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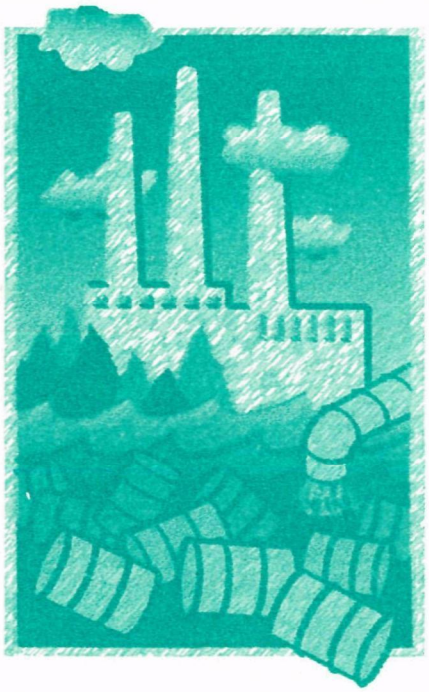

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QUALITY ASSURANCE

FLORIDA's LABORATORY CERTIFICATION PROGRAM: 1994 AND BEYOND

S. E. Garlington, Laboratory Consultant, P. J. Legge, Laboratory Consultant, C. M. Oakley, Laboratory Consultant, and C. C. Kircher, Program Administrator, FL Department of Health and Rehabilitative Services, Office of Laboratory Services, Jacksonville, Florida 32231

ABSTRACT

The Florida Department of Health and Rehabilitative Services (HRS) operates two laboratory certification programs. Currently, 300 Safe Drinking Water testing laboratories and 500 Environmental testing laboratories are certified in each program. Because these programs are fairly large and involve laboratories nation-wide that support Florida projects, the following issues regarding certification are routinely addressed:

- Reciprocal certification with other states and the National Environmental Laboratory Accreditation Program.

- Use of approved, standardized, performance-based, or alternate analytical testing methods.

- Expanding certification for newly regulated contaminants, such as asbestos, dioxin, and disinfectant by-products.

- Formats and documentation of quality systems, both for laboratories and for accreditation agencies.

- Representative on-site laboratory surveys and scope of accreditation among various states and 3rd party agencies.

Many of these issues are common to other state laboratory certification programs. The purpose of this paper is to present Florida's approach to these issues and to stimulate discussions among the regulatory agencies, testing laboratories, water supply systems, and the public.

INTRODUCTION

The State of Florida offers two certification programs to accredit laboratories. One program is for Safe Drinking Water (SDW) testing, and the other is for Environmental Water (ENV) testing. The Department of Health and Rehabilitative Services (HRS) Office of Laboratory Services

has assumed primacy for the enforcement of the Safe Drinking Water Act. The SDW program thus serves to fulfill the requirement that drinking water testing be performed by certified laboratories. Approximately 300 laboratories are certified or pending certification in this program.

Statutory authority for the ENV program is derived from the Florida Air and Water Pollution Control Act. Laboratory certification for this program is required only for analyzing domestic effluents and wastewater during treatment and discharge. Due to laboratory demand, certification is also offered for hazardous waste, soils and sediments, groundwater, and other environmental systems. Defining "environmental water samples" as essentially any source that can impact Florida water quality allows our program to offer this expanded certification. Thus, although the ENV certification is largely voluntary, many laboratories choose to become certified because this accreditation enhances their marketability, public trust, and client relations. Approximately 500 laboratories are certified or pending certification in this program.

The legal framework for Florida's certification programs is encompassed in chapter 10D-41 Florida Administrative Code (FAC). Sections 10D-41.050 through 10D-41.062 FAC pertain to the SDW program, and sections 10D-41.100 through 10D-41.113 FAC pertain to the ENV program. HRS shares responsibilities with the Florida Department of Environmental Protection (DEP) to establish the criteria for laboratory accreditation.

Florida's laboratory certification program is one of the larger programs in the nation. Support for the program is based on the extreme importance Florida places on maintaining the quality of its surface waters and groundwater. Based on regular collaborations with other Florida officials and other state certification agencies, our program routine addresses issues that relate to Reciprocal Certification with other states, National Environmental Laboratory Accreditation, and Performance-based, newly approved, or Alternate Analytical Methods. The purpose of this paper is to present our approach to date on these issues, to describe the implementation and operation of our program, and to stimulate discussions so that the direction of this program will meet the needs of Florida's citizens, other accreditation agencies, U.S. EPA, and the public.

CERTIFICATION CATEGORIES AND REQUIREMENTS

Certification for Safe Drinking Water Testing Laboratories is offered in the following categories:

- PRIMARY INORGANIC CONTAMINANTS
  - Metals
  - Lead and Copper
  - Nitrate and Nitrite
  - Fluoride
  - Cyanide
  - Asbestos
- SECONDARY INORGANIC CONTAMINANTS
- PESTICIDES AND PCB's
  - Insecticides
  - Herbicides
  - Carbamates
  - Disinfectant BP's/VOC's
  - Miscellaneous SOC's
  - Adipates and Phthalates
  - PCB's
  - PAH's
- OTHER REGULATED CONTAMINANTS
  - VOC's
  - THM's
- GROUP I UNREGULATED CONTAMINANTS
  - Herbicides
  - Carbamates
- GROUP II UNREGULATED CONTAMINANTS
  - Purgeables
  - Acid Extractables
  - Base/Neutral Extractables
- DIOXIN
- MICROBIOLOGY
- RADIOCHEMISTRY

These categories and subcategories are generally organized according to SDW regulatory program, monitoring requirements, and analytical technique.

Certification for Environmental Water Testing Laboratories is offered in the following categories:

- METALS
- NUTRIENTS
- DEMANDS
- EXTRACTABLE ORGANICS (GC, GC/MS, HPLC)
- GENERAL CATEGORY I
- GENERAL CATEGORY II
- MICROBIOLOGY
- PESTICIDES-HERBICIDES-PCB'S (GC, GC/MS, HPLC)
- PURGEABLE ORGANICS (GC, GC/MS)
- BIOASSAY
- HAZARDOUS WASTE CHARACTERIZATION
- RADIOCHEMISTRY
- BASIC ENVIRONMENTAL LABORATORY

Some of the analytes offered in the Metals and Nutrients categories are also offered in General Category I and General Category II. The intent for inclusion in the general categories is for smaller laboratories to analyze these contaminants with colorimetric/titrimetric methods or with test kits where ultratrace sensitivities are not required. Also, to save smaller, in-house water utility and wastewater treatment laboratories the expense of being certified in 4-5 categories, selected contaminants from Nutrients, Demands, Microbiology, General Category I, and General Category II categories are combined in the Basic Environmental category. However, laboratories certified in this category may also be certified in only one other additional category of choice. Otherwise, the laboratory is not considered "basic" and must select analytes from the other categories in order to become certified.

As with other state certification agencies, Florida's laboratory certification requirements include completion of an application form, satisfactory analysis of proficiency test samples, formulation of a quality assurance plan, demonstrating compliance with certification requirements during an on-site laboratory inspection, and payment of certification fees. The applications are reviewed for completeness (including the Personnel and Quality Assurance (QA) sections), for original signatures from the Laboratory Director and QA Officer attesting to compliance with certification rules and regulations, and for appropriate analytical methods with each pending analyte. All regulated SDW contaminants must be analyzed with EPA-approved methods. Analytical methods selected for other pending analytes must include the analytes in their titles or their compound lists, or else be referenced by EPA in the Code of Federal Regulations (CFR).

Pending SDW laboratories are enrolled in EPA's Water Supply (WS) proficiency testing (PT) program, and pending ENV laboratories are enrolled in the EPA Water Pollution (WP) program. To be eligible for certification for a particular analyte, the laboratory must produce acceptable results at all available concentration levels for that analyte during the latest WS or WP testing round. If a pending analyte is not available during a round, the laboratory is still eligible for certification for that analyte if the laboratory passes at least 75% of all available analytes pending certification that are in the same category as the unavailable analyte. In general, as a Standard Operating Procedure (SOP), our program will classify a pending laboratory as ready for the on-site inspection if the laboratory passes at least 75% of all available pending analytes at all available concentration levels in any one

category during the latest PT testing round. To maintain certification, a laboratory must produce acceptable results at least once per year for each available certified analyte at all available concentration levels. With prior permission from HRS, a laboratory may analyze commercially available PT samples that are determined to be equivalent to the corresponding EPA program.

For SDW certification, the laboratory must have a QA plan available for review during the on-site inspection, if requested. For ENV certification, the laboratory QA plan must be reviewed and approved prior to the on-site inspection. If the pending ENV laboratory is analyzing only domestic effluents and wastewater, HRS is authorized to review and approve the QA plan. If the laboratory is analyzing other types of samples, such as hazardous waste, then the QA plan must be reviewed and approved by the Florida DEP Quality Assurance Section.

Laboratories located in Florida are generally inspected on-site once per year; out-of-state laboratories are surveyed once every two years. The duration of the on-site survey ranges from a half-day for SDW Microbiology and Basic Environmental laboratories to two days for full-service SDW and ENV laboratories. In general, the laboratory surveys are conducted to verify that the laboratory has performed the Initial Demonstration of Capability, instrumental calibration, and on-going QA requirements in the analytical methods and to verify fulfillment of sample preservation, holding time, and data reduction/reporting requirements for the regulatory compliance programs. Our certification program uses in-house checklists as guidelines to assist in the inspection process. Laboratory consultants are trained by EPA as certification officers in both Chemistry and Microbiology; consequently, one inspector generally conducts the entire survey of the laboratory. Deficiencies observed during the survey are noted on a standard report form, and the laboratory must respond in writing to each deficiency with a Plan of Correction and completion date.

When the above requirements are met, the laboratory is invoiced for certification fees. For each program, SDW and ENV, these fees are $400 per category up to a maximum of $1500 for 4 categories or more. If the laboratory meets the requirements in the middle of the Florida fiscal year, the certification fees are prorated on a quarterly basis. Out-of-State laboratories are also invoiced for the inspector's travel expenses to conduct the on-site survey. Because Radiochemistry certification for both programs is handled through the HRS Office of Radiation Control rather than the Office of Laboratory Services, certification fees for

Radiochemistry are $400 per year in addition to any other certification fees assessed for Chemistry and Microbiology. Laboratory certification is valid for the current fiscal year between July 1 and June 30, and the laboratory is assessed the same certification fees for renewal for the next fiscal year.

When the certification fees are paid and the Plan of Correction is accepted, HRS assigns the laboratory a 5-digit certification number based upon the laboratory's geographic location, type of laboratory (commercial, public utility, research institution, etc.), and numerical sequence relative to previously certified laboratories. A certificate showing all categories certified and an Analyte Sheet showing all analytes and test methods certified are mailed to the laboratory.

