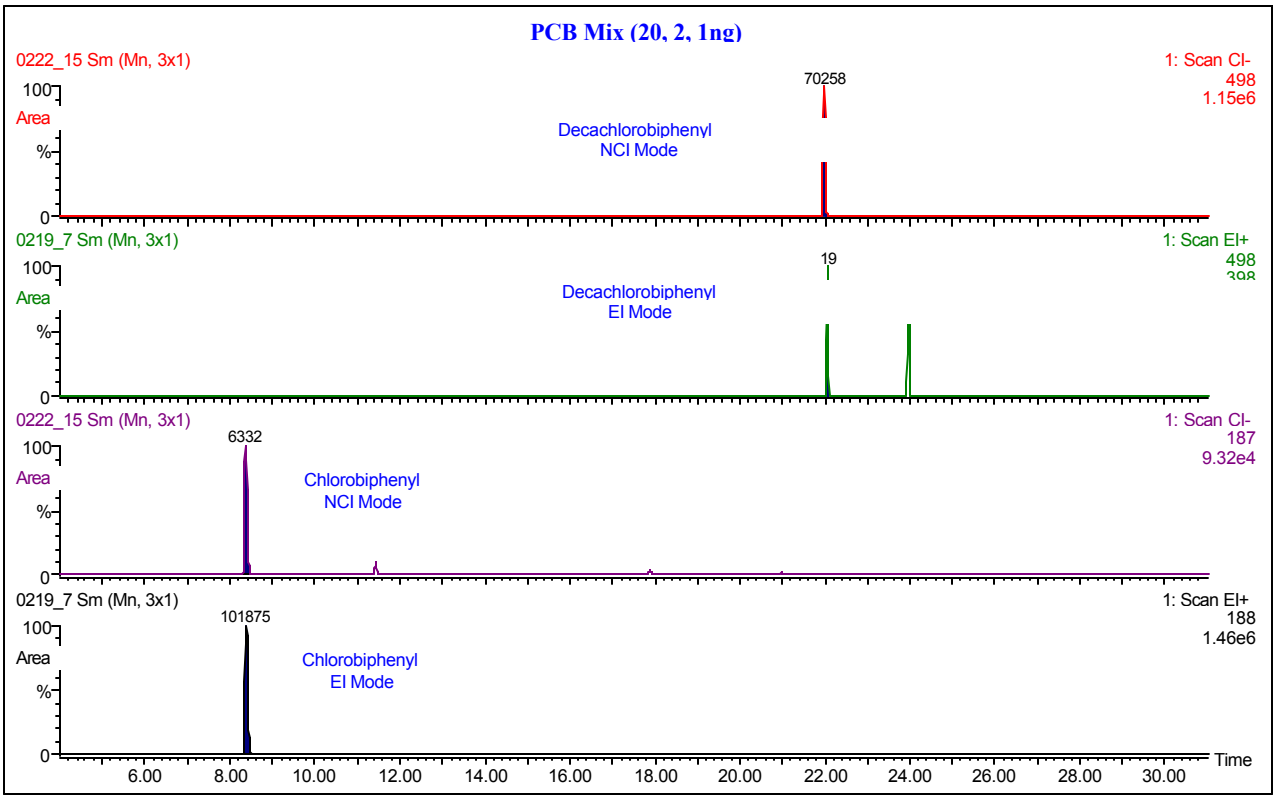

Figure 3. Monochlorinated and Decachlorinated biphenyls using EI & NCI.

SUMMARY

Electron capture negative chemical ionization provides a high level of discrimination. It can selectively detect halogenated compounds, such as polychlorinated biphenyls. Selectivity also helps to greatly minimize interferences. Generally, for the congeners examined in this paper, NCI shows a much higher response for the more highly chlorinated compounds, although this will depend on the degree of isomerization. The dramatic increases in sensitivity realized for the more highly chlorinated biphenyls using NCI ordinarily reflects the increasing level of PCB chlorination.

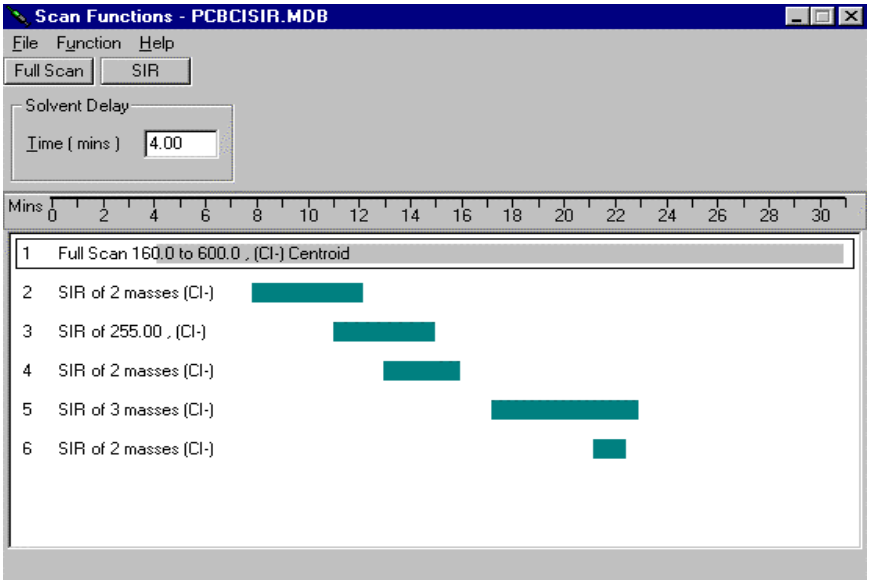

Figure 4. Simultaneous Full Ion and Selected Ion Scanning using Negative Chemical Ionization

The less highly chlorinated biphenyls, and particularly tri- and tetra-chlorobiphenyl, are not as responsive to EC NCI. EI may provide a better solution for these congeners. An even more accurate compound profile can be obtained by the efficient use of both forms of ionization. Fast and simple switching between EI and CI modes of operation affords the most efficient technique for optimum analyte characterization. However, CI is not without it's drawbacks. More frequent source maintenance is required for CI and incurs the added cost of reagent gas. Since chemical ionization is new to the environmental laboratory, it will require additional method development and increased operator skill level. With a sensitive detector and an efficient technique for alternating sources, NCI can be a powerful tool for use in the environmental laboratory, providing the ability to use both electron and chemical ionization for the determination and characterization of PCB contaminated material.

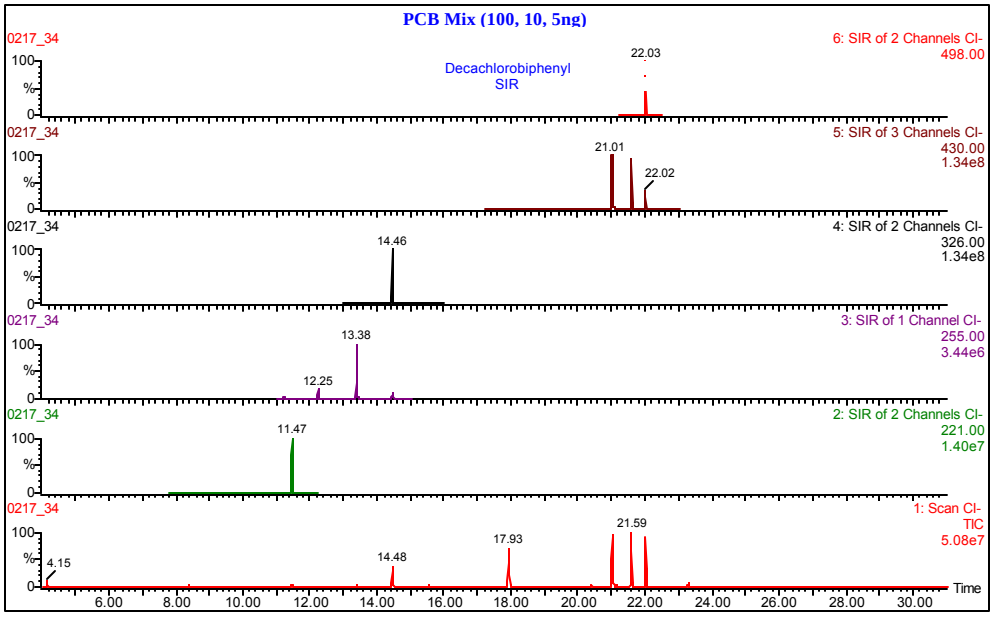

Figure 5. Simultaneous Selected Ion and Full Ion Scans for a biphenyl standard mixture.

The selected ion currents for five of the biphenyls are show in **Figure 5** along with the total ion chromatogram acquired at the same time. **Figure 6** emphasizes the sensitivity gains realized using SIFI and NCI. The less responsive chlorobiphenyl at a concentration of 10 ng/uL shows over a factor of 40 increase in area using the selected ion monitoring mode as compared to the full ion scannning mode. In one analysis, selected ion monitoring can be implemented for chlorobiphenyl and other poorly responding analytes, while full ion monitoring is more than sufficient for the more responsive biphenyls, such as Decachlorobiphenyl.

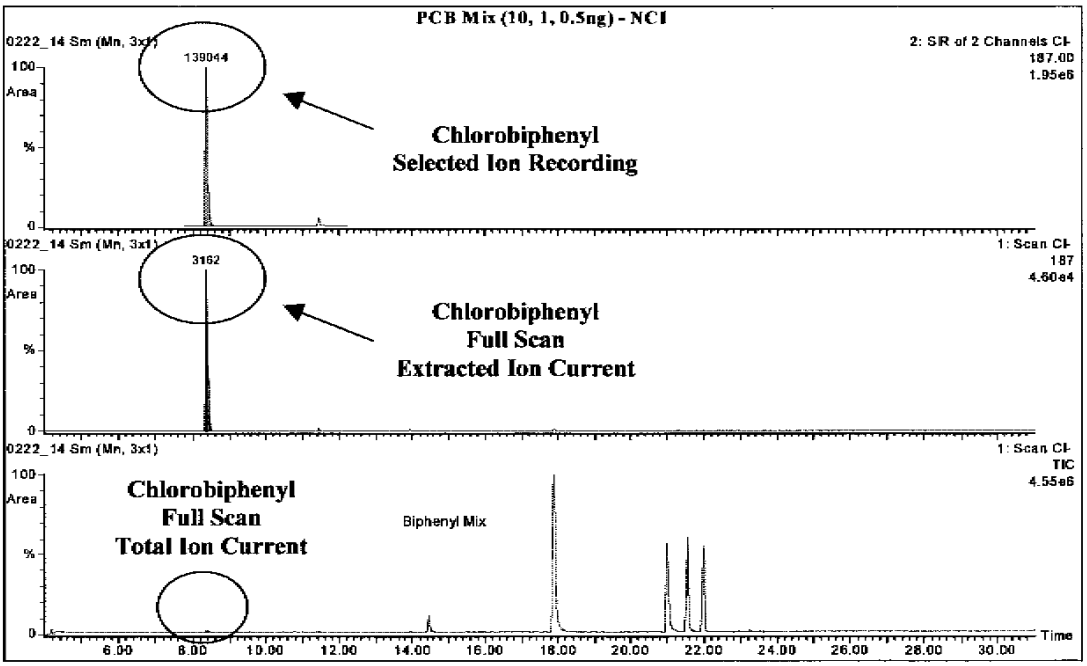

Figure 6. Chlorinated biphenyl peak areas using simultaneous SIFI in NCI mode.

Additionally, simultaneous full ion and selective ion (SIFI) monitoring in one analysis can provide the ultimate combination of sensitivity and productivity. SIFI can be combined with either ionization technique, increasing sensitivity only where it is needed. It can extend the analytical range for analytes with widely disparate responses thereby eliminating many additional analyses.

THE USE OF SULFURIC ACID CLEANUP TECHNIQUES TO MINIMIZE MATRIX INTERFERENCES FOR THE ANALYSIS FOR TOXAPHENE IN SOIL, SEDIMENT, AND GROUNDWATER

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ABSTRACT

Toxaphene is a chlorinated camphene insecticide, containing more than 170 components, which yields a complex, multi-component gas chromatogram. Accurate identification and measurement of toxaphene in environmental samples depend on the removal of matrix interferences from the sample extracts before analyses by gas chromatography using an electron capture detector (GC-ECD). The successful analysis of complex soil and sediment samples, which contain natural and synthetic substances, by gas chromatographic techniques, has long been a challenge for analytical chemists. The use of selective detectors and cleanup techniques has assisted in this endeavor. With respect to the analyses for extractable chlorinated pesticides and polychlorinated biphenyls (PCB) in environmental samples, the U.S. EPA has published a variety of cleanup techniques. The intent of these procedures is to minimize co-extracted interfering substances, while maintaining the qualitative and quantitative integrity of the target analyte(s) of interest. On two projects involving the collection of varying soil, sediment, and groundwater samples, multi-laboratory method validation studies were performed to assess the viability of using sulfuric acid cleanup techniques for the analyses for toxaphene. Extraction techniques, analytical conditions, method validation data, and on-going laboratory control recovery data indicate that sulfuric acid is an effective cleanup technique which significantly reduces co-extracted matrix interferences and that sulfuric acid does not affect the qualitative and quantitative integrity of toxaphene. Based on these studies, the authors conclude that SW-846 Method 3665A should include toxaphene as a validated analyte.