PROGRAM ORGANIZATION

The laboratory certification program consists of fifteen full-time employees: four clerical staff, four in-house professionals, six laboratory consultants, and one program administrator. The clerical staff of secretaries and data entry personnel are responsible for typing correspondence, keying in laboratory and PT data into databases and spreadsheets, maintaining office equipment and supplies, and filing data into various hardcopy files. The in-house professionals are chemists and microbiologists who review certification applications, coordinate PT samples and results, update computer databases and hardcopy files, and provide administrative consultation to laboratories and the public. The laboratory consultants are chemists and microbiologists who are responsible for conducting the on-site laboratory surveys, reviewing QA plans, and providing technical consultation to laboratories and the public. The program administrator is a senior executive who is responsible to the Chief of Laboratory Services and who directs the policy decisions and procedural implementations of the certification program, resolves disputes and complaints from laboratories and the public, delegates defined activities for the program to individuals or committees, and promotes a working environment where accreditation decisions are free from conflict-of-interest or other influences.

Information on pending and certified laboratories is stored in hardcopy files and electronic computer files. For the hardcopy files, data for each certified laboratory is organized in color-coded sections that correspond to certificate, invoices, and certification-decertification correspondence; certification application; analyte sheet; PT

results; on-site survey reports and Plans of Correction; QA plan; and miscellaneous correspondence. Information on certified laboratories that is over two years old is stored in purge files. Information on applicant laboratories is stored in pending file folders. Generally, separate pending files are kept for laboratories pending certification and for certified laboratories that have applied for additional certification. Information on laboratories that are no longer involved in the certification program are stored in inactive files.

Laboratory information is also stored electronically in various computer databases and spreadsheets. The certification program operates a dedicated Novell network (Version 1.22) in which a fileserver is linked to eight personal computers, four printers, and one modem. Access to the network and to databases is controlled through logon ID's and passwords. Most laboratory information is organized in the databases through dBase-IV, Version 1.1. This particular software allows searching for specific records, sorting and organizing laboratories according to specific criteria, and varying the output formats for reports and mailing labels as needed. Analyte Sheets, PT results, and certification status based on PT results are stored in spreadsheets created through Lotus 123, Version 2.2. Standard forms and templates have been prepared with Microsoft Word, Version 5.0.

Florida's laboratory certification program is committed to operating this program in accordance with generally accepted international standards of quality. Because many laboratories use this program as an integral part of their individual quality systems, the certification program documents its quality system in various Standard Operating Procedures (SOP's) and in Appendices that contain the various forms, templates, checklists, and other materials used by the program. This quality system is intended to comply with the guidelines established in ISO Guides 25, 54, and 55[1-3] and in NISTIR 4576[4].

RECIPROCAL CERTIFICATION FOR OUT-OF-STATE LABORATORIES

Florida's certification program is one of the larger programs in the nation and currently certifies laboratories in 34 states and Puerto Rico. Additional laboratories in Canada and Mexico are pending Florida certification. Consequently, this program deals with reciprocal certification with out-of-state laboratories on a regular basis. Some states are known to certify their out-of-state laboratories based upon the laboratories' Florida certifications. However, Florida's current legal system

does not allow for third-party reciprocal certification, and a laboratory must be certified by its home state for the same analytes and test methods to be eligible for reciprocal certification in Florida.

In general, Florida's program handles a laboratory's request for reciprocal certification on a case-by-case basis. The applicant laboratory must submit copies of its state's certificate, analyte sheet, PT results (if applicable), QA plan (if applicable), survey report from the most recent on-site laboratory inspection, and certification rules and regulations. This information is reviewed to verify compliance with all sections of 10D-41 FAC and to ascertain whether Florida's laboratory consultants would observe the same condition of the laboratory as noted in the home state's survey report if Florida's consultants had conducted the inspection. If these requirements are met, the requirements of the on-site laboratory inspection and the laboratory paying for the inspector's travel expenses are waived, and the laboratory is recommended for Florida certification by reciprocity.

Reciprocal certification occurs most frequently with out-of-state laboratories that are seeking Florida certification for a specific analytical function, such as Bioassay, Asbestos analysis, or Dioxin analysis. In these cases, it is comparatively easy to confirm the home state's certification and to verify the representativeness of the inspection criteria used. In other cases, Florida HRS can grant certification by reciprocity for some of the analytes and test methods, but the on-site survey by Florida's consultants would be required for the other pending analytes in the laboratory's application.

Florida's program does accommodate another state's certification by compound class or analytical technique. As an example, an out-of-state laboratory certified in its home state to analyze drinking water by Purge-and-Trap GC/MS would be reciprocally certified by Florida for all Volatile Organic Contaminants, Trihalomethanes, and Purgeable Organics that Florida regulates, by EPA Method 524.2.

Florida's certification program is currently prepared to enter into a Memorandum of Understanding (MOU) with other state programs that require a formal reciprocity agreement. This MOU confirms that the laboratory must meet each state's certification requirements and specifies the differences between the two states' requirements. For example, Florida would require formal approval of the out-of-state laboratory's QA plan, but the Florida laboratory would have to fulfill the other state's existing PT or application

requirements (which Florida agrees is equivalent to or more stringent than its own requirements).

NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION

From the State of Florida, Dr. E. C. Hartwig, Chief of HRS Laboratory Services, and S. Labie, head of DEP's Quality Assurance Section, currently serve on various task forces and working groups in EPA's Committee for the National Accreditation of Environmental Laboratories (CNAEL). Both of these individuals have close associations with the certification program; consequently, there has been considerable information exchange on CNAEL's activities and providing input for task forces and working groups.

Despite the current situation with different states implementing their own certification programs, there is considerable precedent and framework already in place for a national accreditation program. 49 out of 50 states have assumed primacy for the enforcement of the Safe Drinking Water Act and thus have laboratory certification programs of various sizes. In addition, 43 of these programs utilize EPA's WS and/or WP PT samples as integral parts of their certification requirements. Furthermore, all other states' rules and regulations reviewed thus far contain various forms of application, proficiency testing, quality assurance, on-site laboratory inspection, and fee payment requirements for certification.

From a laboratory certification perspective, two of the biggest barriers to national laboratory accreditation are the scope of the certification that will be offered and the representativeness of the on-site laboratory survey among the various organizations that will operate the accreditation program. The scopes of accreditation among the states vary widely. States certify laboratories by categories, chemical compound class, analytical technique, individual analytes, test methods, and/or sample matrix. One way to resolve these differences is to adopt a hierarchical structure for national laboratory accreditation such as the one proposed by the CNAEL.[5]

Because the on-site laboratory survey is important in determining a laboratory's certification status, ensuring that the inspection criteria are completely defined and uniformly applied is critical to the efficacy of a national program. Florida HRS has requested and obtained inspection checklists from other states' programs and has compared these checklists with our own. These checklists have been helpful for improving our own checklists and for deciding

whether an out-of-state laboratory should obtain reciprocal certification.

In addition, Florida's certification program has reviewed an EPA draft document "Data Audits for Drinking Water Laboratories."[6] This document was authored by EPA personnel and is being proposed for inclusion as a chapter or appendix in the EPA "Manual for the Certification of Laboratories Analyzing Drinking Water."[7] Although many of the guidelines need to be tailored to specific analytical methods, the "Data Audit" document has excellent quality in content, organization, and presentation. Its details are pertinent to a laboratory performance audit as well as a conventional data audit. Incorporation of a document such as this one in the National Environmental Laboratory Accreditation Program and the implementation of its guidelines by all accrediting organizations will go a long way in reinforcing the viability of the National Program, addressing the concerns of laboratories regarding uniform treatment, and serving the needs of the public in health and safety.

Thus, from a laboratory certification perspective, the authors see the national accreditation program as having three different components, oversight, implementation, and operation. In general, CNAEL's conclusion of the national program having federal oversight and implementation by the various state agencies is consistent with this view. Specific roles and responsibilities will be assigned to each component, and particular interactions among the components will be defined. The infrastructure of the state accrediting agencies that is already in place would be preserved, and state agencies would have the option of operating the national program on behalf of their respective states, or of delegating these operations to a third party accrediting agency.

EXPANDING CERTIFICATION PROGRAMS

Florida's certification program attempts to be as proactive as possible to changing monitoring requirements in the SDW Act and to updates in CFR. HRS has the fudiciary responsibility and statutory authority to amend its certification rules whenever EPA or Florida DEP promulgate their rule amendments. Certification personnel gain technical competence in new and revised test methods through in-house training in the HRS Central Laboratory (the SDW Primacy laboratory for Florida) and through participation in workshops sponsored by EPA's Environmental Monitoring and Systems Laboratory in Cincinnati and by EPA Region IV. When these options are not available, we can employ outside

consultants to assist in the necessary training for the on-site inspection process. For example, J. Webber from the New York Department of Health instructed our laboratory consultants in the on-site surveys of the first Florida-based laboratories to be certified for Asbestos in drinking water with the Transmission Electron Microscope method. We are attempting to develop expertise in the analyses of Giardia, Cryptosporidia, viruses, disinfectant by-products, and other contaminants should our certification program become involved in any laboratory approval process associated with the Information Collection Rule, Phase VIb, or other SDW monitoring changes.

ALTERATIVE AND PERFORMANCE-BASED ANALYTICAL METHODS

Because Florida laboratory certification is based on test method as well as analyte, our program relies greatly on the references of approved methods in CFR and the references of analytes in each method. In current practice, the use of alternative test methods is allowed in two cases. The most common situation occurs when laboratories exercise their options of modifying approved analytical methods to consolidate analysis procedures and improve performance. For example, a laboratory can use a mass spectrometer as allowed in Sections 6.8.3 and 10.4 of EPA Method 507 as long as the laboratory achieves the Initial Demonstration of Capability precision and accuracy objectives in Section 10.3 and obtains method detection limits that are reliably and consistently below the regulated Maximum Contaminant Level for each analyte. But the laboratory's Analyte Sheet will show certification for these analytes by EPA Method 507.

Alternatively, the laboratory may elect to submit its analytical method to the Alternative Test Method approval process, or to obtain a variance from EPA Region IV allowing the use of its method. When the Alternative Test Method is published in Federal Register or a letter of variance is received from EPA officials, we can offer certification for that method. Examples of variances received to date include analyzing wastewater samples for anions by Ion Chromatography and for metals by ICP/MS.

Our program recently reviewed an EPA draft document "Guidance on the Evaluation of Safe Drinking Water Act Compliance Monitoring Results from Performance-Based Methods."[8] The possible use of Performance-Based Methods (PBM's) represents EPA's approach to rapid changes and improvements in scientific analytical technology, and EPA's departure from the "command and control" style of environmental rule enforcement. Technically, PBM's are most useful in analyses of environmental samples that are

impossible to complete with approved methods. Drinking water samples are less susceptible to matrix interferences, and the current approved SDW methods do allow for considerable flexibility already. Nevertheless, the promulgation of PBM's may result in lower laboratory operating costs and reward the laboratories economically for developing new methods to meet data quality objectives. The chief disadvantage to PBM's is that reliable conclusions may not be reached from data among different water supplies and geographical regions, especially since different PBM's may not be universally applicable to all sampling conditions, site locations, sets of analytes, concentration ranges, or time of year. PBM's will be a challenge to implement in a certification program, and the proposed national accreditation program may be affected if primacy states choose to set their own data quality objectives.