INTRODUCTION

Toxaphene had been a widely used pesticide in the United States until most uses were banned in 1982[1]. Over the past several years, Hercules has collected environmental samples as part of monitoring and remediation activities and has submitted those samples to contract laboratories for the determination of toxaphene. Because toxaphene is a chlorinated camphene insecticide that contains more than 170 components, a multi-component gas chromatogram is obtained[2]. Therefore, in order to identify and measure toxaphene accurately, it is particularly important to eliminate from the sample matrix interferences such as single-response organochlorine pesticides and other electron capture-sensitive compounds[3,4,5].

With respect to the analyses for extractable chlorinated pesticides and PCBs in environmental samples, the U.S. EPA has published[6] a variety of cleanup techniques. The intent of these cleanup procedures is to minimize co-extracted interfering substances, while maintaining the qualitative and quantitative integrity of the target analyte(s) of interest. In particular, the U.S. EPA has published SW-846 Method 3665A, which is a sulfuric acid cleanup procedure. This procedure is identified in the method as being specific to the analyses for PCBs, since these compounds have been shown to be relatively unaffected by this cleanup technique. Conversely, as noted in the method, this cleanup technique "cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate." As a result, sulfuric acid has been exclusively relegated for use as a cleanup technique for the analysis for PCBs during many environmental investigations.

Two projects involved the collection of a significant number of soil, sediment, and groundwater samples collected at sites in the Southeast and on the West Coast. Due to the nature of these sites, significant chromatographic interferences were suspected in the form of co-extracted non-target analytes. Because of this concern, both of the laboratories retained to perform the analyses were first required to perform independent formal method validation studies, inclusive of method detection limit (MDL) studies and precision and accuracy studies, to assess the viability of using sulfuric acid cleanup techniques for the analysis for toxaphene.

EXPERIMENTAL METHODS

Soil, sediment, and groundwater samples were extracted using SW-846 Methods 3550A and 3510C. The resulting extracts were exchanged to hexane and concentrated to a final volume of 10 mL. The final hexane solutions were cleaned up by shaking with concentrated sulfuric acid (SW-846 Method 3665A). The hexane layer was then

analyzed by GC-ECD, following SW-846 Method 8081A with additional, project-specific data quality objectives (DQOs) and analytical requirements. All samples were injected into two different GC columns for quantitation and confirmation: DB-1701 and DB-5, respectively.

RESULTS AND DISCUSSION

The QA/QC samples from the investigations at two different commercial laboratories working on samples from two different sites were examined for evidence of changes in the GC profile of toxaphene. Comparisons of the chromatograms of the toxaphene calibration standard; the soil, sediment, or groundwater samples; the matrix spikes (MS) and matrix spike duplicates (MSD); and the laboratory control samples (LCS) were made to determine if changes in the GC patterns were generated as a result of the H_2SO_4 cleanup. A secondary comparison was made to ascertain if the use of H_2SO_4 had any effect on the recoveries of the two surrogate compounds: tetrachloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB).

Comparisons of the chromatograms in Figure 1 and Figure 2 demonstrate that there were no discernable changes in the toxaphene after exposure to the H_2SO_4 cleanup step. In Figure 1, the chromatograms of the soil samples (980672-006) show no changes in the GC peak pattern for the MS and MSD samples. The few peaks that are different from the toxaphene standard originate in the soil extract, and they are not removed by the H_2SO_4 treatment. They are not related to changes in the toxaphene during the acid cleanup step. In Figure 2, the chromatogram of the water sample (980674-001) after H_2SO_4 cleanup shows only traces of peaks. In the MS and MSD samples, the GC patterns of the toxaphene after cleanup clearly demonstrate a peak-for-peak match for the components in the toxaphene standard. The toxaphene standard is a calibration solution, which had no contact with H_2SO_4.

The quantitative recoveries for toxaphene in the MS and MSD samples, the LCS's, and the surrogate compounds TCMX and DCB from a number of representative samples collected from Site 1 are presented in Table 1. Excellent recoveries were achieved for toxaphene in the MS and MSD samples and the LCS's, ranging from 88 % to 110%. Similarly, acceptable recoveries were observed for TCMX and DCB, which ranged for 73% to 123%. The quantitative recoveries for toxaphene in the MS and MSD samples, the LCS's, and the surrogate compounds TCMX and DCB from a number of representative samples collected from Site 2 are presented in Table 2. As was the case for Site 1, excellent recoveries were also obtained for Site 2 for toxaphene in the MS and MSD samples and the LCS's, ranging from 78% to 110%. Similarly, acceptable recoveries were observed for TCMX and DCB, which ranged from 67% to 97%.

SUMMARY

The work presented within this study is a summary of research performed on a significant number of soil, sediment, and groundwater samples collected from two different sites and analyzed at two independent commercial laboratories. This research has demonstrated that sulfuric acid is an excellent cleanup option for the analysis for toxaphene. There are no discernable changes in the toxaphene GC-ECD profile after sulfuric acid cleanup. The recovery of toxaphene, TCMX, and DCB indicate that there is no destruction of those compounds as a result of contact with concentrated sulfuric acid. The application of the research presented herein, complete with thoughtful project planning, project-specific DQOs, and analytical requirement specifications, represents the essence and appropriate application of the U.S. EPA performance-based measurement systems (PBMS). It is recommended that, during the next update period, toxaphene be added to the list of analytes that have been validated for use in SW-846 Method 3665.

REFERENCES

1. United States Public Health Service, Agency for Toxic Substances and Disease Registry, "Toxicological Profile for Toxaphene (Update)," August, 1996.
2. M.A. Saleh, "Toxaphene Chemistry, Biochemistry, Toxicity, and Environmental Fate," Rev. Environ. Contam. Toxicol. **118**: 1-85 (1991).
3. J.W. Gooch and F. Matsumura, "Evaluation of Toxic Components of Toxaphene in Lake Michigan Trout," J. Agr. Food Chem. **33**: 844-848 (1985).
4. F. Matsumura, R.W. Howard, and J.O. Nelson, "Structure of the Toxic Fraction of Toxaphene," Chemosphere **5**: 271-276 (1975).
5. J.O. Nelson and F. Matsumura, "Separation and Comparative Toxicity of Toxaphene Components," J. Agr. Food Chem. **23**: 984-990 (1975).
6. United States Environmental Protection Agency, "Test Methods for Evaluation of Solid Waste, Volume 1B: Laboratory Manual, Physical/Chemical Methods, (SW-846)," Method 8080A, Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography, Revision 1, November 1992.

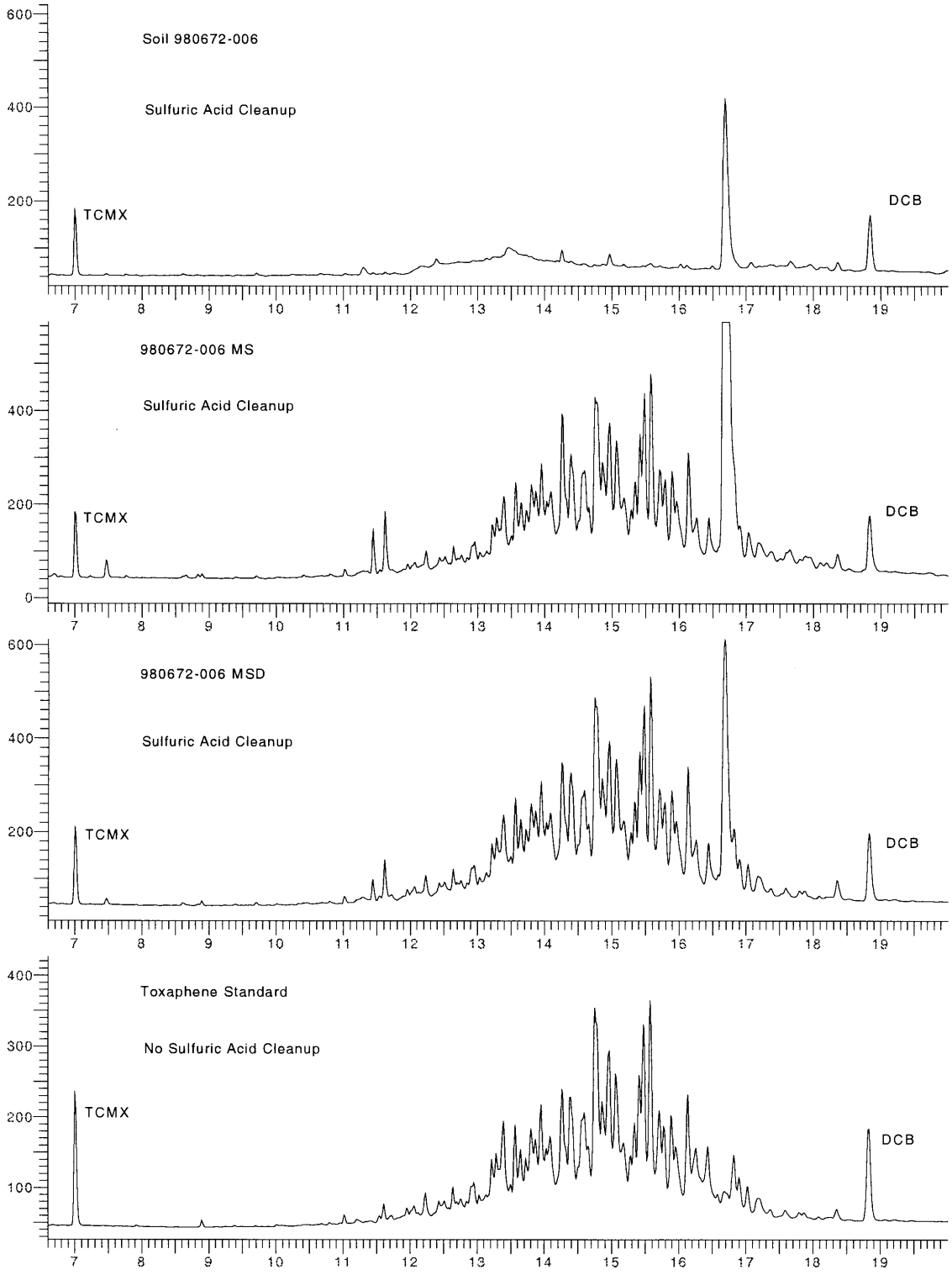

Figure 1. Comparison of Chromatograms of a Toxaphene Standard with Extracts of a Soil Sample and Matrix Spike Samples

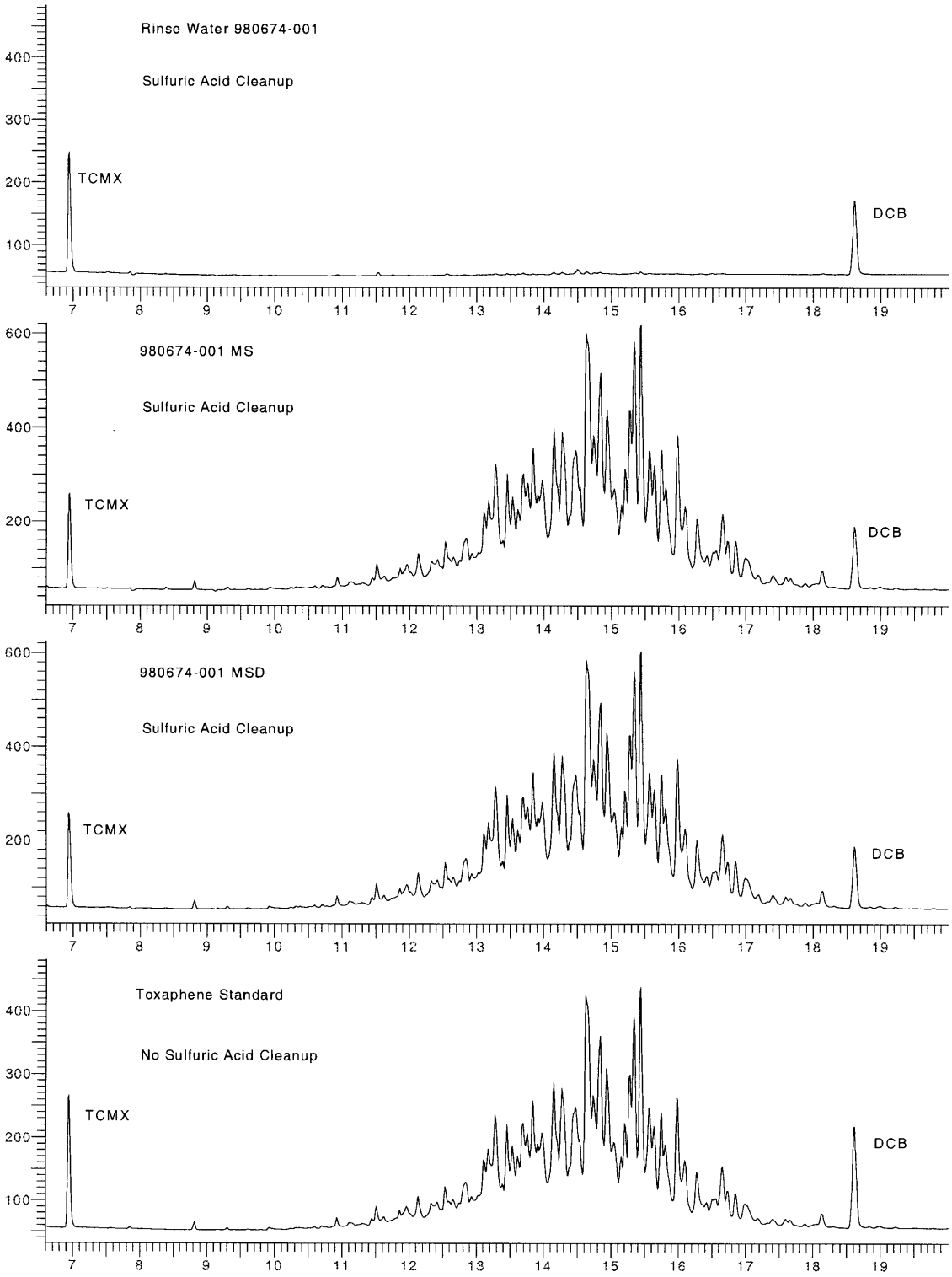

Figure 2. Comparison of Chromatograms of a Toxaphene Standard with Extracts of a Water Sample and Matrix Spike Samples

Table 1. Summary of Recovery Data from Laboratory 1 and Site 1

SAMPLE NUMBER	SAMPLE TYPE	MATRIX	ANALYTE	% RECOVERY
9020127-BLK1	Blank	Soil	Toxaphene	ND
			TCMX	77.8
			DCB	72.7
9020127-BS1	LCS		Toxaphene	90.9
			TCMX	88.9
			DCB	83.8
9020127-MS1	MS	Soil	Toxaphene	88.0
			TCMX	90.7
			DCB	80.8
9020127-MSD1	MSD	Soil	Toxaphene	91.0
			TCMX	92.8
			DCB	83.8
9020258-BLK1	Blank		Toxaphene	ND
			TCMX	77.2
			DCB	79.3
9020258-BS1	LCS		Toxaphene	95.4
			TCMX	79.0
			DCB	91.0
9020258-MS1	MS	Soil	Toxaphene	122
			TCMX	123
			DCB	114
9020258-MSD1	MSD	Soil	Toxaphene	106
			TCMX	111
			DCB	101

ND = Not Detected

Table 2. Summary of Recovery Data from Laboratory 2 and Site 2

SAMPLE NUMBER	SAMPLE TYPE	MATRIX	ANALYTE	% RECOVERY
980675-005	MS	Sediment	Toxaphene	88
			TCMX	78
			DCB	85
	MSD	Sediment	Toxaphene	92
			TCMX	79
			DCB	86
	LCS 1		Toxaphene	78
			TCMX	67
			DCB	80
	LCS 2		Toxaphene	86
			TCMX	68
			DCB	84
980788-007	MS	Sediment	Toxaphene	92
			TCMX	87
			DCB	97
	MSD	Sediment	Toxaphene	94
			TCMX	88
			DCB	92
	LCS 17		Toxaphene	91
			TCMX	85
			DCB	94
	LCS 18		Toxaphene	95
			TCMX	89
			DCB	92
980674-001	MS	Water	Toxaphene	110
			TCMX	82
			DCB	78
	MSD	Water	Toxaphene	107
			TCMX	93
			DCB	78
	LCS 98		Toxaphene	100
			TCMX	80
			DCB	91

ND = Not Detected

THE ANALYSIS OF ARMY CHEMICAL AGENTS: GB, VX, MUSTARD, AND LEWISITE IN SOIL AT ROCKY MOUNTAIN ARSENAL

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ABSTRACT

A critical need in the ongoing remediation of Rocky Mountain Arsenal (RMA) is the ability to quickly determine whether various solid materials are free of military chemical agent contamination. The analysis must be performed and results available within two hours of receipt of the sample at the onsite laboratory. The reported results must exhibit a high degree of confidence and accuracy. Suitable methods for bis(2-Chloroethyl) sulfide, (Mustard,H), Isopropylmethylphosphonofluridate, (Sarin,GB), O-ethylS(2-diisopropylaminoethyl)methylphosphonothiolate(VX), and 2-chlorovinyl dichloroarsine (Lewisite,L) have been validated at the Environmental Analytical Laboratory (EAL) at RMA under the Comprehensive Analytical Laboratory Services (CALS) contract (CALS contractor URS Greiner Woodward Clyde). These techniques are used in support of the remediation at RMA.

GB, VX and H are first extracted from solid matrices in a fluid containing chloroform and 2-(diisopropyl amino) ethanol. The extract is decanted, centrifuged, and analyzed on two separate gas chromatographs (GC) equipped with dual flame photometric detectors (FPD). The first GC is configured in the phosphorous mode with a 525-nm filter for the analysis of GB and VX. The second GC is configured in the sulfur mode with a 393-nm filter for the analysis of Mustard (H). Simultaneous second column confirmation is used on both gas chromatographs to provide confirmatory analysis.

Lewisite is first extracted in a fluid containing 0.01% 1,3-propanedithiol in hexane. The 1,3-propanedithiol derivatizes Lewisite and its breakdown products into a similar derivative (LD) which is chromatographically stable. The derivatization of Lewisite and its breakdown products allow for a quick qualitative and quantitative analysis by a gas chromatograph for the presence or former presence of Lewisite in solid matrices. The extract is analyzed on a GC equipped with dual flame photometric detectors configured in the sulfur mode, dual columns and injectors for simultaneous qualitative and quantitative analysis.

These methodologies have been subjected to a performance-based validation process which for GB, VX, H and L resulted in the following Method Reporting Limits (MRL) and accuracies. Method validations for these four Army chemical agents were performed using non-agent RMA standard soil:

- The MRL for Mustard was determined to be 0.250 µg/g, with a method accuracy of 113%.
- The MRL for GB was determined to be 0.320 µg/g, with a method accuracy of 85.1%.
- The MRL for VX was determined to be 0.353 µg/g, with a method accuracy of 74.5%.
- The MRL for Lewisite was determined to be 0.275 µg/g, with a method accuracy of 80.3%.

The following poster material will explain in detail how these methods are performed. These methodologies have been critical in furthering the remediation at RMA by providing a means to establish that various solid materials are free of military chemical agent contamination.

INTRODUCTION

Chemical agent production at RMA occurred under a variety of different programs for numerous years. Mustard was manufactured at the facility from December 1942 until May of 1943. Mustard was also found at RMA at various other times for many different projects including the filling of munitions and demilitarization. The production of Lewisite began in April of 1943 and ended in November of 1943. The production of nerve agent GB (Sarin), occurred at the Arsenal from 1953-1958. Demilitarization occurred in 1972,1973, and 1976. Finally VX was stored at RMA in what is now known as the Toxic Storage Yard. These activities lead to the need to develop analytical techniques that quickly determine that various solid matrices are free of these four chemical agents. The analyses must be performed and results available within two hours of receipt at the onsite laboratory. These analyses can be performed within the necessary framework using two different methods on three different GCs.

THE ANALYSIS OF GB, VX, AND H IN SOIL

Reagents:

1. Chloroform, $CHCl_3$, Residue grade (assay 99.95%) or better

2. 2-(diisopropylamino)ethanol. $[(CH_3)_2CH]_2$-N-CH_2-CH_2-OH
3. Extraction Mixture, (Prepare by placing 500 mL of chloroform in a 1L volumetric flask. Add 25 mL of 2-(diisopropylamino)ethanol and 5.0 mL of distilled water. Shake until all components are dissolved. Dilute to final volume with chloroform. The solution is stable indefinitely and is stored at room temperature in it's volumetric flask.)
4. Hypochloric Acid (bleach)
5. Non-agent RMA standard soil

Analytes: Chemical Agent Standard Analytical Reference Materials (CASARM) are received as dilute solutions sealed in 5-mL glass ampules under a blanket of dry inert gas from the Chemical Research and Development and Engineering Center (CRDEC) in Aberdeen, Maryland.

1. Mustard: bis(2-Chloroethyl) sulfide, Cl-CH_2-CH_2-S-CH_2-Cl (CAS No 505-60-2). A dilute CASARM stock solution in hexane is obtained from CRDEC at approximately 2000µg/mL.
2. GB (Sarin): Isopropylmethylphosphonfluoridate, $CH_3P(O)(F)$-$OCH(CH_3)_2$.(CAS No.107-44-8). A dilute CASARM stock solution in isopropyl alcohol is obtained from CRDEC at approximately 250 µg/mL.
3. VX: O-ethyl S-(2-diisopropylaminoethyl) methyphosophonothiolate (CAS No. 50782-69-9), CH_3-$P(O)(OC_2H_5)$-S-CH_2-CH_2-$N[CH(CH_3)_2]_2$. A dilute CASARM stock solution in isopropyl alcohol is obtained from CRDEC at approximately 100µg/mL.

Sample Preparation: GB, VX, and H are extracted together in one vial.

1. Weigh 5.0 grams of soil into a 40 milliliter (mL) volatile (VOA) vial with a TeflonÔ lined screw cap.
2. Add 5.0 mL of 2-(diisopropyl amino)ethanol/chloroform extraction fluid.
3. Place the sample on a vortex mixer for 15 seconds
4. Allow it to stand for approximately one minute.
5. Transfer the liquid extract into autosampler vials. If necessary, to settle out particulate matter decant the extract into a centrifuge tube and centrifuge at 1800 revolutions per minute (RPM) for 1 minute.
6. Analyze on both the sulfur and phosphorus mode GC's.

Instrumentation: Sulfur-mode GC (Mustard)

A Hewlett Packard 5890 GC equipped with dual FPDs and a 7673 autosampler. The FPDs are operated in the sulfur mode and are each equipped with a 393-nm filter (purple). The primary column is a Restek RTx-5, 0.53 mm I.D. 30 meters, 0.50 µm film thickness and the secondary column is a Restek RTx-200, 0.53 mm I.D. 30 meters, 1 µm film thickness. The primary and secondary columns are joined by a "Y" adaptor. The instrument parameters are: initial oven temperature of 120°C for 2.0 minutes, then temperature ramped at a rate of 35°C/minute to a final temperature of 300°C and held for 1.0 minute. The injectors and detectors are held constant at 250°C.

Instrumentation: Phosphorus-mode GC (GB and VX)

A Hewlett Packard 5890 GC equipped with dual FPD and a 7673 autosampler. The FPDs are operated in the phosphorus mode and are each equipped with a 525-nm phosphorus filter(yellow). The primary column is a Restek RTx-5, 0.53 mm I.D., 30 meters, 0.50 µm film thickness and the secondary column is a Restek RTx-200, 0.53mm I.D., 30 meters, 1 µm film thickness. The primary and secondary columns are joined by a "Y" adaptor. The instrument parameters are: initial oven temperature of 50°C for 3.0 minutes, then temperature ramped at a rate of 50°C/minute to a final temperature of 300°C and held for 3.50 minutes. The injectors and detectors are held constant at 250°C.

THE ANALYSIS OF LEWISITE IN SOIL

Reagents:

1. Hexane, HPLC grade or equivalent
2. 0.01% 1,3-Propanedithiol extraction fluid (Using a gastight syringe, add 100µL of 1,3-Propanedithiol (1,3-PDT, Aldrich, 99%, Cat. No. P5, 060-9) to a final volume of 1.0 L HPLC grade hexane. Invert to mix. This solution has an expiration date of six months after date of preparation. It should be stored in a hood since 1,3-PDT is a stench irritant.)
3. Hypochlorite Acid
4. Non-agent RMA standard soil

Analyte: The CASARM is received as a dilute solution sealed in 5-mL glass ampule under a blanket of dry inert gas from CRDEC. A new stock is received annually.

1. Lewisite: 2-chlorovinyldichloroarsine, Cl-CH=CH-$AsCl_2$, (CAS No. 541-258-3). A dilute CASARM stock in hexane is obtained from CRDEC at approximately 2000µg/mL.

Sample Preparation: Sample preparation for the analysis of Lewisite is slightly more complex. Lewisite rapidly hydrolyzes to form a variety of products and hydrochloric acid and does not readily lend itself for analysis by GC. The analysis of Lewisite includes a step to derivatize the Lewisite in a stable product (LD) which can be easily analyzed by GC.

1. Weigh 10.0 grams of soil into a 40 mL VOA vial.
2. Pipet 5.00 mL of the 0.01% 1,3-propanedithiol in hexane into the VOA vial.
3. Gently swirl to mix the soil into the solution.
4. Place the sample on a vortex mixer for 10 seconds to throughly mix the solvent and soil.
5. Place in an ultrasonic bath and sonicated for 6 minutes.
6. Let the sample sit undisturbed for 30 minutes. During this time the derivatization of Lewisite and Lewisite Oxide into the stable derivative LD occurs. This reaction has been observed by various authors investigating the derivative and derivative detection.[1] The derivative, LD, is chromatographically stable, and enables the analysis to proceed by normal chromatographic techniques.
7. Transfer the liquid extract into autosampler vials.
8. Analyze on the sulfur-mode GC.