CONCLUSIONS

Florida HRS is committed to operating its laboratory certification program to meet the needs of Florida citizens, the laboratories, US EPA, and the public. The primary purpose of the program is to ensure that laboratories perform analyses according to prescribed methods, produce data that meet defined standards of quality and defensibility, and comply with federal and Florida regulatory programs. Nevertheless, the philosophy of all personnel in the program is to provide cooperation and assistance to the laboratories in meeting these requirements and, when requested, provide technical assistance to the laboratory to improve analytical performance. Because the laboratory pays fees for its accreditation, Florida certification personnel want the product, the Certificate that the laboratory displays, to communicate the laboratory's trust and integrity to the public and quality and commitment to its clients. By pursuing these objectives, Florida's certification program is poised to offer laboratory accreditation that will meet present and future needs, benefit local communities, and provide for testing laboratory acceptance in international markets.

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The Significance of Sample Preparation in the Analytical Process

Gary Robertson, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV 89193
Sujith Kumar, Lockheed Environmental Systems & Technologies Company, Las Vegas, NV 89119

The U.S. EPA is concerned about the quality of analytical data used for making decisions about environmental cleanups. A research project at the Environmental Monitoring Systems Laboratory-Las Vegas relates the results of quality control (QC) activities to specific data quality parameters. Historically, laboratories have placed emphasis on the instrumental measurement system in environmental analysis with less attention paid to sample extraction and cleanup. Generally, in commercial laboratories, extraction personnel are less experienced, less educated and lower paid than instrument operators. This can have a severe impact on data quality unless appropriate controls are in place.

The object of this study was to differentiate between sample preparation errors and instrumental analysis errors and examine the effect of the sample preparation errors. QC data from the Contract Laboratory Program quarterly performance evaluation samples were examined and related to the analytical results obtained by program laboratories. Data from surrogates, internal standards, calibrations, and tunes were evaluated for laboratories with poor or failing scores on the semivolatile and pesticide fractions. The errors relating to the extraction portion of the analysis will be discussed relative to their effect on the analytical results. Case studies will be presented which illustrate the relationship between the QC and the analytical results, with a discussion of the errors likely to be responsible in each case.

The types of data quality defects resulting from sample preparation errors on performance evaluation samples are assumed to also occur from similar sample preparation errors on other samples. Therefore, an increased emphasis on procedures and training in sample preparation can make a significant improvement in the quality of data produced by a laboratory.

IDAHO NATIONAL ENGINEERING LABORATORY ANALYTICAL SERVICES PERFORMANCE EVALUATION PLAN*

Joan M. Connolly, Senior Scientist, S. J. Sailer, R. P. Wells, EG&G Idaho, Inc., Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415; D. A. Anderson, Battelle Pacific Northwest Laboratories, P.O. Box 999, MSIN P7-27, Richland, WA 99352

ABSTRACT

Consistent assessment of laboratory (mobile and permanent) and validator analytical support supplier performance across regulatory programs is a concern for sample management organizations across the Department of Energy (DOE) complex. The use of suspect analytical data for decision making has serious legal and financial implications to the DOE and its contractors. A joint statement issued by DOE, U.S. Environmental Protection Agency (USEPA) and the Department of Defense, and a subsequent DOE memorandum, emphasize the need to develop and implement a consistent and innovative means of preventing suspect data. Past occurrences of fraud in the generation of environmental and waste characterization data have been detrimental to the credibility of the DOE. A recent Federal Register proposed rule indicated that DOE will not be able to rely on other agencies for notification of suspect laboratories or validators.

The Idaho National Engineering Laboratory (INEL) Analytical Services Performance Evaluation Plan (ASPEP) proposes a strategy to ensure that analytical service suppliers provide products of known and appropriate quality for all DOE Environmental Management (EM) activities. The ASPEP emphasizes supplier product quality improvement through integration of real-time with periodic performance evaluation. Periodic evaluation of performance is accomplished using data generated from existing performance evaluation programs (i.e., those administered by DOE, the USEPA, and the Army Corp of Engineers) and audits. Real-time performance assessment is accomplished through evaluation of routine laboratory quality control data, blind performance evaluation samples, INEL-specific performance evaluation materials, deliverables and supplier management practices.

This paper describes the general approach and specific components outlined in the ASPEP for the assessment of analytical laboratory and data validator performance.

INTRODUCTION

The primary responsibility of the Idaho National Engineering Laboratory (INEL) Sample Management Office (SMO) is to ensure that data of known quality are supplied to the INEL by analytical chemistry service organizations. Because high-quality analytical support is vital to the success of the Department of Energy (DOE) Environmental Management (EM) programs at the

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INEL, the performance of organizations providing these services must be routinely monitored and assessed. This will be accomplished through the implementation of a Performance Evaluation (PE) Program.

The INEL Analytical Services Performance Evaluation Plan (ASPEP) documents the approach of the INEL PE program. The framework described in this document will ensure that laboratory and validator analytical service suppliers used by the SMO meet requirements and maintain an appropriate quality level. The ASPEP was developed to provide a proactive tool for prevention and detection of suspect analytical support supplier products. This system provides an objective means to measure and assess performance.

Program Scope

The INEL ASPEP is an integrated approach that assesses analytical supplier performance supporting all EM programs (i.e., environmental monitoring, environmental restoration, and waste management) at the INEL. The approach includes specific supplier evaluations of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Safe Drinking Water Act (SDWA), Clean Water Act (CWA), Resource Conservation and Recovery Act (RCRA) and Clean Air Act (CAA) analytical services.

Analytical service suppliers evaluated through the INEL PE program include analytical laboratories and data validators from both private and government sectors that have achieved SMO approval. The analytical disciplines for which ongoing performance is monitored are 1) metals, 2) organics, 3) radiochemistry, and 4) classical analyses.

Program Philosophy

The intent of the INEL PE program is to augment existing PE programs administered by the Environmental Protection Agency (EPA), the Department of Defense (DOD) and DOE by expanding into areas not addressed by these programs. Supplier performance monitoring based solely on existing PE program results occurs too infrequently to allow prompt correction of quality problems. There are no formal programs addressing the evaluation of data validation supplier performance. Therefore, the ASPEP integrates periodic and real-time supplier performance evaluation with quality improvement tools for a comprehensive approach to quality management of laboratory and data validation analytical services.

Multiple tools are available for assessing performance. The performance assessment tools chosen for this program fit into one of the following approaches to quality assurance:

1. *Periodic Supplier Performance Evaluation:* consists of evaluation of laboratory performance data generated from participation in existing PE programs administered by EPA or DOE, supplier audits, and evaluation of data validator performance on blind prevalidated data packages.

2. *Real-time Supplier Performance Evaluation:* consists of evaluation of laboratory quality control (QC) and blind PE sample data generated concurrently with INEL field samples, supplier management practices, and evaluation of supplier deliverables.

3. *Quality Improvement:* consist of matrix-specific QC materials provided to suppliers for use as known laboratory controls and feedback to suppliers on performance to encourage process improvements.

Data generated by participation in existing PE programs will be used as a tool to determine the general ability of a supplier to perform the required work. However, existing PE programs administered by EPA or DOE primarily manage quality by inspection because they are too infrequent to ensure that real-time control of data quality is maintained. The INEL ASPEP addresses quality through prevention, and augments data available from existing PE programs by:

1. Use of real-time quality assurance tools to monitor laboratory and validator performance when INEL samples or data packages are being processed

2. Performance assessment of validation support suppliers

3. Creation and use of INEL-specific PE soil samples to identify and correct analytical problems affecting actual INEL samples

4. Use of commercially available PE samples

5. Tracking performance indicators that reflect supplier management practices.

PROGRAM COMPONENTS

The program approach to performance evaluation is schematically represented in Figure 1. The components of the approach are performance tools, performance indicators associated with these tools, performance criteria for each indicator, an indicator assessment process and determination of supplier performance status. The status of analytical service supplier performance is determined by their records of conformance to criteria. Individual sections of supplier organizations will have a unique performance status based on the nature of their nonconformances. This performance status will determine the eligibility of a supplier to receive work from the INEL SMO.

Performance Evaluation Tools

Several performance evaluation tools and the required frequency for their use have been identified for use in evaluating analytical support suppliers. The analytical laboratory performance tools include: general laboratory operation assessment tools (audits or desk evaluations, assessment of deliverables, time management information) and method or analytical discipline-specific performance tools (existing PE program sample data, blind real-time PE sample data, and routine laboratory QC sample data, field split data, and field spike sample data). Validation supplier performance tools include: general assessment tools (audits or desk evaluations) and analytical discipline-specific assessment tools (assessment of deliverables, dual validation of data packages, and blind test data packages). These tools were selected to provide information regarding the supplier's management practices as well as their performance in specific analytical disciplines.

For purposes of this discussion, PE tools are referred to as "periodic" or "real-time", depending on the nature of their use. Periodic tools are used at a set frequency to provide information on supplier performance, either general or discipline-specific, which is not specifically associated with a particular batch of INEL field samples. Information supplied by periodic PE tools is indicative of overall performance or capabilities in a particular analytical discipline or method. Information provided by real-time PE tools is directly associated with supplier performance on specific batches of INEL field samples. Real-time tools are those which are either processed by the supplier at the same time as INEL field samples (e.g., a blind PE sample or laboratory QC) or data (e.g., a blind previously-validated data package) or involve assessment of supplier deliverables for actual INEL field samples.

Participation in existing periodic performance evaluation programs administered by EPA, DOE, or DOD is one tool used to assess laboratory performance. Supplier participation in these PE programs is dependant on the scope of the supplier's support to INEL (e.g., a laboratory supporting the drinking water program exclusively would not be required to participate in the Water Pollution program). Table I reflects the participation requirements associated with existing PE programs.

Performance Indicators and Performance Criteria

Performance indicators are associated with each of the tools. These performance indicators are the basis for qualitative and quantitative assessment of analytical laboratory and data validator performance. Acceptable performance criteria are defined for each performance indicator. The indicators and acceptable performance criteria are organized into general laboratory performance, specific laboratory analyses, and data validation performance categories. Analytical service supplier performance for each indicator is tracked, trended, and compared to the acceptable performance criteria. The frequency of nonconformance to these performance criteria are the basis for evaluating supplier performance.

General laboratory performance indicators are used to assess laboratory management and operational processes. Areas of assessment include holding times, turnaround times, completeness and accuracy of deliverables, audit results, and responsiveness. These parameters are assessed for either the laboratory as a whole, or for specific analytical disciplines and analysis types (e.g., VOCs, SVOCs, ICP metals, GFAA metals) as appropriate. The general laboratory performance indicators and performance criteria are listed in Table 2.