Instrumentation; Sulfur Mode GC (Lewisite)

A Hewlett Packard 5890 GC equipped with dual FPDs and a 7673 autosampler. The FPDs are operated in the sulfur mode with 393-nm filter(purple). The primary column is a Restek RTx-1701, 30 meters, 0.53 mm ID, and a 0.50µm film thickness and the secondary column is a Restek RTx -5, 30 meters, 0.50µm film thickness. The instrument parameters are: initial oven temperature of 120°C for 3.0 minutes, then temperature ramped at 35°C/minute to a final temperature of 270°C and held for 2.71 minutes. The injectors and detectors are held constant at 250°C.

GB/VX/H RESULTS

The FPDs display good selectivity and sensitivity to the analytes of interest in comparison to the wide range of background contamination present at the RMA. (See chromatograms #1 and #2 pages 7 and 8). No problems have been experienced with false positives due to non-agent contamination. During the performance-based method proficiency process the following results were obtained. The method proficiency matrix was non-agent RMA standard soil:

Tested Concentration Range: The tested concentration ranges for GB, VX, and H on both columns are 0.25 to 2.5 µg/g.

Sensitivity:

Column	Analyte	MRL	Accuracy
Restek RTx-5 GB		0.130µg/g	0.957
	VX	0.320µg/g	0.847
	H	0.220µg/g	1.1
Restek RTx-200	GB	0.320µg/g	0.849
	VX	0.350µg/g	0.745
	H	0.200µg/g	0.920

Method Reporting Limits (MRL): The MRLs will be the worst case scenario obtained from the performance-based method proficiency listed above in order to include the performance of each column. Mustard is assigned the MRL of the lowest proficiency spike that was analyzed, since the calculated MRL for Mustard was less than the lowest spike analyzed (see table below).

Analyte	MRL	Upper Limit	Accuracy
GB	0.320µg/g	2.50µg/g	0.851
VX	0.353µg/g	2.50µg/g	0.745
H	0.250µg/g	2.50µg/g	1.13

LEWISITE

The FPDs displayed good sensitivity and selectivity for Lewisite in comparison to the wide range of background contamination and interferences (Chromatogram #3 page 8). No problems have been experienced with false positives

due to non-agent contamination. During the performance-based method proficiency process the following results were obtained. The method proficiency matrix was non-agent RMA standard soil.

Tested Concentration Range: The tested concentration for Lewisite on both columns was 0.125 to 1.25 µg/g.

Sensitivity:

Column	Analyte	MRL	Accuracy
Restek RTx-1701	Lewisite	0.121µg/g	0.803
Restek RTx-5	Lewisite	0.275µg/g	0.924

Method Reporting Limit (MRL): The MRL will be the worst case scenario obtained from the performance-based method proficiency listed above in order to include the performance of each column.

Analyte	MRL	URL	Accuracy
Lewisite	0.275µg/g	1.25µg/g	0.803

SUMMARY

These methods provide a quick qualitative and quantitative means to determine if various solid matrices are free of these four chemical agents. Some of the matrices that have been tested using these procedures are soil, concrete, chlorinated parafilm, fume hood filter remnants, and various other waste materials. In each case the methodologies have been able to determine that these matrices are free of GB, VX, H and L. The use of the FPDs with simultaneous confirmatory analysis has filled a critical need in providing high quality, defensible data that has enabled to cleanup of RMA to move forward.

FOOTNOTES

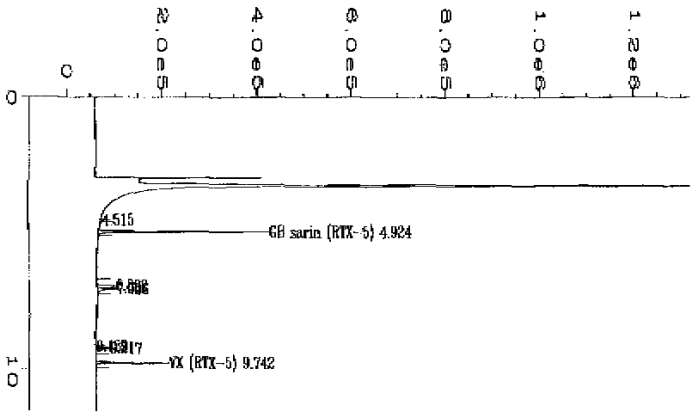
1. Albro, Thomas., Field Determination of Lewisite and It's Breakdown Products by Flame Photometric and Photoionization (PID) Detectors in Soil and Water Matrices: September 1994, Page 2

ACKNOWLEDGMENTS:

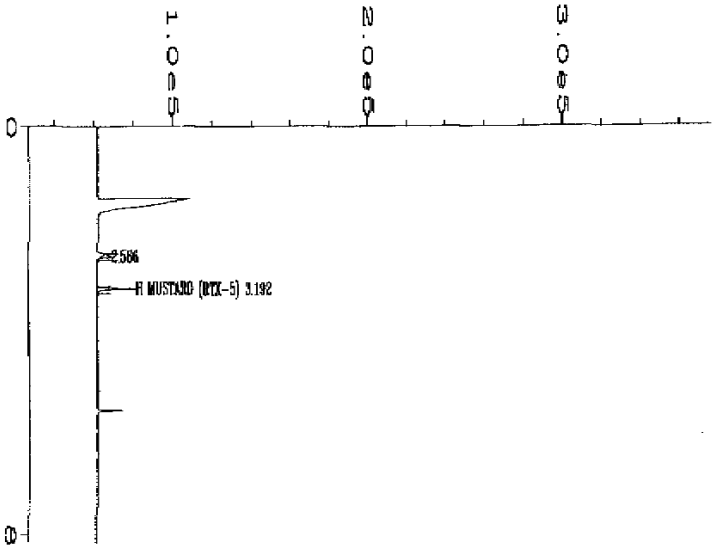
The Comprehensive Analytical Laboratory Services Team at the Rocky Mountain Arsenal comprised of the RVO Support Team. URS Greiner Woodward Clyde, Lockheed Martin, Oak Ridge National Laboratory, and Roybal Corporation.

REFERENCES

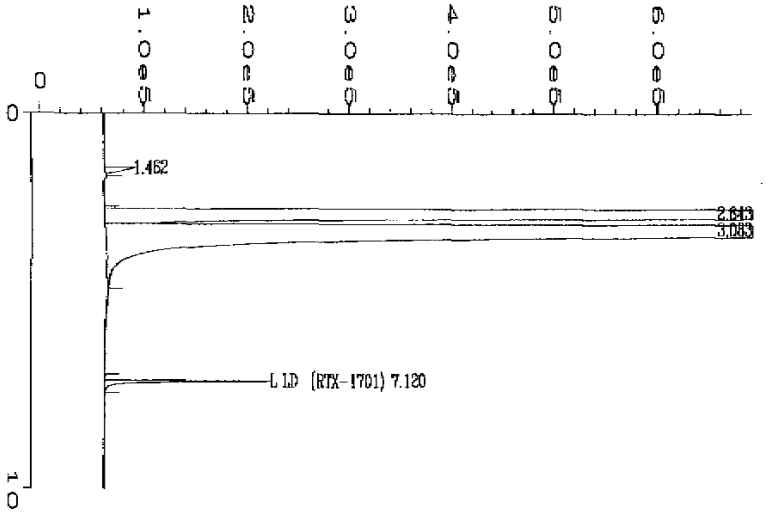
1. Albro, Thomas., Field Determination of Lewisite and It's Breakdown Product by Flame Photometric and Photoionization (PID) Detectors in Soil and Water Matrices: September 1994.
2. Chemical Agent Standard Analytical Reference Material Quality Assurance Plan for Chemical Agent Air Monitoring, Revision II, US Army CBDCOM Quality Directorate, August 1995.
3. Comprehensive Analytical Laboratory Services, Laboratory Quality Control Plan, April 1999.
4. Comprehensive Analytical Laboratory Services, Quality Assurance Management Plan, April 1999.
5. Environmental Analytical Laboratory, Rocky Mountain Arsenal, SOP 301, Analytical Method for the Determination of Mustard, Sarin and VX in Soil using 2-(Diisopropyl amino) ethanol Extraction Followed by Gas Chromatography with Flame Photometric Detection Method Number LO03, October 1998.
6. Environmental Analytical Laboratory, Rocky Mountain Arsenal, SOP 310, Lewisite in Soil by 1,3-Propanedithiol Derivatization Certified Method LL13, December 1998.
7. Kuznear, Casimir and Trautmann William, L. History of Pollution Sources and Hazards at Rocky Mountain Arsenal. September 1980.
8. Program Manager Rocky Mountain Arsenal, Chemical Quality Assurance Plan, April 1996.
9. Program Manager Rocky Mountain Arsenal, Chemical Hygiene Plan, Revision 4, October 1996
10. Toxic Chemical Agent Safety Standards, US Army, 31 March, 1997.



Chromatogram #1. GB and VX @ 1.0 µg/g, sample B05403 MS, Restek RTx-5 0.53 mm ID, 0.50µm film thickness, 30.0 meter capillary column.



Chromatogram #2. Mustard @ 1.0 µg/g, sample B05403 MS, Restek RTx-5 0.53mm ID, 0.50 µm film thickness, 30.0 meter capillary column.



Chromatogram #3. Derivatized Lewisite @1.0 µg/g, sample B05403 MS, Restek RTx-1701 0.53mm ID, 0.50µm film thickness, 30.0 meter capillary column.

COMPARISON OF SAMPLING PROTOCOLS FOR THE ZERO HEADSPACE EXTRACTION (ZHE) FOR TCLP AND SPLP

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With the introduction of SW846 Method 5035 for soil volatile organic analysis, the large method bias that existed with SW846 Method 5030 was mostly eliminated. However, protocols for sampling soil and waste for TCLP and SPLP still rely on the bulk sampling protocol. In regulatory programs that allow for either TCLP/SPLP or Method 5035 to assess contamination risk, there may be a very large discrepancy between the two options. Since soils cannot be preserved for TCLP/SPLP, there are limited sampling options that will maintain soil integrity.

We compared two sampling protocols, the bulk sampling option (Option A) and the En Core™ sampler (Option B). Samples were prepared by mixing a soil consisting of 5 lbs sand, 2 lbs farm topsoil and 18 lb of garden soil with a TCLP standard mixture. The soil was rotated in a mixing drum for 18 hours and then sampled for the TCLP protocol. Two oz jars with new, high-performance sealing Teflon™ inserts obtained from QEC, Inc. were used for Option A and the 25 gm En Core™ was used for Option B.

Spiked samples were analyzed at zero time to obtain the initial total concentration. Sets of samples prepared by Options A or B were leached by TCLP protocol on Day 4, Day 7 and Day 14. Leachates were analyzed by SW846 Method 5030.

Table 1

Day	1,1 Dichloroethene		Benzene		Tetrachloroethene	
	Bulk	En Core™	Bulk	En Core™	Bulk	En Core™
Day Two	7.3	12.1	28.1	52.4	37.7	51.4
Day Seven	ND	12.7	10.1	50.6	25.5	56.8

Results of representative compounds are presented in Table 1. Data are the mean of five replicates and are expressed as µg/l of leachate.

As expected, the more volatile compounds showed significantly more time dependent losses than the less volatile compounds. Data will be presented on the completed time study to fourteen days of soil hold time and for the full list of TCLP volatile compounds. In addition, two types of bottles with different Teflon™ seals will be compared.

FIELD APPLICATION OF A PORTABLE GAS CHROMATOGRAPH FOR GROUNDWATER HEADSPACE SAMPLING

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Abstract
For many years portable instrumentation has been widely accepted as a screening tool for a variety of environmental monitoring needs. Technology advances have made accurate identification and quantification of numerous contaminants possible in the field. End users, however, remain skeptical of field data except as a screening tool. As a result, most groundwater samples are still collected, preserved in the field and sent to a laboratory for analysis using EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry. While this is a widely accepted practice, problems associated with sample handling and storage can lead to erroneous results. Advantages of field sampling and analysis are an immediate answer to questions about the presence and concentration of VOCs, reduced sampling costs, and the ability to quickly respond to a spill with remediation techniques appropriate to the area, concentration and content of a spill. This paper will demonstrate the applicability of a field portable gas chromatograph for the characterization of volatile organic compounds (VOCs) in groundwater headspace, thus building confidence in field quantitative data.

In 1997, Perkin-Elmer Photovac participated in EPA's Environmental Technology Verification Program for Field Portable GCs. In the ETV program field analysis results obtained with the Voyager portable gas chromatograph were compared to laboratory analysis generated using EPA Method 8260B. As a result of PE Photovac's participation at two ETV field sites and subsequent data review in the ETV Program, a field sample handling method was developed to minimize errors, allowing very accurate readings down to ppb levels while maintaining high sample throughput. A second comparative project was executed in early 1998 to improve accuracy and repeatability. Excellent correlation between lab and field data was demonstrated in this study.