Performance indicators for specific laboratory analyses are listed by analytical discipline in Table 3. The listed indicators are applicable for all sample matrices listed in the Applicable Matrices column of the table unless otherwise indicated by a parenthetical clarification.

Specific laboratory performance indicators are identified for existing PE programs, INEL-sponsored blind PE samples, and routine laboratory QC. These indicators provide data for overall discipline performance and method and analyte-specific performance. The list may be subject to modification as the Performance Evaluation Program evolves and the usefulness of each indicator is assessed. Performance indicators for analysis of other matrices not specified in this section will be developed as needed.

Areas of data validation supplier performance assessment are turnaround times, deliverable accuracy and completeness, audit results, and responsiveness. The specific indicators with their associated

acceptable performance criteria are presented in Table 4. These parameters are indicators of general organization management and technical performance, and are assessed for the organization as a whole or on an analytical discipline or analysis type basis, as appropriate.

Performance Indicator Assessment Process

Performance indicator results and compliance with the associated acceptable performance criteria will be tracked for each supplier over time, using frequency histograms, control charts, and statistical analysis, as appropriate. Failure to meet the acceptable performance criteria for any performance indicator constitutes a supplier nonconformance (SNC). These SNCs will be communicated to the supplier, and corrective action approaches and closure times negotiated, documented, and tracked. Additionally, trends that indicate possible future problems (e.g., analyte recoveries dropping over time) will be communicated to the supplier. A form has been created to simplify and expedite these communication processes.

In certain limited instances, suppliers will be granted a variance from the acceptable performance criteria for circumstances which would incur a SNC through no fault of their own. For example, if samples arrive at a laboratory after holding times have expired, the laboratory would be granted a variance from the holding time performance criteria for those samples.

Supplier Performance Status

Supplier performance status categories have been established and are defined as follows: satisfactory, probation (warning), suspension (work stopped), and termination of SMO approval. The performance status of a supplier may be changed for part or all of their organization. Individual functions within the supplier organization may be affected independent of one another. The current performance status for each SMO-approved analytical service supplier is determined from results of performance indicator assessments. The nature and number of the SNCs incurred in the indicator assessment process determines the status categories assigned to individual supplier areas.

Tables 5 and 6 are performance status matrices constructed to outline the grounds for changing supplier performance status. The matrices reflect the scope and severity of performance problems causing status change. Progression from left to right across the matrices reflects increasingly pervasive impacts due to a performance problem. Progression from top to bottom indicates increasing severity of a performance problem. An example of increasing pervasiveness is nonconformances affecting several analytes, which in turn impact an entire multi-analyte method, and which ultimately, if unresolved, could affect the entire analytical discipline within a laboratory. The severity of a performance problem increases with multiple occurrences or unresolved corrective actions in the preceding categories. Repeated or unresolved performance problems will roll a supplier's status further toward the bottom right of the matrices.

The manner in which the performance indicators are tracked dictates the entry point into the status change matrices. For analytical laboratories, performance status changes may be invoked on an analyte, method or analytical discipline basis, or for the entire laboratory. In some cases, laboratory performance status changes may also be invoked for certain analysis types within the discipline (e.g., VOC, SVOC, GFAAS methods), where the performance status change effects more than one method but not the entire discipline. The performance status of data validators may be changed on an

analytical type or analytical discipline basis as well as for the entire organization. All changes in supplier performance status involve procurement concurrence; changes involving Stop Work orders (i.e., suspension and termination of approval) are handled according to DOE procurement practices.

Table 7 summarizes actions and responsibilities associated with performance status changes. If a supplier (or area within the supplier organization) has had a probation or suspension status change invoked, corrective actions (CAs) are mandatory to reinstate satisfactory status. CAs (CA) are negotiated between the supplier and the INEL SMO and closure times established. Contingencies exist for suppliers to appeal status change actions.

Status records are maintained for analytical laboratory general operations and for analytes, methods, analysis types, and analytical disciplines, as appropriate for the laboratory's support to the SMO. Status records for data validation suppliers are maintained for analytes, analysis types, analytical disciplines and overall performance. Since recurrences of performance problems can immediately force a supplier into probation or suspension, provisions exist to recognize successful corrective action. When sufficient time lapses after CA closure without a repeat occurrence of the same performance problem, the past occurrences will not be held against the supplier when determining future status changes.

SUMMARY

The ASPEP proposes a strategy for ensuring that analytical service suppliers provide products of known and appropriate quality to support INEL EM programs. This strategy is a proactive objective approach to identify and correct situations that may lead to the generation of suspect analytical products. Objective data for all analytical service suppliers will be compiled and assessed to ensure that suspect suppliers are not used by INEL projects. The iterative nature of the approach with an emphasis on communication between the supplier and the customer ensures that total quality management is acheived by all parties involved.

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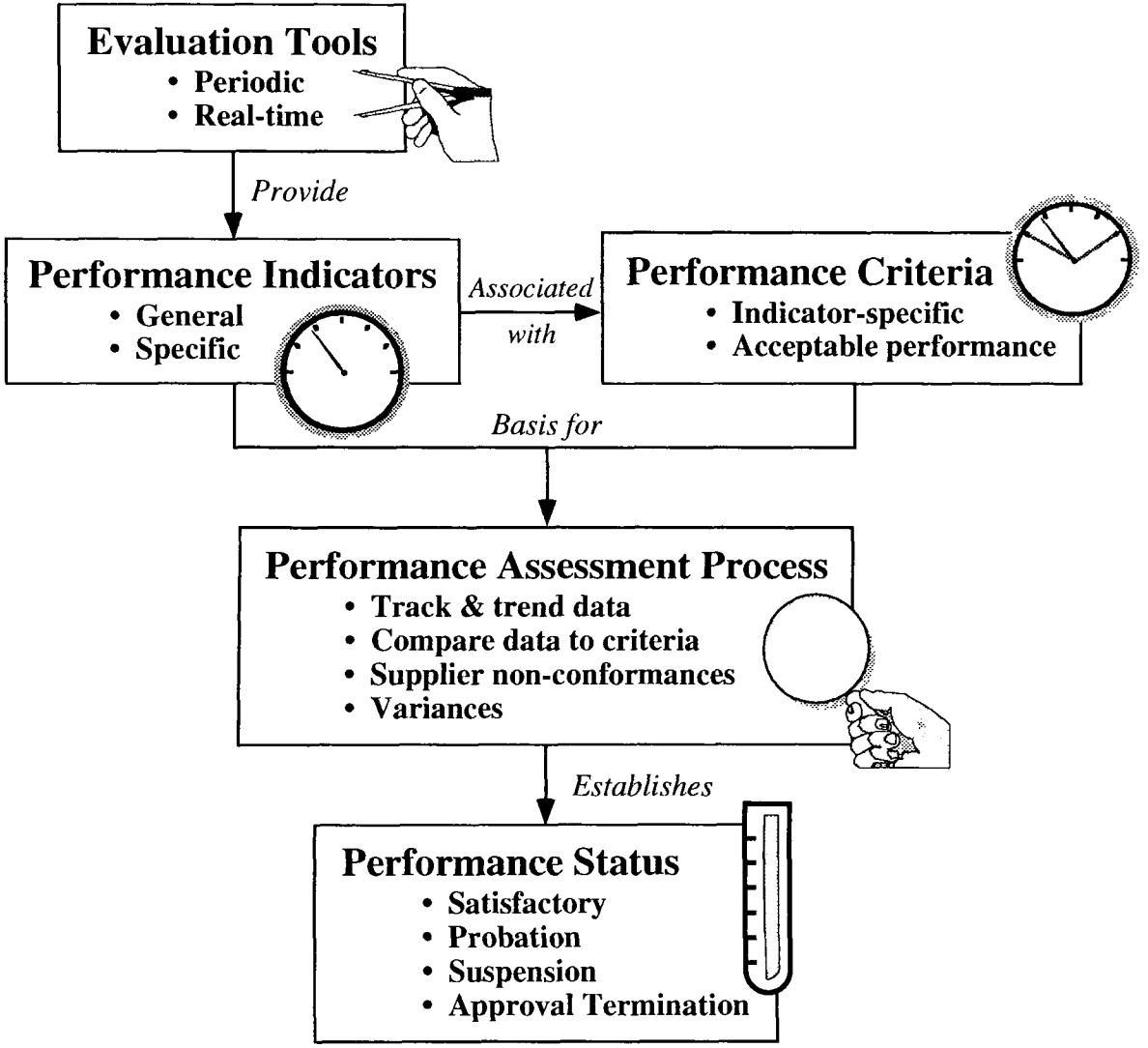

Figure 1. Performance Evaluation Approach

Table 1. Required participation in existing PE programs.

Existing Performance Evaluation Programs and Required Participation Frequency		Idaho National Engineering Laboratory Environmental Program											
		Environmental Restoration				Waste Management				Environmental Monitoring			
	Mandate Source	Rad	Org	Metals	Other	Rad	Org	Metals	Other	Rad	Org	Metals	Other
EMSL RIS Semiannual	DOE	F,W				F,W				F,W			
EML QAP Semiannual	DOE	F,W S,B				F,W S,B				F,W S,B			
USEPA CLP QB Semiannual	CERCLA & INEL ASPEP		W,S	W,S	W,S (CN)		W,S	W,S					
EMSL-CI WP Semiannual	CWA & INEL ASPEP		W,S	W,S	W,S		W,S	W,S	W,S		W,S	W,S	W,S
EMSL-CI WS Semiannual	SDWA & INEL ASPEP		W	W	W						W	W	W
WIPP PDP Semiannual	WIPP & INEL ASPEP		G (HCV)				G (NVG)		G				
Corp. of Eng. PE Program for High Explosive Residues As Needed	INEL ASPEP				S,W (HER)				S,W (HER)				
RESL MAPEP Under Development Semiannual	DOE	W,S		W,S		W,S		W,S		W,S		W,S	
Commercial PE Program As Needed	INEL ASPEP	W,S		W,S		W,S		W,S		W,S		W,S	

Sample Matrix Key: F = Air Filter, W = Water, S = Soil, B = Biota, G = Gas

Special Analyses Key: HER = High Explosive Residue; HCV = High Concentration Volatiles; NVG = Non-VOC Gases; CN = Cyanide

Table 2. General laboratory operations performance indicators and acceptable performance criteria.

Area of Assessment	Performance Indicator	Performance Criteria	Tracked by:
Holding Time & Turnaround Time	• Total number of sample delivery groups (SDGs) having holding time violations per analysis type	• Zero (0) SDGs with holding time violations	• Analysis type
	• Total number of SDGs with turnaround time violations	• Zero (0) SDGs with turnaround time violations	• Analysis type
Completeness & Accuracy of Deliverable	• Number of SDGs for which resubmissions are requested due to missing, incomplete, or inconsistent forms and COCs, during Level B or Level C validation per analysis type	• ≤ 1 SDG for which resubmissions are requested	•Analysis type
	• Number of SDGs for which resubmissions are requested by the data validator due to missing, incomplete, or inconsistent forms, COCs, or raw data) during Level A validation per analysis type	• ≤ 1 SDG for which resubmissions are requested	• Analysis type
	• Number of SDGs requiring full resubmission per analysis type	• Zero (0) SDGs requiring full resubmission	• Analysis type
	• Number of SDGs in which specified methods were not used (i.e., method change not approved by SMO) per analytical discipline	• Zero (0) SDGs in which incorrect methods were used	• Analytical discipline
Audits	• Number of findings per audit or desk evaluation repeated from a previous audit or desk evaluation	• Zero (0) repeated findings	• Organization
Responsiveness	• Number of corrective action responses not received within required response time frame	• Zero (0) corrective action responses not received within required response time frame	• Organization
	• Number of corrective actions not closed within the required closure time frame	• ≤ 3 corrective actions not closed within the required closure time frame	• Organization

Table 3. Analysis-specific laboratory performance indicators and acceptable performance criteria.

Analytical Discipline	Applicable Matrices	PE Program and INEL-Sponsored Blind PE Sample Results				Routine Laboratory QC (Analyte- and Method-Specific)	
		Overall Performance (Analytical Discipline or Analysis Type)		Analyte- and Method-Specific Performance			
		Performance Indicators	Performance Criteria	Performance Indicators	Performance Criteria	Performance Indicators	Performance Criteria
Radiochemistry	W, S, F, B	• Number of analytes misqualified (i.e., not correctly identified) per PE sample • Number of analytes misquantified per PE sample	• ≤ 1 per PE sample • ≤ 10% of total number of requested analytes per PE sample	• % Recovery of Analyte	• Within defined acceptance limits for PE sample	• % Recovery of laboratory LCS • % Recovery of LCS PESM (soil) • Mean difference of laboratory duplicates • Number of reported blanks > MRDL or CRDL • Number of SDGs having analytical yields outside of required limits	• Within method/SOW requirements • Within established control limits • Within method/SOW requirements • ≤ 1 • ≤ 1 SDG affected by any out-of-control analytical yield
Metals	W, S, F	• CLP QB score, when applicable • Number of analytes misqualified per PE sample • Number of analytes misquantified per PE sample	• CLP QB Score ≥ 75 • ≤ 1 per PE sample • ≤ 10% of total number of requested analytes per PE sample	• % Recovery of Analyte	• Within defined acceptance limits for PE sample	• % Recovery of laboratory LCS • % Recovery of LCS PESM (soil) • % Recovery of detection-level QC standard (e.g., CRI,CRA) • Number of reported blanks > MRDL or CRDL • % Recovery of surrogate spikes (filters) • Number of SDGs having ICV, CCV, or ICSAB QC results outside required limits	• Within method/SOW requirements • Within established control limits • ± 50% of true value • ≤ 1 • Within method/SOW requirements • ≤ 1 SDG affected by any out-of-control ICV, CCV, or ICSAB
Organics	W, S, G	• CLP QB score, when applicable • Number of analytes misqualified per PE sample • Number of analytes misquantified per PE sample	• CLP QB Score ≥ 75 • ≤ 1 per PE sample • ≤ 10% of total number of requested analytes per PE sample	• % Recovery of Analyte • RPD between field sample splits (gas matrix samples only)	• Within defined acceptance limits for PE sample • RPD ≤ (Method lab duplicate RPD control limit + 50%)	• % Recovery of laboratory LCS (gas) • Number of reported blanks > CRQL or PRQL • % Recovery of surrogate standards (water and soil) • RPD for MS/MSD (water and soil) • Number of SDGs w/ICAL, CCAL or internal standard areas outside of required limits	• Within method/SOW requirements • ≤ 1 • Within method/SOW requirements • Within method/SOW requirement • ≤ 1 SDG affected by any out-of-control ICAL, CCAL, or internal standard areas

Matrices: W = Water; S = Soil; G = Gas; F = Air Filters; B = Biota

Table 4. Data validation performance indicators and acceptable performance criteria.

AREA OF ASSESSMENT	PERFORMANCE INDICATORS	PERFORMANCE CRITERIA	TRACKED BY:
Turnaround Times	• Total number of turnaround time violations per analytical discipline	• Zero (0) L&V reports with turnaround time violations	• Analytical discipline
Deliverable Completeness & Accuracy	• Total number of L&V Reports for which resubmissions are requested by the SMO per analysis type	• ≤ 1 L&V for which resubmissions are requested	• Analysis type
Deliverable Assessment of Periodic Blinds and Real-Time Dual Validation	• Number of problems associated with the data package identified by the data validator as a percentage of the total number of problems identified by referee validation per analysis type	• 95% - 100% of problems identified by referee validation	• Analysis type
	• Number of L&V Reports affected by errors evaluating the following critical parameters: COC, rejected data points, and incorrectly assigned data qualifier flags (i.e., those assigned which should not have been assigned, and those which were not assigned when they should have been) per analysis type	• ≤ 1 L&V Report affected by critical parameter errors	• Analysis type
Audits	• Number of findings per audit or desk evaluation repeated from a previous audit or desk evaluation	• Zero (0) repeated findings	• Organization
Responsiveness	• Number of corrective action responses not received within required response time frame	• Zero (0) corrective action responses not received within required response time frame	• Organization
	• Number of corrective actions not closed within the required closure time frame	• ≤ 3 corrective actions not closed within the requried closure time frame	• Organization

Table 5. Grounds for change in laboratory performance status.

Performance Status	Scope of Impact				
	Single Analyte Method or Single Analyte from Multiple-Analyte Method	Multiple-Analyte Method	Analysis Type	Analytical Discipline	Analytical Support Supplier Organization
Satisfactory	• Failure to meet performance criteria for any specific laboratory analysis indicator tracked by analyte or method	• Failure to meet performance criteria for any specific laboratory analysis indicator tracked by method	• Failure to meet assessment criteria for any general performance indicator tracked by analysis type	• Failure to meet performance criteria for any general performance indicator tracked by discipline	• Failure to meet performance criteria for any general performance indicator tracked by organization
Probation	• SNC on 2 or more indicators • 2 SNCs on a single indicator • SNC on an indicator which was the cause of previous probation or suspension	• 2 or more probations affecting a single analyte • SNCs on multiple analytes • SNC within a method which has had a previous probation or suspension	• Probation on multiple methods within analysis type • SNCs in 2 or more single-analyte methods within analysis type • 2 SNCs on a single general indicator tracked by analysis type • SNCs on multiple general indicators tracked by analysis type • SNC on a general indicator which was cause of previous probation or suspension	• Probations in multiple analysis types in discipline • 2 SNCs on a single general indicator tracked by analytical discipline • SNCs on muliple general indicators tracked by analytical discipline • SNC on a general indicator which was cause of previous probation or suspension • SNC on CLP QB Score	• Probation in 2 or more disciplines • Multiple SNCs on a general performance indicator tracked by organization • SNC on multiple general performance indicators tracked by organization • SNC on a general indicator which was the cause of previous probation or suspension
Suspension	• Failure to close probation CA within allowed response time frame • 2 open probation corrective actions on a single indicator • Open probation corrective actions on 2 or more indicators	• Failure to close CA for mutilple-analyte method probation within allowed time frame • 2 open probations affecting the method • Suspension of 1 or more analytes	• Failure to close analysis type probation CA within allowed time frame • 2 open analysis type probation corrective actions • Multiple method suspensions within analysis type	• Failure to resolve analytical discipline probation CA within allowed time frame • 2 open analytical discipline probations • Suspension of multiple analysis types in discipline • Sequential SNCs for any WS PE sample analyte recovery indicator	• Failure to close CA for supplier organization probation within allowed time frame • 2 open supplier probation corrective actions • Suspension in 2 or more disciplines
Termination of Approval	• Failure to resolve suspension CA within negotiated time frame • 3 suspensions on a single indicator	• Failure to close method suspension CA within allowed time frame • 3 method suspensions • Termination of any analyte	• Failure to close analysis type suspension CA within allowed time frame • 3 analysis type suspensions • Termination of multiple methods within the analysis type	• Failure to close analytical discipline suspension CA within allowed time frame • 3 analytical discipline suspensions • Termination for multiple analysis types per discipline	• Falsification of records/data • Failure to close CA from supplier organization suspension within allowed time frame • Termination of 2 or more disciplines

CA = Corrective Action; SNC = Supplier Nonconformance

Table 6. Grounds for change in data validator performance status.

Performance Status	Scope of Impact		
	Analysis Type	Analytical Discipline	Analytical Support Supplier Organization
Satisfactory	• Failure to meet performance criteria for any indicator tracked by analysis type	• Failure to meet performance criteria for any indicator tracked by analytical discipline	• Failure to meet assessment criteria for any indicator tracked by organization
Probation	• 2 SNCs on a single indicator • SNCs on multiple indicators within the analysis type • SNC on an indicator which was the cause of previous probation or suspension	• 2 SNCs on a single indicator (tracked by discipline) • SNCs on mulitiple indicators tracked by discipline • 2 or analysis type probations within the discipline • SNC on an indicator (tracked by discipline) which was the cause of previous probation or suspension	• 2 SNCs on a single indicator (tracked by organization) • SNCs on mulitiple indicators tracked by organization • Probation in multiple analytical disciplines • SNC on an indicator (tracked by organization) which was the cause of previous probation or suspension
Suspension	• Failure to close probation CA within allowed time frame • 2 open probation CAs within the analysis type	• Failure to close CAs for discipline probation within the allowed time frame • 2 open probation CAs within for indicators tracked by discipline • Suspension of multiple analysis types within the discipline	• Failure to close CA for supplier organization probation within the allowe time frame • 2 open probation CAs within for indicators tracked by organization • Suspension of multiple disciplines
Termination of Approval	• Failure to close suspension CA within allowed time frame • 3 suspensions within the analysis type	• Failure to close CA due to discipline suspension within the allowed time frame • 3 suspensions for an indicator tracked by analytical discipline • Termination of multiple analysis types within the discipline	• Falsification of L&V reports • Failure to close CA for supplier organization suspension within allowed time frame • 3 suspensions for an indicator tracked by organization • Termination multiple disciplines

Table 7. Supplier performance status resolution.