Introduction

It is a common practice to check for the presence of volatile organic compounds such as BTEX or TCE in groundwater samples during site assessment or site remediation. The groundwater samples are collected and sent to a lab for analysis often using Method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry. As with any lab method the major disadvantages can be sample handling prior to analysis and turnaround time. Samples often deteriorate during collection or transport reducing the accuracy of the lab data. Site managers may be faced with critical project decisions while waiting for lab data which could result in project delays or unnecessary costs associated with additional sampling. This paper will present a means to sample and analyze groundwater samples quickly and accurately in the field. Field analysis often results in significant cost or time savings.

Environmental Field Sampling

At most groundwater assessment or remediation sites that involve groundwater sampling, the samples are collected in 40 mL VOA vials. The samples are preserved using an appropriate method to prevent sample deterioration, transported as quickly as possible to a lab, stored at the lab, and analyzed using EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry. There are many potential problems when collecting field samples of groundwater. The field technician can aerate the sample while filling the VOA vial causing a loss or dilution of the analytes. Poor sampling technique can allow the analytes to escape into ambient air. Headspace may remain in the vials causing dilution of the sample with trapped ambient air resulting in low concentrations of analytes in the vial compared to the source groundwater. If samples are not properly preserved with a compound such as hydrochloric acid then bacteria in the sample that were inactive due to the lack of oxygen in groundwater can now "bioremediate" the sample in the vial causing a breakdown or alteration of the sample compounds. During transport the vials can offgas volatile organic compounds if the vial is not properly capped or the temperature during transport reaches high levels. Vials can be broken resulting in a total loss of that sample. Numerous sampling factors can determine the accuracy of the lab results.

Traditional Field Sampling Methods

There are a wide variety of portable analysis kits and instrumentation that have been long accepted as screening tools in the field. These include portable photoionization detectors and flame ionization detectors for non specific analysis of total VOCs in the headspace over groundwater, immunoassay field kits, colorometric tests, and detector tubes. These screening tools often have several significant drawbacks. The PID or FID cannot speciate compounds so the technician or engineer in the field will learn the total concentrations of VOCs in a sample but not identify specific compounds or concentrations in the sample. Certain techniques that do speciate are often less accurate or subject to interference from other compounds in the matrix. Training of the sampling technician as well as ambient conditions during sampling can also affect accuracy.

Field Sampling Today

Despite these limitations field screening remains an important tool to delineate the extent of contamination at a site. Valuable time and money can be saved using field screening. Over the past ten to twenty years several new ways have evolved to accurately assess samples on site with a more rapid turnaround. At larger sites a mobile lab can be used. A mobile lab consists of lab instrumentation installed in a large trailer or van. The groundwater is placed into VOA vials, brought to the mobile lab and analyzed quickly. This allows the project manager to make rapid decisions about the site remediation. There is also a new generation of portable or transportable instruments available in the market. Field portable gas chromatographs as well as transportable gas chromatograph/mass spectrometers can be brought to a site to perform near real time analysis on a wide variety of samples. This type of instrumentation provides an immediate answer to questions about which compound is present and at what concentration. Advantages of portable field instrumentation are reduced sampling costs and the ability to respond quickly to contamination. This quick response can provide substantial savings to a remediation project by reducing idle time for field personnel and equipment. Immediate response to new contamination allows more rapid completion of projects at a lower cost.

Field Sampling Reality

Unfortunately, field data is often seen as suspect or unacceptable by regulators or clients. The quality control methods for field data is perceived to be less rigorous than the quality control normally practiced by a certified lab. Lab data is seen as "the gold standard". Yet by implementing many of the same quality control techniques used in a certified lab it is possible to attain the same accuracy and data confidence using field instrumentation. As the advantages of performing sample analysis in the field have become more widely recognized, regulators, environmental consultants and PRPs are all becoming more interested in implementing new technology to remediate sites more rapidly and at lower cost. The move to field sampling using portable instrumentation seems logical. Yet this has not happened to date. The main reason is a lack of confidence in the data quality.

EPA ETV Program

The US EPA's Environmental Technology Verification (ETV) program was established to facilitate deployment of innovative environmental technology, provide a verification of performance and disseminate this information to potential users of environmental technology. ETV is not an approval program but a verification of vendor claims about their technology. The ETV program was intended to give potential end users of field technology, such as environmental consultants, a higher level of confidence in the accuracy of field technology.

Wellhead Demonstration Program

In September 1997 the ETV program sponsored a demonstration project to verify the performance of several instruments designed to analyze volatile organic compounds in groundwater. Two sites were selected to provide the groundwater samples, Savannah River Site (SRS) in Aiken, SC and McClellan Air Force Base in Sacramento, CA. Certain compounds were targeted for detection and analysis at each site. At SRS those compounds were trichloroethylene (TCE) and tetrachloroethylene (PCE). At MAFB the compounds were 1,2 DCA, 1,1,2, TCA, 1,2 Dichloropropane, trans-1,3 Dichloropropene. Other compounds were also expected to be present. The Perkin-Elmer Photovac Voyager portable gas chromatograph was one of the portable instruments selected to participate in the demonstration project at both sites. By inviting the Voyager to participate, both the ETV sponsors and Photovac hoped to validate the field performance claims for the Voyager as well as elevate field instrumentation from a screening technique to a quantitative technique that could be used in place of a fixed lab. This would allow the Voyager to meet user needs for a more rapid accurate field method for VOC analysis in groundwater. Samples possibly containing VOCs in groundwater were provided at each site by the ETV program and were analyzed on the Voyager portable GC. Duplicate samples of the groundwater matrix obtained at each site were sent to a certified lab for analysis. This would allow direct comparison of data obtained using the Voyager with data obtained by a lab using Method 8260B.

Technology Description

The Voyager portable gas chromatograph uses a three column design that allows the separation of compounds on one of three built-in columns. The three built-in columns allow analysis of a wide range of compounds without having to physically change columns. The Voyager is equipped with a dual detection system. Most volatile organic compounds are detected using a photoionization detector equipped with a 10.6 eV lamp. Some chlorinated VOCs such as carbon tetrachloride are detected on an electron capture detector (ECD) with a 15 millicurie Nickel-63 source. Samples are injected or pumped into a heated injection port and then introduced onto the isothermally heated column set. The user selectable temperature range of the injection port and oven is 30 to 80 degrees Centigrade. Ultra high purity nitrogen is used as the carrier gas. The Voyager is completely self contained and weighs 15 pounds. Figure 1 shows the column type and configuration used in the Voyager.

Assay Development

An assay was developed for the Voyager that allowed for detection and accurate quantification of the compounds expected at the SRS and MAFB sites. The assay included a single column analysis for optimum separation of up to twenty four compounds. A three point calibration curve for each compound was incorporated into the method.

Original Sample Method

At the Savannah River Site, the following sampling method was used for performing the analysis on the Voyager GC. A three point calibration curve was established for each compound. A calibration was performed daily before the first analysis. The ETV personnel provided each groundwater sample to the Voyager field technicians at the SRS site. The vial was placed in a water bath for 15 minutes at 30 degrees C to allow equilibration. After equilibration the vial was uncapped and 20 mL of the sample was poured into another VOA vial. The second vial with 20 mL of sample and 20 mL of headspace was shaken for two minutes and placed in the water bath at 30 degrees for five minutes.

After five minutes the vial was removed from the water bath, a 500 uL gas tight syringe was used to remove 500 µL of headspace in the vial and the sample was injected onto the Voyager columns. Voyager results from each completed analysis were automatically stored in the Voyager's internal datalogger. The contents of the datalogger were later downloaded to a PC for archiving the results and printing the chromatograms. At McClellan Air Force Base, a slightly modified method was used. A three point calibration curve was run for each compound. A calibration was performed daily before the first analysis. A 40 mL VOA was filled with a groundwater sample and provided to the Voyager field technicians. The vial was placed in a water bath for 15 minutes at 30 degrees C to allow equilibration. In this modified method, after equilibration 20 mL of sample was removed using a 20 mL glass syringe. The 20 mL withdrawn from the vial was discarded. The vial, which now contained 20 mL of sample and 20 mL of headspace, was returned to the water bath at 30 degrees for five minutes. After five minutes the vial was removed from the water bath, a 500 µL gas tight syringe was used to remove 500 µL of headspace in the vial and the sample was injected onto the Voyager columns. After the Voyager completed the analysis results were automatically stored in the Voyager's internal datalogger. The contents of the datalogger were later downloaded to a PC in order to archive the results and print the chromatograms. The results of the field analysis at both sites for selected compounds are shown in Figure 2. Overall mean percent recovery is an average of how closely all reported Voyager concentrations for each sample matched the concentrations found in the laboratory analysis as a percentage. One hundred percent would indicate perfect Voyager concentration correlation with laboratory concentrations.

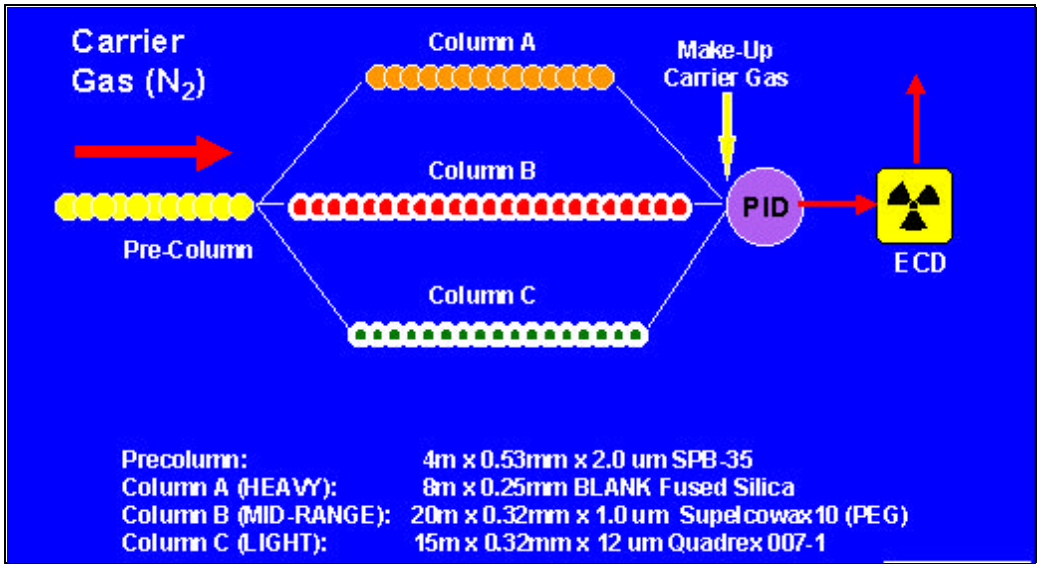

Figure 1. Voyager Configuration

Figure 2. Results of SRS/MAFB ETV Demonstration

Target Compound	Site	Overall Mean % Recovery
Trichloroethylene	SRS	92-164
	MAFB	231-344
1,2 Dichloroethane	SRS	55-86
	MAFB	0-170
1,2 Dichloropropane	SRS	55-86
1,2 Dichloropropane	MAFB	0-170
1,1,2 Trichloro-ethane	SRS	
	MAFB	50-116
Tetrachloro-ethylene	SRS	1-124
	MAFB	
t-1,2 Dichloropropene	SRS	106-162
	MAFB	95-143

The results did not correlate as well as the Photovac had hoped. Possible reasons for the poor correlation include loss of analytes due to sample handling technique used by the vendor field personnel. In particular, uncapping the vial and pouring off part of the sample as was done at SRS most likely resulted in loss of analytes. The stability of the water bath temperature was also called into question. During sampling the Voyager and water bath were inside a minivan. Since ambient temperatures were high, the air conditioning was running in the minivan but the doors were frequently opened and closed. Some of the compounds may have coeluted on the columns leading to false high readings for some compounds and no detection indications for other compounds. Since the concentration of compound varied widely in each sample matrix, there could have been errors induced by using only a three point calibration curve.

Improved Sample Methodology

The outcome of the field sampling at SRS and MAFB prompted development of a new methodology to improve the accuracy, repeatability, and detection of all compounds. A five point calibration curve was developed for each compound at 0, 0.005, 0.05, 0.5 and 5 mg/L. More frequent calibrations were performed throughout the day. A temperature block was substituted for the water bath. The temperature block maintained a more stable temperature during the VOA vial hold time. A reduced volume of headspace sample was injected into the Voyager to reduce the possibility of coelutions. Modifying the Voyager assay reduced analysis time and increased sample throughput.