Condition	Impact on Data Quality	SMO Approval Status	Actions		
			PE Program Office	EG&G Procurement	Supplier
Trend Condition	None	Satisfactory (Not Affected)	• Document • Counsel supplier	None	Discretionary
Supplier Nonconformance	Minor	Satisfactory (Not Affected)	• Document • Counsel supplier • Review disposition • Review CA (if needed)	None	• Respond by dispositioning SCN • Submit & implement CA (discretionary)
Probation	Major	Conditional (Qualified)	• Document • Obtain procurement concurrence • Notify supplier • Evaluate appeal • Approve CA • Resolve probation	• Sign probation notice	• Respond by: Appeal or Submit & implement CA (mandatory)
Suspension	Critical	Suspended (On Hold)	• Document • Notify Procurement • Evaluate appeal • Approve CA • Resolve suspension	• Notify Supplier • Issue Stop Work Order • Forward CA to PE Office • Lift Stop Work Order	• Respond by: Appeal or Submit & implement CA (mandatory)
Termination of Approval	Fatal	Terminated (Revoked)	• Document • Notify procurement • Recind supplier approval & PE program participation	• Notify Supplier • Issue Stop Work Order • Terminate contract (discretionary)	• Reapply through supplier approval process

QUALITY BY DESIGN - IT CAN BE ACHIEVED!
A Review of Two Projects with Different Levels of Project Planning

Robert J. Thielke, Technical Operations Manager, Kerri G. Luka, Quality Assurance Manager, QuantaLex Inc., 300 Union Boulevard, Suite 600, Lakewood, Colorado 80228

ABSTRACT

Because data validation services are often obtained late in the remediation process after sample analysis has occurred, these quality control activities are too frequently viewed as added costs to project budgets as well as frustrating delays to project schedules. These impressions are often valid. Data validation performed under this scenario serves as either an expensive inspection function that limits the usability of data or as an even costlier data rehabilitation activity. However, if quality control activities are designed into a project from the beginning, data validation activities are transformed from an expensive inspection process to a more efficient, less costly evaluation and assessment process. The process then becomes one in which project data quality objectives (DQO's) are utilized to determine that they were met as planned in the design process. Therefore, a most effective and efficient use of data validation experts in environmental activities is to utilize their experience and knowledge in the up-front project planning process.

The same expertise used in the design of a validation system that satisfies project-specific needs should also be used to develop the following:

- Comprehensive analytical statements of work
- Usable data management systems
- On-site laboratory evaluation plans
- Performance evaluation sample programs/test data packages for compliance to statements of work
- Laboratory surveillance programs based upon validation results
- Project planning start-up sessions to communicate project requirements in advance to all project participants (DQO development process)

The value added to the environmental project planning process by involving highly-skilled validation staff up-front in the project design process is demonstrated through two scenarios of environmental remediation projects. The first scenario is a medium-sized project in which the validation staff were introduced into the process after the procurement of analytical services. A significant amount of the data in this project proved to be unusable because of problems that could have been prevented if adequate pre-planning of the project had occurred. The unusable data resulted in the need for expensive re-sampling efforts and jeopardized important project schedules. The second scenario is a larger, more complex project in which the validation staff were involved in all of the pre-planning and surveillance activities. The data for this project satisfied all project DQOs as a result of the pre-planning activities and project schedules were not compromised due to re-work.

This paper also describes the necessary elements of each of the pre-planning activities and describes the skills that knowledgeable Project Managers should look for when selecting validation personnel to participate project planning.

INTRODUCTION

Analytical quality control activities are too frequently viewed as added costs to project budgets and the cause of frustrating delays to project schedules. These impressions occur because data validation and analytical support services are frequently obtained late in the environmental project process, often after laboratory analyses have been completed. Unfortunately, these impressions are usually valid because data validation and other quality control actions performed under this scenario serve as either expensive inspection functions that limit the usability of data or as even costlier data rehabilitation activities. However, when quality planning activities are designed into a project from the beginning of the project, data validation and other quality control activities are transformed into cost effective verification activities. Using qualified analytical support services to implement project quality planning activities can reduce project cost overruns and scheduling delays.

The cost effectiveness of analytical quality planning can be demonstrated by performing cost-benefit analyses of two environmental project scenarios. The first scenario is on an environmental project that did not have sufficient up-front quality planning of environmental chemical analyses and the second scenario is on a project that had sufficient analytical quality planning built into the project from the beginning of the project. The scenarios presented are derived from actual environmental projects and demonstrate the financial risks, scheduling risks, and other risks that can occur when planning is not designed into projects. However, the costs of project activities are estimated based upon similar available project information.

Determining the optimal cost of analytical quality planning can be accomplished by performing a cost-benefit analysis on the cost of analytical quality planning. The analysis will consist of identifying the costs of analytical quality planning, determining the cost-benefits of analytical quality planning, and specifying the desired probability of success. The probability of success can be factored into the quality planning evaluations by performing a sensitivity study of the costs and benefits at a low, medium, and high probability of success.

Performing quality planning on a project does not guarantee success on a project. Conversely, a project is not doomed to fail if planning does not occur. However, quality planning activities generally increase the probability of project success. This probability can be increased if the activities are designed and performed with the help of knowledgeable analytical services personnel. Identifying the most effective analytical quality planning tools and understanding their intended purposes are crucial to maximizing the cost effectiveness of analytical quality planning.

PROJECT SCENARIO NUMBER 1

The analytical requirements for this environmental project consisted of 50 groundwater samples and 200 surface soil samples. The site consisted of a singular operable unit and was not associated with any other ongoing environmental project. The samples were taken to determine the level of metals contamination in an effort to determine whether further cleanup was required. The samples were collected over a ten week period and sent to the laboratory for analysis. The metals analyses were diluted to the point that the detection limits were above the levels required to determine whether further action was necessary. In addition, the appropriate frequency of duplicate precision and other quality control analyses specified in the quality assurance plan were not met.

As a result, all the metals data points were rendered useless and new samples and analyses were required. Re-analysis of the previous samples was not possible because the laboratory disposed of the samples shortly after analysis. The quality criteria identified in the project Quality Assurance Plan were not addressed in the laboratory statement of work (SOW) and these requirements were not conveyed to the laboratory. In addition, neither the laboratory operations or analytical techniques were evaluated prior to the project. The only analytical quality planning that was performed was to give laboratory personnel the opportunity to review and comment on the Quality Assurance Plan.

The costs of quality planning for this project scenario were as follows:

Activity	Hours	Labor Rate	Extended Cost (Labor X Hours)
QA Plan Review	8	$50/hour	$400
		Labor Cost Total	**$400**

There were no travel or non-labor costs associated with quality planning for this project.

The costs associated with analytical failure on this project are the actual costs of repeating the sampling and analysis of these samples and other external costs are not easily quantifiable. The Project Manager decided to re-sample 190 of the soil samples and 45 of the groundwater samples because the Quality Assurance Plan specified that 90 percent of the data must be usable. Repeating 95 percent of the samples allowed for a small amount of unusable data in the second sampling episode. The costs of re-taking all of the samples that were rendered useless for this scenario were as follows:

Labor Costs

Activity	Hours	Labor Rate	Extended Cost (Labor X Hours)
Water sampling[1]	275	$120/hour	$33,000
Soil sampling[2]	380	$120/hour	$45,600
		Labor Cost Total	**$78,600**

Additional costs associated with re-sampling for this scenario were:

Laboratory analysis[3]	$110,500
Travel[4]	$7,600
Re-validation[5]	$8,225
Total Additional Costs	**$126,325**
Total Costs of Re-sampling	**$204,925**

The cost of re-sampling must also be adjusted for the time value of money because the costs of planning occur in the present while the costs of re-sampling occur in the future. The adjusted cost of re-sampling becomes **$198,961** if the current annual interest rate is 3 percent and the re-sampling will take place approximately one year after quality planning activities. However, the cost of failing to obtain acceptable data on this project due to insufficient quality planning was manifested in more than just financial terms.

The time needed to take, analyze, and evaluate the additional samples caused project deadlines to be missed. Determining the impact of a missed deadline will vary between projects. However, it is safe to assume that impacts of missed deadlines are all negative and could include additional indirect project costs, a loss of future work, and reduced public confidence in the cleanup effort. Although these costs are not easily quantifiable they must be considered when determining the level of quality planning to perform on a project.

This scenario is an extreme example of what can go wrong on an environmental project. However, it is an indicator of why quality planning is necessary.

PROJECT SCENARIO NUMBER 2

This environmental project consisted of an operable unit that was part of a larger site with other operable units. The analytical requirements for this environmental project for purposes of comparison also consisted of 50 groundwater samples and 200 surface soil samples taken over a ten week period. The samples were taken to determine the level of metals contamination in an effort to determine whether further cleanup was required. The analytical quality planning that was performed for this site included the following activities:

> Development of a laboratory SOW that specified detection limits, quality control requirements, reporting requirements, and sample handling requirements.
>
> Pre-award laboratory evaluation to determine if laboratory procedures, personnel, and equipment were adequate to perform the work.
>
> Project set-up meeting with all project participants to discuss the requirements of the statement of work and clarify any ambiguous issues.
>
> Analysis of test samples by the laboratory. The analytical results were then sent to qualified data validation staff to determine if the data satisfied all project requirements. The findings of this evaluation were discussed with the project participants prior to beginning work on samples collected from the site.

Less than 2 percent of the 6800 metals data points were rejected and only 3 of the groundwater samples required re-analysis.

The costs of pre-planning for this project were as follows:

Labor Costs

Activity	Hours	Labor Rate	Extended Cost (Labor X Hours)
Prepare SOW	60	$60/hour	$3,600
Project Set-up	16	$50/hour	$800
	24	$60/hour	$1,440
	8	$100/hour	$800
Perform Audit	80	$60/hour	$4,800
Evaluate Test Data	10	$60/hour	$600
		Labor Cost Total	**$12,040**

Additional costs associated with planning were:

Laboratory analysis[6]	$1,000
Two Test Samples[7]	$500
Total Additional Costs	**$1,500**
Total Costs of Analytical Quality Planning	**$13,540**

Costs of Re-sampling

The costs associated with analytical failure on project scenario 2 were as follows:

Labor Costs

Activity	Hours	Labor Rate	Extended Cost (Labor X Hours)
Water sampling[8]	20	$120/hour	$2,400
		Labor Cost Total	**$2,400**

Additional costs associated with re-sampling were:

Laboratory analysis[9]	$1,350
Travel[10]	Not Applicable
Re-validation[11]	$105
Total Additional Costs	**$1,455**
Total Costs of Re-sampling	**$3,855**

The cost of re-sampling adjusted for the time value of money **$3,743** if the current annual interest rate is 3 percent and the re-sampling will take place approximately one year after quality planning activities.

This scenario demonstrates the additional sampling costs that can be avoided if effective quality planning is performed on a project.

Both of these project scenarios illustrate the ultimate cost of failing to build in quality planning into the project design and the possible cost savings if adequate analytical quality planning is performed. The level of analytical failure for an environmental project will fall somewhere in between these two scenarios. Judicious project management would dictate that some level of analytical quality planning should occur on a project.