Redesigned Method testing

This modified sample method was tested by mixing Supelco prepared reference standards of benzene, toluene, ethylbenzene, m-xylene, trichloroethylene, tetrachlorethylene, bromodichloromethane, and dibromochloromethane with organic free deionized water. A sample matrix of all eight compounds was prepared at concentrations of 7, 30, 700, 3000 µg/L. A spike matrix of 300 µg/L of benzene, toluene, ethylbenzene, m-xylene, bromodichlormethane, and dibromochloromethane and 5000 ug/L of trichloroethylene and tetrachlorethylene was also prepared. Four samples of each concentration were analyzed on the Voyager using the modified sample method and assay. Duplicate samples were sent to a reference lab for analysis using Method 8260B. The results of the redesigned test method are shown in Figure 3.

Figure 3. Redesigned Method Results

Compounds	% Recovery at 7 µg/L	% Recovery at 30 µg/L	% Recovery at 700 µg/L	% Recovery at 3000 µg/L	% Recovery at 300/5000 µg/L	Overall Mean Percent Recovery
Benzene	82	139	112	94	66	99
Toluene	139	115	106	92	85	107
Ethylbenzene	11	155	98	93	60	83
m-Xylene	11	157	74	93	52	77
Trichloroethylene	89	145	102	89	66	98
Tetrachloro-ethylene	136	56	115	98	95	100
Dibromochloromethane	121	75	101	102	79	96
Bromodichloromethane	93	206	97	102	73	114

Conclusions

The Voyager portable gas chromatograph can be used to analyze the headspace over groundwater for the presence and quantification of volatile organic compounds. Participation in the EPA's ETV program allowed Photovac to compare Voyager data with certified lab data for samples provided by the ETV managers at two field sites. The initial correlation was not as close as Photovac had expected. A new assay was developed for the Voyager to target the specific compounds and a new field sampling technique was implemented. Data obtained using the new method showed improved recovery (Voyager versus lab) and the elimination of coelutions. The new Voyager assay and sampling methodology increased sample throughput by reducing total analysis time required to run the samples on the Voyager portable GC. This reduced analysis time provides quicker results to field personnel and increases the number of samples per day that can be analyzed. Most importantly, the Voyager now meets the vendor performance goals established for the ETV program. Meeting the performance goals set for the Voyager should lead to increased confidence in Voyager field data by regulators and end users. Ultimately, increased field sampling can reduce the cost of environmental site assessment or remediation and shorten the time needed to complete a project.

References
Voyager Portable Digital Gas Chromatograph User's Manual, Revision C, December 1997
Environmental Technology Verification Report, Field Portable Gas Chromatograph, Perkin-Elmer Photovac, Voyager by Wayne Einfeld, Sandia National Laboratories, Albequerque, NM EPA/600/R-98/144 November 1998
Phoenix Lab Report, Phoenix Laboratories, Manchester, CT

ON-SITE DETERMINATION OF VOLATILE ORGANIC HALIDES (VOH) IN WATER BY UV-INDUCED COLORIMETRY

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Abstract
A novel UV-induced colorimetric field test kit, Quick Test® VOH Water Test Method, for the quantitation of volatile organic halides in water has been developed by Envirol Inc. (Logan, UT). An average method detection limit (MDL) of 4 Φg/L (ppb) was achieved for TCE, PCE, chloroform and carbon tetrachloride with a dynamic range up to 200 Φg/L. With dilution, the dynamic range can be up to 200 mg/L (ppm). The accuracy and precision results for the analysis of TCE in water were comparable to standard laboratory methods validated by SW-846. The independent performances of Quick Test VOH Water Test Method in the field were compared with laboratory results. Statistical analysis by linear regression and non-parametric t-test (Wilcoxon test) confirms that the Quick Test VOH Water Test Method meets U.S. EPA Superfund Innovation Technology Evaluation (SITE) Level 2 criteria for field testing.

Introduction
Trichloroethylene (TCE) is widely used in industry as a degreasing solvent and perchloroethylene (PCE) is used as a cleaning agent in dry-cleaning facilities. From 1987 to 1993, the TCE and PCE releases into water and land were estimated to be more than 291,000 lbs. for TCE and more than one million lbs. for PCE. The U.S. EPA has classified TCE and PCE as possible carcinogens and has set the MCL (Maximum Contaminant Level) at five parts per billion (ppb) for TCE and PCE in drinking water.[1, 2]

Current approaches for evaluating TCE, PCE and other volatile organic halides in water at field sites involve obtaining and preserving field samples for transport to a laboratory where samples are stored until analysis by gas chromatography at a cost of approximately $80-$200 per sample. Storage and time constraints for samples taken in the field often limit the number of samples that can be processed and therefore limit the number of results that can be obtained. The lag time between sample collection and quantification, and reporting of results can often be from many days to several weeks. The traditional approach is limited with regard to 1) the number of samples that can be analyzed due to cost and time, 2) the statistical validation due to the number of samples taken, 3) decisions concerning site management (removal actions, treatment technologies) are delayed or postponed due to the relatively long time required from sampling to analyzing results, and 4) evaluation of treatment effectiveness cannot be determined until results are available.

A novel UV-induced colorimetric field Quick Test kit, Quick Test VOH Water Test Method, for the quantitation of TCE, PCE and other volatile organic halides in water has been developed by Envirol, Inc. The process is based on a photochemical-induced oxidation-reduction reaction between the organic halide and the chemical reagent. The

purpose of this study was to characterize the performance of the Quick Test VOH Water Test Method for the analysis of VOH in water and to test the suitability of this new method for field investigation of VOH-contaminated sites. The characterization study includes quality-control parameters specified in Test Methods for Evaluating Solid Waste (SW-846)[3], in Lesnik and Marsden[4] and our previous research paper,[5] including detection limit, dynamic range, accuracy and precision, interference analysis, and matrix specificity. The Quick Test VOH Water Test Method was also performed under field conditions, and the results for TCE/PCE in water were compared with approved U.S. EPA procedures for analysis of TCE/PCE by an independent, certified laboratory.

Experiment

Material and Method

All inorganic chemicals used in this study were reagent grade and the organic chemicals used were optical or HPLC grade. Quick Test VOH Water Test Method contains all components for water extraction and solution preparation analysis. The procedure started with a 290 mL water sample being extracted with 2.0 mL of octane and 30 inches of Teflon® tape. The mixture is shaken manually for three minutes. After this shaking, the Teflon tape is removed from the solution and placed into a 10-cc syringe. The syringe plunger is used to force the extraction solvent (octane) and the analyte from the Teflon tape to the extraction solvent vial. The clear extraction solvent is transferred to a drying vial containing 50 mg sodium sulfate, eliminating residual water, and then transferred from the drying vial to the liquid/liquid transfer vial containing 1.0 mL acetonitrile. After one minute of shaking, 0.60 mL of acetonitrile (bottom layer) is pipetted into a vial containing 0.4 mL of the reagent. The mixture is placed directly into Envirometer™, a field instrument developed by Envirol, Inc.,[5] for UV exposure and quantitation. The kit also provides two sets of premeasured standards (5, 90, 190 Φg/L) of VOH (TCE, PCE, CCl_4 or $CHCl_3$) for instrument calibration and two calibration verification samples (90 Φg/L).

The spiked concentrations of VOH (TCE, PCE, carbon tetrachloride, chloroform) were verified by GC/ECD (SHIMADZU, GC-17A) with purge and trap (Tekmer™ 3000) (Method 5030). For performance of the Envirol VOH test kit the user needs the Envirometer and an adjustable mechanical pipetter capable of measuring 0.60 mL solution with less than 1 percent absolute error (equivalent to Wheaton No. 851268).

Results and Discussion

Method Detection Limit

The method detection limit (MDL) for the Quick Test VOH Water Test Method was determined with the method specified in SW-846.[3] TCE, PCE, carbon tetrachloride and chloroform were each tested individually. Type II water (organic free water) was spiked with each of the test chemicals individually at several levels to determine a primary spiking concentration where the signal/noise ratio was in the range of 2.5-5.0. The primary spiking concentration was then multiplied by a number from 3-5 to obtain the secondary spiking concentration. In this study, the multiplier value chosen was four. Once the appropriate secondary spiking concentration was determined, Type II water was spiked at that concentration and then16 replicates were extracted and analyzed using the Quick Test VOH Water Test Method. The mean and standard deviation of the TCE, PCE, carbon tetrachloride and chloroform concentration for the16 samples was determined. The standard deviation was then multiplied by the appropriate t-statistic to determine the method detection limit of each chemical. To determine the method quantitation limit (MQL), the same data was used, but with a t-statistic for the 99.9 percent confidence level. The results of this analysis are summarized in Table 1.

The MDL listed in Table 1 are appropriate for determination of TCE, PCE, carbon tetrachloride and chloroform in water at regulatory levels above the MDL. The average MDL across all analytes is 4 Φg/L, which is below the MCL of TCE and PCE (5 ppb) set by the U.S. EPA. The dynamic range of this method is 4 to 200 Φg/L(ppb). Figure 1 shows the standard curve for TCE in water. With dilution, the dynamic range may be extended up to 200 mg/L (ppm). Three points (5, 90, and 190 Φg/L) all fall within the dynamic range of the method, and thus were chosen as the standardization points for the Envirometer.

Specificity of Reaction

The photochemical reaction which is utilized for the detection of volatile organic halides is interspecific towards various organo halides, thus the method displays varying sensitivity toward different test compounds. This necessitates understanding of the dominant analyte of interest for proper screening and quantitation. Relative sensitivities of various volatile organic halides to TCE, PCE, carbon tetrachloride and chloroform are given in Table 2. Sensitivity is clearly related to the extent of halogenation, with carbon tetrachloride being the most sensitive compound and vinyl chloride the least.

Table 1. Quick Test VOH Water Test Method Detection and Quantitation Limits.

Chemical	Primary Spike Level Φg/L	Multiplier Value	Secondary Spike Level Φg/L	Standard deviation for (8) 16 repli-cate analyses	t-statistic multiplier for (8) 16 replicates	MDL Φg/L	t-statistic multiplier for (8) 16 replicates	MQL Φg/L
TCE*	5	4	20	1.4	3.00	4	5.405	8
PCE	4	4	16	1.7	2.60	4	4.073	7
Carbon Tetrachloride	4	4	16	1.1	2.60	3	4.073	4
Chloroform	5	4	20	1.8	2.60	5	4.073	7

*TCE spiked at two concentrations and each concentration was analyzed 8 times.

The MDL was calculated for each of the spiked concentrations and the two MDLs were averaged.

All other chemicals were spiked at one concentration and analyzed 16 times.

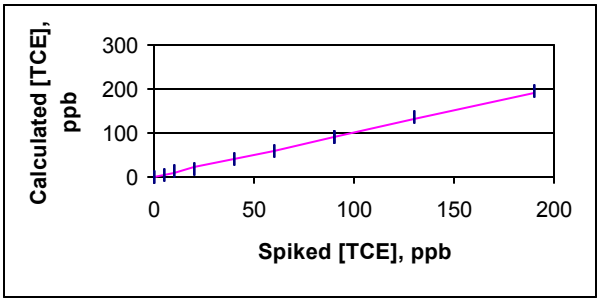

Table 2. Method Performance Data as Percent Relative Sensitivity to TCE, PCE, Carbon Tetrachloride and Chloroform

	Compared with TCE	Compared with PCE	Compared with carbon tetrachloride	Compared with chloroform
Trichloroethene	**100**	122	88	122
Perchloroethene	82	**100**	72	100
Carbon tetrachloride	114	139	**100**	139
Chloroform	82	100	72	**100**
1,1-Dichloroethene	69	84	61	84
Vinyl chloride	0.8	1.0	0.7	1.0
trans-1,2-Dichloroethene	61	74	54	74
cis-1,2-Dichloroehtene	43	52	38	52
Dichloromethane	20	24	18	24
1,1,1-Trichloroethane	112	137	98	137
1,1,2-Trichloroethane	80	98	70	98
1,2-Dichloroethane	15	18	13	18
Bromoform	77	94	68	94
Bromodichloromethane	75	91	65	91
Chlorobibromomethane	71	87	63	87

Method Accuracy (Bias)

Method accuracy was determined by evaluating the percent recovery of TCE spiked in Type II water. Data was generated using the field instrument for the spike concentrations shown in Table 3.

Method accuracy, as recovery, for the Quick Test ranged from 91-110 percent. The reported method accuracy for halogenated volatiles by Method 8021B (U.S. EPA, 1996) is 96 percent for TCE and 86-109 percent for other volatile organic halides. The recovery data obtained with the Quick Test Method for TCE exceed that reported using Method 8021B. The reported method accuracy range using the Quick Test is within limits for other volatile organic halides as reported in Method 8021B.

Table 3. Method Accuracy Determined by Spiking Type II Water with 20 and 150 Φg/L TCE.

TCE Fortification Φg/L	TCE Concentration Determined by Standard Methods* Φg/L	TCE Concentration Determined by Quick Test Φg/L (s)**	Number of Samples	Mean Percent Recovery (range)
20 150	17.3 153	22 (1.6) 137 (8.8)	10 10	110 (95-120) 91.1 (84-104)

* GC/ECD with purge and trap (Method 5030) was used for analysis of all spiked samples.
**For the purposes of this report, (s) refers to the sample standard deviation.