DETERMINING THE OPTIMAL LEVEL OF QUALITY PLANNING

Although a certain level of quality planning does not guarantee project success, the probability of success will increase as the level of quality planning increases. The optimal amount of quality planning for a project is determined when the marginal cost of quality planning equals the marginal benefits of the quality planning at a desired probability of success. Each Project Manager should evaluate the need for quality planning and the costs of project failures. The amount of resources committed to quality planning should vary from project to project. The benefits of analytical quality planning

are the cost savings of not having to re-sample and the avoidance of other social costs. Some relatively small quality planning expenditures will have a large benefit by improving data quality. However, additional expenditures on quality planning will eventually exceed the benefit obtained after a certain level of quality is reached. An example curve of quality costs versus quality benefits was developed by Harris and Chaney[12] and has been adapted for this paper and included as Figure 1. The optimal level of quality planning is determined by performing a cost-benefit analysis of the costs of quality planning, the costs of analytical failure, and the required probability of success. High costs of quality planning in relation to the costs associated with re-sampling would encourage a lower level of quality planning. Conversely, high costs associated with re-sampling in relation to the costs of quality planning would encourage a higher level of quality planning.

The costs of quality planning are usually easily determined since the same basic quality planning activities are generally performed for each project. The various types of analytical quality planning activities that can be performed are discussed later in this paper.

The costs of analytical project failure are more difficult to evaluate because of the variability of projects, the uses of the data, and the impact of external costs. An evaluation of the costs of re-sampling should incorporate a number of project variables. These variables include, but are not limited to, the following:

> The number of samples taken and the requested analyses for each sample. Some analyses can be very expensive or have very short holding times that would prevent the original sample from being re-analyzed if the first analysis failed.
>
> The cost of re-sampling different types of samples. For instance, the cost of drilling additional boreholes are much greater than obtaining additional surface water samples.
>
> The location of the site can have a significant impact on the costs of re-sampling. Remote or inaccessible locations would be more expensive to re-sample than nearby or accessible locations.
>
> The geological and hydrological conditions of the sampling location can increase the costs of re-sampling. Deep bedrock wells would be more difficult and more expensive to re-sample than shallow alluvial wells.
>
> Some types of samples can realistically only be taken one time because of the nature of the sample or the sampling process. These types of samples would include samples taken to test singular events, or samples taken from studies or situations that could only be duplicated at extreme costs.
>
> External costs of failure would include the public sensitivity towards the project, fines, and the impact of schedule delays on future project activities.

An initial judgment of the benefit of planning activities would indicate that the investment would be extremely prudent. However, spending money on planning and quality assurance does not guarantee success on a project. In addition, the probability of predicting success on a project is difficult and will vary from project to project.

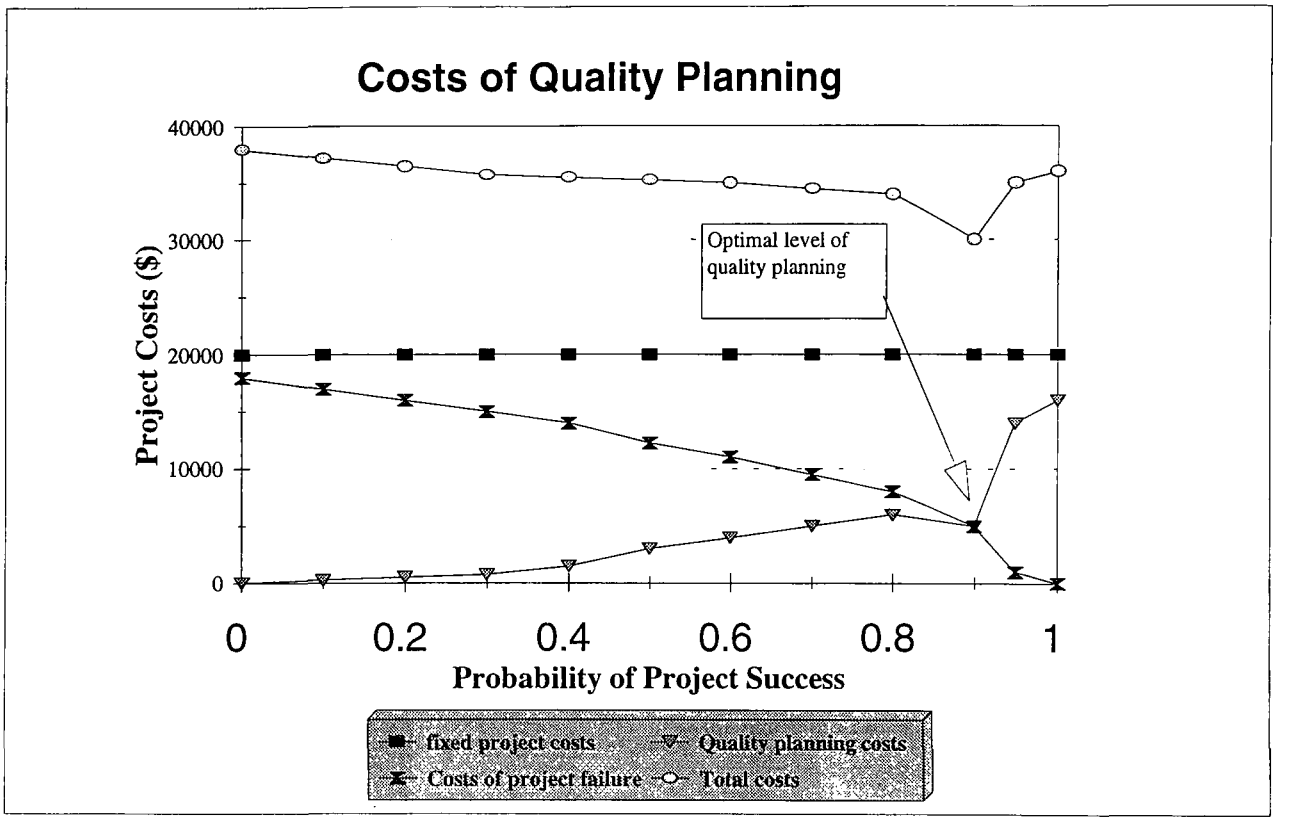
Costs of Quality Planning
40000
30000
20000
10000
0
Project Costs ($)
Optimal level of quality planning
0
0.2
0.4
0.6
0.8
1
Probability of Project Success
fixed project costs
Quality planning costs
Costs of project failure
Total costs

Figure 1

Mansfield indicated that economic decisions based upon risk are a function of the probability of success and failure and the economic return associated with each outcome. The benefits of quality planning are best determined by performing a prior risk analysis based upon the costs of re-sampling and the probability that the project will fail. The probable adjusted cost savings are estimated based upon the assumption that the Project Manager is indifferent to risk and will choose the option that maximizes monetary wealth. The calculation will change based upon the Project Manager's aversion to risk or acceptance of risk.

A sensitivity study evaluating the costs and benefits of planning at different probabilities of success would demonstrate the effectiveness thresholds of quality planning on a project. A benefit analysis of quality planning at a 90 percent (high) probability of success, a 50 percent (medium) probability of success, and a 10 percent (low) probability of success would demonstrate the probability at which analytical quality planning activities would be cost effective. The probable cost savings are determined by:

$C(a) = C(r) \times P$

Where:

C(a) = The probable adjusted cost savings of quality planning
C(r) = The adjusted cost of re-sampling
P(s) = The probability of avoiding re-sampling because of pre-planning[13]

The table below illustrates the cost savings at low, medium, and high probabilities of avoiding re-sampling costs for project scenario 1 if the analytical quality planning activities in project scenario 2 had occurred.

Quality Planning Cost	$P_{(s)}$	Probable Adjusted Cost Saving of Quality Planning
$13,540	0.9	$179,065
$13,540	0.5	$99,481
$13,540	0.1	$19,896

For this scenario the benefits of quality planning exceeds the costs at each level of sensitivity. Analytical quality planning would be beneficial if the cost of the quality planning did not exceed the benefit gained as a result of project success at a given probability of success. This decision would be influenced by the willingness of the Project Manager to accept the risk of failure. The benefits of quality planning would exceed the costs for this example if the quality planning had greater than a 6.8% probability of success. The Project Manager would have to decide if the costs of quality planning would be beneficial in comparison to the costs of project failure and the probability of success. The levels of quality planning for a project will vary based upon the scope of the project and the potential costs of failure. Small projects or projects with minimal re-sampling costs (such as a preliminary site assessment for a small site) may not require the same level of quality planning costs as a politically sensitive project or a project with extremely high costs associated with re-sampling (such as pilot studies or borehole soil sampling in remote locations.) The desired probability of project success must also be factored into the cost of project failure. Although a Project Manager would not usually be willing to pay for complete assurance of project success, tight budgets and tight schedules would require some level of quality planning with a reasonably high

probability of success. The required probability of success becomes much greater at sensitive or high profile sites.

Determining the marginal benefit associated with a marginal unit of quality planning cost is difficult to predict. This objective probability of marginal benefit is most easily determined by the conjecture of probability.[14] The example Sinn uses to explain this statement is that of oil exploration. The objective probability of finding oil in a location is determined by the relative rate of success in locations with similar geological and topographical characteristics. A conjecture is made as to the probability of success based upon the probability of success at similar locations. Obtaining more information about the location or adding more controls to variables will increase the objective probability of finding oil. Eventually the amount of information that can be obtained about a location will be limited by technology and cost. This analogy can be applied to environmental projects. Based upon the characteristics of a project, the Project Manager can conjecture about the probability of success by assessing the level of success of similar projects using a defined level of quality planning. The project will have a higher expected probability of success as more quality planning is performed. Some measures of control such as detailed SOWs with specific liquidated damages upon failure to perform have proven to be a low cost quality planning measure with a high probability of success. Other quality activities such as inter-laboratory comparison studies may be considerably more expensive and provide limited quality benefits. A Project Manager should evaluate the effectiveness of quality planning activities on similar projects to determine which activities provide the greatest benefit to cost ratios.

QUALITY PLANNING ACTIVITIES

Analytical quality planning activities can help alleviate the probability of project failure if they are implemented by experienced analytical support staff and in the proper sequence of events. Experienced analytical support staff could help effectively develop and implement the following analytical quality planning activities:

- Comprehensive analytical statements of work
- Usable data management systems
- On-site laboratory evaluation plans
- Performance evaluation sample programs/test data packages for compliance to statements of work
- Laboratory surveillance programs based upon validation results
- Project planning start-up sessions to communicate project requirements in advance to all project participants (DQO development process)

ANALYTICAL STATEMENTS OF WORK

Comprehensive laboratory analytical SOWs are the primary method of specifying:
- Project objectives
- Analytical methods
- Required detection limits
- Analytical quality control requirements
- Documentation requirements
- Data package compilation requirements

Analytical SOWs should reflect the requirements of all primary quality assurance documents such as the project Quality Assurance Project Plans. The analytical SOW and the analytical services contract are also the appropriate documents to reference contractual provisions that can either enhance the quality of the analysis or help recover costs if the analysis fails due to laboratory error. The types of provisions that should be included in these procurement documents are analytical holding times, reporting turnaround times, sample disposition and disposal requirements, and quality control limits that would prompt re-analysis or re-preparation of samples.