Method Precision

Information on method precision was obtained by repeatedly analyzing the same spiked water sample and then examining the variation in the results. Type II water was fortified at two concentrations, 20 and 150 Φg/L TCE, and was analyzed using the Quick Test procedure. The results obtained from this study are shown in Table 4.

Table 4. Method Precision Determined by Spiking Type II Water with 20 and 150 Φg/L TCE.

TCE Fortification Φg/L	Number of Samples	Mean TCE Concentration Determined by Quick Test Φg/L	Standard Deviation (s)	Coefficient of Variation (100*s/mean)	Range of Concentration Φg/L
20 150	10 10	22 137	1.6 8.8	7.3 6.4	19-24 126-156

For Method 8021B, precision was reported as 3.5 of the average recovery for a single operator using GC/HECD for TCE and 1.5 to 9.9 for other volatile organic halides (U.S. EPA, 1996). For the Quick Test the standard deviation of recovery for TCE was 7.3 and 6.4 for the two concentration levels. It is concluded that the method precision for Quick Test VOH Water Test Method is comparable to standard method precision and is acceptable.

Chemical Interferences

An analysis of chemical interferences was performed using 250 mL of Type II water to assess the degree to which other related or pertinent compounds would affect the measured TCE concentration. Table 5 is a summary of this analysis.

No significant interference was observed for the compounds tested. 2,2,2-trichloroethanol had an interference effect at 2,000 Φg/L (100-fold) but no significant interference at 200 Φg/L (10-fold).

Table 5. Results of Interference Analysis for the Quick Test for TCE Interfering Substance. TCE Spiked in Type II Water at a Concentration of 20 Φg/L.

Interference=s	Concentration Required for a Detectable Interference (Φg/L)
Benzene	>2,000
Methanol	>2,000
Toluene	>2,000
Oxalic Acid	>2,000
Sodium Trichloroacetate	>2,000
Sodium Dichloroacetate	>2,000
2,2,2-trichloroethanol	>200

False Positive/False Negative Study

False positive analysis for the Quick Test was performed using Type II water as the clean test matrix. The suggested concentration of TCE for the false positive test is one-half of the MDL or 2.2 Φg/L (Lesnik, 1992). Twenty replicate samples of the fortified water were analyzed using the Quick Test. The results of the false positive analysis indicate

that this method meets the criteria of no more than 10 percent false positive. The false negative analysis for the Quick Test was performed using Type II water spiked at two times the MDL or 8.8 Φg/L. Twenty replicates were analyzed using the Quick Test. The results of the false negative analysis indicate that this method meets the criteria of zero false negatives.

Matrix Suitability

Matrix specific performance data was evaluated using the Quick Test VOH Water Test Method. Four water matrices: Type II water, Type II water with 20 mg/L humic acid, Type II water with 1,000 mg/L suspended solids and buffered (pH 9) Type II water. Prior to fortification, each matrix was analyzed using the Quick Test and with GC/ECD. All matrices were uncontaminated with respect to volatile organic halides. Matrix specific performance data was generated by spiking the water matrices at 20 Φg/L and 150 Φg/L TCE. The four water matrices were spiked at two concentrations and analyzed using Method 8021B for verification of the spiking concentration. The results obtained with the Quick Test VOH Water Test Method and Method 8021B were comparable and both are subject to variability. There is no evidence of matrix interferences with the sample types tested.

Correlations Study

An independent evaluation of the test kit was preformed by the University of Waterloo. Samples were prepared by spiking Type II water with TCE only or TCE with PCE. The prepared samples were analyzed in duplicate using the test kit and standard methods. Results are presented in Table 6. For comparison of results, the reported amount of PCE quantified using the standard method was adjusted by its sensitivity relative to TCE (Table 2).

Table 6. Inter-method Comparison between the Standard Laboratory Method and the Quick Test VOH Water Test Method

Sample ID	Test Kit (Φg/L)			Standard Method (Φg/L)			Percent Difference
	Replicate 1	Replicate 2	Mean	Replicate 1	Replicate 2	Mean	
TCE-1	30	31	31	16	12	14	121
TCE-2	57	62	60	68	65	66	9
TCE-3	192	65	129	309	319	314	59
TCE-4	1410	1270	1340	1541	1528	1534	13
TCE-5	O/L	O/L	O/L	2834	2867	2850	
TCE/PCE-1	35	35	35	22	26	24	46
TCE/PCE-2	98	100	99	135	133	134	26
TCE/PCE-3	610	540	575	577	602	590	2.5
TCE/PCE-4	NA	2400	2400	3283	3228	3256	26
TCE/PCE-5	O/L	O/L	O/L	6287	5245	5766	

The Quick Test VOH Water Test Method has been used to measure volatile organic halides at the field site contaminated with TCE. Table 7 outlines comparison data between the Quick Test and Method 8260 for measuring volatile organic halides in water samples. For this comparison, the concentrations determined using GC/MS were adjusted by their relative sensitivities compared with TCE as determined for the Quick Test (Table 2).

Regression analyses were used to determine if there was a relationship between the Quick Test and the confirmatory laboratory procedure. Similar analyses have been used by the U.S. EPA Superfund Innovative Technology Evaluation (SITE) program to evaluate intermethod comparisons.[6] Three components of the regression were evaluated, the y-intercept, the slope and the coefficient of determination, r^2. To meet Level 3 accuracy requirements, the r^2 value must be between 0.85 and 1.0 and the slope and y-intercept must be within the 90 percent confidence interval of their ideal values of 1.0 and zero, respectively.[6] To meet Level 2 accuracy the r^2 values must be between 1.0 and 0.75 when the slope and intercept do not meet their ideal values. A Level 2 accuracy requirement indicates a consistent relationship between the test and the confirmatory method but the relationship is not 1:1. Table 8 displays the results from the regression analysis by Wilcoxon test method using data from Tables 6 and 7. The Quick Test VOH Water Test Method meets Level 2 criteria, that is, there is a relationship between the methods but the relationship is not 1:1.

Table 7. Total VOH Quick Test Kit Results Comparison with Laboratory Data

Sample Number	Total Volatile Organic Halide by the Quick Test Φg/L	Total Volatile Organic Halide by Standard Methods Φg/L	Percent Difference
1	890	959	7.2
2	270	206	31
3	<4	<10	NC
4	6.4	<10	NC
5	99	102	2.9
6	172	145	19
7	153	165	10
8	57	66	14
9	1670	1703	1.9
10	3025	4858	38
11	2900	4040	28
12	300	339	12
13	119000	98208	21
14	12.9	<10	NC

Table 8. Statistical comparison of Quick Test and Standard Methods Results for Data in Tables 6 and 7

concentration range Φg/l	n	r^2	y intercept	slope
5 to 4000	18	0.974	91.7*	0.678

* y-intercept was not statistically different from 0 at a 90 percent confidence limit

Meeting Level 2 accuracy requirement indicates that there is a consistent relationship within the samples tested, however the relationship between methods cannot be assumed to be statistically equivalent. Regression analysis can be performed on select samples from a site to determine the relationship between methods, and therefore Quick Test VOH results can be corrected using the regression equation generated.

Conclusions

The performance characteristics of a new field test, based on a photo-induced oxidation-reduction reaction producing coloration proportional to the concentration of VOH (volatile organic halides) present, have been evaluated. The average method detection limit (MDL) for the Quick Test VOH Water Test Method for volatile organic halides is 4 Φg/L in water. The dynamic range is 4 to 200 Φg/L (ppb), which is useful for sites where cleanup levels are within the stated dynamic range. With dilution the dynamic range can be extended up to 200 mg/L (ppm). The Quick Test VOH Water Test Method meets standard method=s criteria, set by the U.S. EPA for accuracy and precision. The matrix suitability study results show that the Quick Test VOH Water Test Method is not subject to matrix effects. Independent correlation studies between Quick Test results and those reported for field water samples analyzed by standard methods confirm that the Quick Test VOH Water Test System meets U.S. EPA Superfund Innovation Technology Evaluation (SITE) Level 2 criteria for field testing. The quality control (QC) procedures prescribed for the Quick Test are adequate and flexible to accommodate the intended uses of this method. The Quick Test procedure is simple, easy to use and is optimized for quantitation of volatile organic halides.

Reference

1. National Primary Drinking Water Regulations, TRICHLOROETHYLENE, US EPA, Office of Ground Water and Drinking Water, Revised December 23, 1998.
2. National Primary Drinking Water Regulations, TETRACHLOROETHYLENE, US EPA, Office of Ground Water and Drinking Water, Revised December 23, 1998.
3. U.S. Environmental Protection Agency, Test Method for Evaluating Solid Waste, Physical/Chemical Method, SW-846, U.S. Government Printing Office, Washington, DC, 1992.
4. B. Lesnik and P. Marsden, A Demystifying Methods Development @ Environ. Lab. Mag. July 1995.

5. Dong Chen, David Shattuck, Mark Hines and Joan McLean, Field Analytical Chemistry and Technology 2(1):29-37, 1998.
6. U.S. Environmental Protection Agency, APCP Immunoassay Technologies, Innovative Evaluation Report, @ Report No. EPA/540/R-95/514, 1995.

LAB AUDITING AND ACCREDIDATION

THE ROLE OF A COMPLIANCE PROGRAM AND DATA QUALITY REVIEW PROCEDURE UNDER PBMS

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INTRODUCTION

The trend away from sole reliance on method specified quality control (QC) to a performance based measurements system (PBMS) creates the need for a broader based oversight program to ensure that environmental project and regulatory program requirements are met. A strict QC program based on method compliance will not be sufficient to ensure compliance with PBMS guidelines. Further, strict QC programs have not always been effective in ensuring method and project compliance and in preventing ethics violations.

Under PBMS, a comprehensive compliance program is warranted to help ensure compliance of all activities and ethical performance of work, regardless of the method or project requirements. New approaches to data review are needed to ensure that performance standards can be met. This paper provides guidance on key elements that should be included in an effective compliance program and presents a data quality review procedure to use for determining if data of acceptable quality can be generated.

IMPLEMENTING A COMPLIANCE PROGRAM

Ethics Policy or Statement

A compliance program must have an ethics policy or statement. This policy or statement should define the company or organization's position on ethics and state what is expected of its employees or members with regards to ethical behavior.

For example, a company's ethics policy may be the following:

> "All employees at all times shall conduct themselves and the business of the Company in an honest and ethical manner. Compliance with this policy shall be strictly enforced."

The ethics policy should be documented and posted for all employees to view. Companies may wish to further affirm and document employee commitment to compliance with the ethics policy through an Employee Ethics Agreement that each employee must sign as a condition of their employment.

Compliance Program Management

The compliance program should be managed by a senior management employee with the authority, skills and availability to perform such an assignment. The compliance program manager should report to upper management on a regular basis on the status of ethics activities within the organization. Companies may also elect to form an Ethics Committee with members from their upper management staff or Board of Directors that meets on a regular basis to set ethics policy and discuss ethics related matters.

Ethics Procedures

Policies and procedures for ethical conduct and for reporting and investigating suspected ethics violations should be developed and included in the company's policy and procedures manual. An ethics procedure should define ethical conduct and what constitutes unethical behavior and how it is handled. Disciplinary action for ethics violations, up to and including termination, should be stated in the ethics procedure. Fair procedures for reporting and investigating alleged unethical behavior should be included in an ethics reporting and investigation procedure. These procedures as well as other company procedures should be accessible to all employees.

Zero Tolerance Policy

Companies should have a zero tolerance policy on unethical activities and non-compliance with required procedures. Unethical behavior or fraud may be defined as intentional falsification of data or records, such as sampling or sample handling records, laboratory worksheets or logbooks, instrument settings or data, sample results or data, and laboratory analysis reports. Unacceptable behavior may be defined as deliberate lack of adherence to company and method requirements, such as procedures for instrument calibration, quality control, standards and reagents preparation, sample handling, and sample preparation and analysis.

Laboratories may wish to go one step further and issue a policy that defines specific unacceptable and fraudulent

activities. Since most laboratory procedures define what employees are required to do, this policy ensures that employees are educated as to what they are not allowed to do. Such a policy may include the following unacceptable and fraudulent activities: 1) making up data (dry labbing) or other sampling and analysis information; 2) misrepresentation of QC samples and spikes as being extracted or digested when in fact they were not extracted or digested; 3) improper clock setting (time traveling) or improper date/time recording; 4) improper peak integration (peak shaving or enhancing); 5) improper GC/MS tuning; 6) improper calibration/QC analysis; 7) file substitution; 8) deletion of non-compliant data; 9) improper alteration of analytical conditions; 10) unwarranted manipulation of computer software; and 11) lack of notification to management on identified sample or data errors.

Laboratories that are proactive in informing employees of what constitutes unacceptable and fraudulent behavior have a better chance of preventing fraud than laboratories that do not.

Ethics Assistance and Reporting Mechanism

Companies should a have a single point of contact for assisting employees with questions on ethics related matters and for reporting observations of suspected unethical behavior or business conduct. A Helpline or Hotline is such a mechanism where phone calls, faxes or other correspondence on ethics concerns, questions or reports of suspected unethical behavior can be directed and then addressed appropriately. The phone numbers and addresses for the Helpline or Hotline should be documented and readily available to all employees. The Helpline or Hotline can be manned by a senior management employee, such as the compliance program manager, or by an outside service.

Compliance Plan

A compliance plan should include or refer to all of the procedures used by an organization for ensuring compliance with company, client and government requirements. The compliance plan should include or refer to company policies and procedures on business conduct, especially ethics. Also include or refer to technical and quality assurance procedures used by the laboratory and required by client, method or regulatory agencies to ensure that data are accurate and traceable. The compliance plan should further include or refer to environmental management activities and procedures used for chemical and waste handling to comply with federal, state and local regulations. A compliance plan may also include a quality management program such as ISO 9002.

Compliance Training

Compliance training should be provided to all employees and include, at a minimum, training on the ethics policy and procedures. Ethics training should be documented on training forms and included in the employee training or personnel files. Training on laboratory procedures should be ongoing and based on each individual and their work assignments.

Compliance Audits

Adherence to the compliance plan and associated procedures/requirements should be checked on a regular basis via on-site audits. The compliance officer, quality assurance staff or outside consultants may conduct compliance audits. Any findings of non-compliance with company, client or government requirements should be documented and provided to management. Prompt and effective corrective action should be taken on any findings and reported back to the auditing body for review and approval.

DATA QUALITY REVIEW

Despite the number of laboratory audits that are conducted at environmental testing laboratories, many of these audits do not address data quality and thus do not identify data quality problems. Traditional audits tend to focus on laboratory procedures and QC criteria rather than data quality. Probably the most important area that affects the usability of sample data is not receiving the critical attention it should have.

A data quality review should be performed to determine if data of acceptable quality can be and are being generated by a given laboratory. This review does not replace on-site assessments that evaluate method compliance or tape audits that evaluate the accuracy of reported data. The following items should be included in a data quality review of organic analysis data, whether for PBMS methods or traditional methods. Similar principles apply to inorganic analysis data.

Initial Demonstration of Competency Data

An initial demonstration of competency (IDC) study (also referred to as initial demonstration of capability or proficiency study) demonstrates the ability of each analyst and instrument to achieve acceptable accuracy and precision for each analyte in each test method performed. It should be performed prior to performing sample analyses and

whenever there is a new analyst or major change in the instrumentation. An IDC study involves the preparation and analysis of a minimum of four spiked samples at concentrations of 20 µg/L for volatiles, 100 µg/L for semivolatiles and 2-50 µg/L for pesticides and PCBs.

First determine if IDC studies have been performed for each analyst and instrument. If not performed, note which studies are needed for immediate action. If performed, review the data from each study and determine if each target analyte was included. For each analyte, evaluate the spike value, found values, average percent recovery and standard deviation (SD). Compare the average percent recovery and SD for each analyte to the method or project specified acceptance range or values. If the average percent recovery is within the acceptance range, then acceptable accuracy can be achieved. If the SD is less than the maximum allowable value, then acceptable precision can be achieved. If either criteria were not met, then note the analytes that require immediate action (repeat of study.)

Method Detection Limits

A method detection limit (MDL) determination or study establishes the lowest concentration that the laboratory can measure an analyte with 99% confidence. Using the procedure in 40 CFR Part 136 Appendix B, a MDL study involves the preparation and analysis of a minimum of seven spiked samples at a concentration 1-5 times the estimated MDL. The MDL is calculated by multiplying the standard deviation obtained for the seven measurements by 3.14.

First determine if MDL studies have been performed for each method and analyte. If not performed, note which studies are needed for immediate action. If performed, evaluate each study to determine if each target analyte was included. For each analyte, evaluate the spike value, found values, average percent recovery, standard deviation (SD) and calculated MDL. Compare the calculated MDL and the spike value. If the calculated MDL is greater than the spike concentration, then the study should be repeated at a higher spike concentration. If the spike concentration is greater than 10 times the calculated MDL, then the study should be repeated at a lower spike concentration.

Laboratory Reporting Limits

Laboratory reporting limits (RLs) are the minimum values used by the laboratory to report sample data. Laboratories typically use quantitation limits or values that are generally 5 to 10 times the MDLs for their RLs. For samples that are diluted, the RLs must be multiplied by the sample dilution factor. Target analytes found in samples at concentrations greater than the RLs are reported as numerical values. Target analytes not detected above the corresponding RLs are reported as “not detected” or at a qualified value greater than the MDL.

First obtain and review the laboratory’s RLs for each method, matrix and analyte. Then evaluate the RLs in water for each method and analyte to determine if the laboratory RLs are greater than the MDLs (data for other matrices may also be reviewed.) If any RLs are less than the associated MDLs, then note which analytes require immediate action (Note: an error here means that the laboratory may be reporting data lower than it can actually measure.) If the RLs are greater than or equal to the associated MDLs, then it can be expected that the laboratory’s reports will provide values that can be detected or backed up by laboratory measurements. Alternately, if MDLs are not available for certain analytes, the lowest calibration standard may be evaluated and compared to the laboratory RLs. If any RLs are less than the lowest concentration calibration standard, then note the analytes that require immediate action. If the RLs are greater than or equal to the lowest concentration calibration standard, then it can be expected that the laboratory’s reports will provide values that can be detected by calibration standards.

Initial Calibration Data

Initial calibration is performed to establish the calibration curve and range for each analyte.

Analyte Presence and Standard Concentration. First review recent initial calibration data for each method and analyte. Also review the source and concentration for each initial calibration standard. Determine if all target analytes were included in the calibration standards. If not, note any missing analytes for immediate action. Next determine if the concentration values used for each analyte in the calibration table or curve match the actual concentrations provided with the calibration standards. If the concentrations do not match, then note any analytes that require immediate action (Note: this error could result in incorrect concentrations in samples.) If the values do match, then the calibration table or curve can be considered accurate with regards to assigned standard concentration. Also evaluate if surrogates were analyzed at multiple concentrations. Previous EPA SW-846 methods allowed single concentrations but recent updates to SW-846, i.e., Update III and Method 8000B, require multi-point concentration for surrogates as well as target analytes. If surrogates were not analyzed at multiple concentrations, then note which analyses are affected for immediate action.

Analyte Identification. Evaluate the data for the lowest concentration standard analysis to determine if the identification data for each target analyte is representative of that analyte, such as GC/MS mass spectrum or characteristic ions, GC/MS "Q" value, GC retention time, elution order, etc. If not, note which analytes are questionable and require immediate action (Note: this error could result in incorrect analyte identification in samples.) If all analytes are included and the data are representative, then the laboratory should be able to correctly identify target analytes in samples.

Analyte Response. Evaluate the analyte response in each calibration standard to determine if the responses are acceptable and proportionate to concentration. For GC/MS analyses, determine if the relative response factors (RRFs) for each analyte are above the minimum required value. For each target analyte, evaluate if the responses increase with concentration (e.g., the area for benzene in a 100 ppb standard should have twice the area as a 50 ppb standard.) If RRFs are below the minimum value or if responses are not proportionate to concentration, then note the analytes that require immediate action. If the analyte responses are acceptable, then it can be expected that the laboratory can acceptably measure responses for target analytes in samples.

Calibration Accuracy. Evaluate the calibration table or curve to determine if all data were used and that no points in the middle of the calibration table or curve were deleted to force the calibration to meet certain criteria. Also evaluate if manual integrations appear to be acceptable. The only points (concentrations) that should be deleted from the calibration are low or high points that are outside the calibration range or points with a known error. If any analytes were deleted from the middle of the calibration or if manual integration appears to be improper, then note the analytes that require immediate action.

Next evaluate the %RSD for average RFs or RRFs for each analyte in the initial calibration and determine the method used for sample quantitation. If the %RSD value for each analyte is less than or equal to 15%, it is acceptable by EPA SW-846 methods to use RRF or RF for quantitation. If the %RSD is greater than 15% for any analyte, evaluate if a linear or higher order calibration curve was used for quantitation and if the minimum number of standards (5 for 1st order, 6 for 2nd order and 7 for 3rd order) were included in the calibration. If not, note the analytes that require immediate action. If the correct number of standards were analyzed and the appropriate technique is used for quantitation, then the initial calibration can be considered acceptable for sample quantitation.

Analytical Conditions. Also evaluate the conditions used for initial calibration to determine if the same conditions were used for sample analysis (such as purging temperature for volatiles). If not, note the analyses that are affected for immediate action.

Calibration Verification

Calibration verification is performed at a regular frequency (every 12 hours for GC/MS analysis and at the beginning, end, and 5 to 10% of the runs for GC analysis) to verify that the current instrument performance is still acceptable in comparison to performance during the initial calibration.

First review recent calibration verification data for each analysis. Also review the source and concentration for the calibration verification analysis. Determine if the concentration values used in the calibration verification matches the actual concentration provided with the calibration standard. If the concentrations do not match, then note any analytes that require immediate action. If the values do match, then the calibration can be considered accurate with regards to assigned standard concentration. Next evaluate the data for the calibration verification standard analysis to determine if all of the target analytes were included and detected in the standard. If any target analytes were not included or not detected, then note the analytes that require immediate action.

Evaluate the % difference (%D) from the expected value or the % recovery compared to the known value for each target analyte in the calibration verification. Determine if the %D or % recovery for each analyte was within the method or project specified acceptance values, generally +/- 15 to 20%. If not, note the analytes that require immediate action. (Note: Action may not be necessary if the analyte(s) in question was not detected in any associated samples and the standard indicates that the analyte could be detected if it was present in a sample.) If the %D or % recovery for each analyte was within the allowable values, then the calibration verification can be considered valid with regard to the initial calibration.

Laboratory Control Sample

A laboratory control sample (LCS) is a purchased or prepared sample with a known concentration of target analytes taken through the entire sample preparation and analysis procedure and used to measure recovery.

First evaluate the analytes that were included in the LCS and their concentration values. Determine if the method or project required analytes were included in the LCS and if the concentration was at the required value(s). Review the source data for the LCS to determine if the LCS was from a different source or lot than the calibration standards and if the concentration values assigned by the laboratory match the values from the source. If any analytes or concentrations are incorrect, note the analytes that require immediate action. For each spiked analyte, evaluate the spike value, found values and percent recovery. Compare the percent recovery for each analyte to the method or project specified acceptance values. If the percent recovery is within the acceptance range, then acceptable accuracy can be achieved. If not, note the analytes that require immediate action.

Laboratory Blanks

Laboratory blanks are analyzed to measure any background contamination introduced by the laboratory during the sample preparation or analysis procedures. Laboratory blanks include method blanks, reagent blanks, calibration blanks and holding or storage blanks.

Review blank data to determine if any analytes are present and at what concentrations. If target analytes are present in the blank, review associated sample data to determine if the background in the blank could have a significant affect on the sample values. If there are no detects for the affected analyte(s) in the sample or if the analyte concentration is the sample is high, then low level background contamination will not have a significant affect. If there are low level concentrations in the sample slightly above or near the blank level, then the sample may be affected. Also review surrogate data in the blank to establish a baseline level with which to compare the sample data. If surrogate recovery is acceptable in the blank, then unacceptable recovery in samples is probably due to the sample and not laboratory performance. Note any unacceptable recovery of surrogates in blanks for immediate action.

Sample Data

Last but not least are the sample data. Review sample data for surrogate recovery, internal standard response (if internal standards are used), and analyte identification and quantitation. Determine if surrogates and internal standards (if applicable) were added to each sample and if the surrogate recovery and internal standard responses were within method or project specifications. If not, determine if corrective action was taken or if additional analyses were performed. If reanalysis data still are not acceptable, then note the impact (low or high bias) on sample results. Evaluate reported analytes in samples to determine if identification characteristics and criteria were satisfied, such as GC/MS mass spectrum, GC/MS "Q" value, GC retention time and elution order. If not, the analyte identification and presence may be suspect and sample results should be handled accordingly (i.e., reprocessed or rejected.) Next determine if concentrations for found analytes were calculated and reported correctly. If not, the analyte concentration may be incorrect and sample results should be handled appropriately (i.e., recalculated or rejected.) Also review matrix spike and duplicate data if available for the same sample to determine if the results for found analytes correlate between each analysis. Determine if non-spiked analytes found in the original sample are also found in the matrix spike and duplicate at similar concentrations. If not, there may be a lack of precision or an error in one or more of the analyses; sample results should be handled appropriately (i.e., qualified or rejected.) Also review all sample documentation to determine if complete and consistent. If not, note what is needed for immediate action.

For any of the items that require action, consult with the laboratory manager for correction and resolution. Data of acceptable quality can be achieved when all of the above criteria are satisfied.

CONCLUSION

With PBMS on the horizon, environmental professionals may wonder what will happen to control of laboratory data quality if adherence to strict method requirements is no longer mandatory. Data quality has not been guaranteed by the traditional focus on method QC limits, and in fact many unethical practices have occurred in environmental laboratories in order to meet QC limits. Change is disconcerting but necessary for improvement. By implementing an effective compliance program and by conducting data quality review with the guidance provided in this paper, ethics awareness and environmental data quality can be improved.

AUTHOR INDEX

NOTES

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