Qualified analytical personnel should help develop the analytical SOW because they have an understanding of the analytical methods and documentation requirements of the project. Less experienced personnel may not be aware of the relative weaknesses and strengths of various methods.

All too often less experienced personnel develop analytical SOWs using modifications of SOWs previously developed for projects. Revised SOWs are functional as long as all non-relevant information is removed from the document. Information mistakenly left in SOWs is usually confusing and costly. Independent experts can assist in developing draft SOWs that are both effective and concise.

DATA MANAGEMENT SYSTEMS

Most sampling projects should utilize data management systems to track project progress and to trend laboratory performance. All data management systems benefit from design and implementation input provided by independent analytical support experts. Analytical data management systems are often designed without the input of the laboratory or data validation experts. As a result, the systems are often inefficient or unusable for their intended purpose. Data management systems are frequently designed by computer programmers and Project Managers that may not have specific knowledge of environmental analysis and, as a result, add fields to document unnecessary analytical information or omit fields that are critical to documenting analytical results, validation results, and data usability information. Unnecessary information in a database that contains millions of data points has a multiplying cost factor because each data element must be generated and reviewed at several points by the analytical, validation, and assessment personnel to ensure the accuracy of information in the database. This data entry and review becomes very expensive as the size of the data base grows. Large data files which house unnecessary information may slow software systems thereby decreasing the efficiency of the data entry and data management activities. In addition, expert analytical personnel could work with computer programmers to develop data management systems that are both streamlined and compatible with existing software used by laboratories to manage and report analytical data to more efficiently.

LABORATORY EVALUATIONS

A critical element of laboratory procurement is the on-site laboratory evaluation. The audits should be of sufficient detail and scope to determine if the laboratory has adequate facilities and equipment to perform the analyses required for the project. The auditors should also have sufficient experience in the laboratory to assess the experience and skill of the laboratory personnel to perform the required analyses. Experienced analytical support personnel could be used to develop comprehensive evaluation checklists and perform the on-site evaluations.

Large sampling programs typically have routine performance evaluation (PE) sample programs that are used to monitor the performance capabilities at analytical laboratories. The composition and content of the PE samples should be consistent with the environmental samples that will be taken. In addition, several different PE samples should be used to provide a representative profile of the conditions at the site. The PE samples should be sent to the laboratory prior to contract award and may also be sent prior to project initiation, after significant changes in laboratory management and staffing, and as a result of laboratory performance as determined through data validation and surveillance results. PE samples may be sent more frequently to laboratories that have had previous performance problems or to laboratories that are receiving critical samples. Experienced analytical services personnel would be helpful in determining the appropriate number and composition of PE samples in conjunction with the Project Manager. PE samples are valuable for determining a laboratory's analytical capability under optimal conditions. They are also useful prior to procurement because they can help both the evaluator and the laboratory management to determine whether the laboratory personnel have a complete understanding of the necessary documentation and package compilation procedures as specified in the laboratory.

On-site laboratory surveillances are also useful in evaluating laboratory performance and capabilities. With shrinking project budgets, regularly scheduled quality assurance activities should be replaced with performance-based quality assurance activities. Data validation can be used to trend laboratory performance by which to base such surveillances. Project Managers can remain apprised on the status of the project, compliance to quality objectives, and the need for additional quality assurance activities (e.g., surveillances and PE samples) through the use of control charts and trending reports. As with audits, surveillances should be of a scope commensurate with the data validation results. Individuals conducting surveillances should have adequate experience to effectively evaluate the laboratories.

PROJECT MEETINGS

Dialogue in the form of meetings is the another effective tool to ensure that analytical and data validation services are designed and delivered in a manner that best serves the needs of the project. Informal project start-up sessions can be set-up by independent experts to ensure that:

- Project participants feel comfortable to freely discuss the requirements and status of the project
- Project participants function as a team
- Project participants have a forum in which questions can be asked and answered without delay
- Problems are discussed and resolved in a timely manner

The frequency and scope of project meetings should be based upon the project funding, project sensitivity, and project size.

INDEPENDENT ANALYTICAL SUPPORT FIRM QUALIFICATIONS

When contracting for an independent analytical support firm, organizations and agencies should consider the following qualifications:

Is the firm truly independent?

The firm should have no vested interest in the procurement of the laboratories if the contract includes the development of a draft SOW. The firm should also have no interest in the outcome of the data validation and analytical results.

Are the Data Validators qualified to perform quality planning activities?

Data Validators should be knowledgeable of the available methods so that they can provide guidance when selecting methods that best suit the needs of the project. Laboratory experience is a qualification requirement that is often solicited when evaluating data validation firms. While laboratory experience can be valuable in the conduct of on-site evaluations, it can be mutually exclusive of method knowledge and general data validation experience. Laboratory experience therefore, may not be an indicator of validator qualifications.

Does the firm have previous experience developing sample data development and tracking systems?

Firms that have previous experience developing such systems have knowledge of what works well and what does not. It is far more beneficial to select a firm that has experience and knowledge of "lessons learned" from other similar projects than to re-invent the wheel with each new project.

Does the firm have personnel with adequate verbal and written communication skills?

Developing a sampling, analysis, and validation program with the quality planning activities previously described demands that the individuals assisting in the development of the program have exemplary communication skills.

Does the firm have a computer software development department that is knowledgeable of programming methodologies that will serve the needs of the project?

Organizations and agencies should seek-out firms that have the expertise in the types of hardware and software required by the project. Software systems can be developed to be compatible with existing software systems. Describing these pre-existing conditions up-front with the firm is essential to ensure that systems will be as functional as possible. Integrating existing systems and newly developed software can be very cost effective and efficient. Software developers should write code in a generic, modular fashion. If function-oriented programming and object-oriented programming methodologies are used, libraries of code should be maintained. A complete library of functions or objects can reduce the cost of software development by reducing the time to write and test code. Object-oriented programming is more easily modified for specific projects than other methodologies because the modules can be re-used without modification. Over time a complete object-oriented library can reduce costs significantly.

SUMMARY

Performing analytical quality planning cost-benefit analysis on environmental projects indicates that quality planning is a worthwhile expenditure even at low probabilities of success. However, as evidenced by the scenario presented in this paper adequate levels of quality planning are not always performed. These failures occur because Project Managers lack the information to choose and execute adequate quality planning activities, because Project Managers fail to account for the possibility of failure when developing project schedules and budgets, and because the irreversible nature of sampling and analysis is not understood. Undertaking adequate cost-benefit analyses and allowing expert analytical support personnel to participate in analytical quality planning activities would enhance the probability of project success. The cost analysis would not be definite because of the uncertainty associated with the project and because of the difficulty in quantifying non-fiscal costs. However, based on knowledge from other projects the Project Manager could determine the objective probability of success for quality planning activities. Using qualified analytical experts will help to ensure that the quality planning activities are effective in meeting project objectives. The current climate in the environmental arena demands that projects are not over budget and that the work is done in a reasonable and timely manner. Analytical quality planning is an essential element of helping to ensure project success.

ENDNOTES

[1] 3.3 wells could be sampled by a two person sampling crew each 10 hour day and the depth of the wells averaged 50 feet. The time requirements include all set-up, decontamination, documentation, and shipping activities. These cost estimates are based on a theoretical sampling costs profile developed by CDM-FPC (Denver). CDM-FPC was not involved in any aspect of this project.

[2] The soil samples were taken within the first six inches of soil. Ten soil samples could be taken by a two person sampling crew each 10 hour day. The time requirements include all set-up, compositing, decontamination, documentation, and shipping activities. These cost estimates are based on a theoretical sampling costs profile developed by CDM-FPC (Denver). CDM-FPC was not involved in any aspect of this project.

[3] The laboratory analysis consisted of 45 groundwater samples and 190 soil samples analyzed for CLP metals with full documentation at a cost of $450/sample for aqueous samples and $475/sample for soil samples. The prices for analysis are used from an actual price guide for a laboratory. However, the identity of the laboratory will not be revealed due to business confidentiality reasons.

[4] The cost of travel was estimated at two airfares at $1,000 per roundtrip airfare and per diem for two samplers at $100/day for 45 days.

[5] The cost of data validation on the additional 360 samples for full documentation CLP metals is $35/sample.

[6] The analysis cost of two CLP metals samples with a full CLP data package for the performance evaluation samples.

[7] The cost of two standard metals performance evaluation samples.

[8] 3.3 wells could be sampled by a two person sampling crew each 10 hour day and the depth of the wells averaged 50 feet. The time requirements include all set-up, decontamination, documentation, and shipping activities. These cost estimates are based on a theoretical sampling costs profile developed by CDM-FPC (Denver). CDM-FPC was not involved in any aspect of this project.

[9] The laboratory analysis consisted of 3 groundwater samples analyzed for CLP metals with full documentation at a cost of $450/sample for aqueous samples. The prices for analysis are used from an actual price guide for a laboratory. However, the identity of the laboratory will not be revealed due to business confidentiality reasons.

[10] There were no travel costs because of the site location.

[11] The cost of data validation on the additional 3 samples for full documentation CLP metals is $35/sample.

[12] Harris, Douglas and Chaney, Fredrick. Human Factors in Quality Assurance. pg 19.

[13] Mansfield, Edwin. Statistics for Business Economics. pg. 520.

[14] Sinn, Hans Werner. 1983. Economic Decisions Under Uncertainty. pg 12.

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ENSURING COMPARABILITY OF DATA GENERATED BY MULTIPLE ANALYTICAL LABORATORIES FOR ENVIRONMENTAL DECISION MAKING AT THE FERNALD ENVIRONMENTAL MANAGEMENT PROJECT

Chris Sutton, Manager, Environmental Division, Barbara Campbell, Supervisor, Environmental Division, Raymond J. Danahy, Manager, Environmental Division, Thomas Dugan, Senior Environmental Scientist, Environmental Division, F. Keith Tomlinson, Senior Environmental Scientist, Environmental Division, Fernald Environmental Restoration Management Corporation (FERMCO), P.O. Box 298704, Cincinnati, Ohio 45239-8704

ABSTRACT

The Fernald Environmental Management Project is a U. S. Department of Energy (DOE)-owned facility located 17 miles northwest of Cincinnati, Ohio. From 1952 until 1989, the Fernald site provided high-purity uranium metal products to support United States defense programs. In 1989 the mission of Fernald changed from one of uranium production to one of environmental restoration.

At Fernald, multiple functional programs require analytical data. Inorganic and organic data for these programs are currently generated by seven laboratories, while radiochemical data are being obtained from six laboratories. Before final cleanup of the Fernald site occurs, numerous additional laboratories may well have provided analytical data for environmental programs.

Quality Assurance (QA) and Quality Control (QC) programs have been established to help ensure comparability of data generated by multiple laboratories at different times. The quality assurance program for organic and inorganic measurements specifies which analytical methodologies and sample preparation procedures are to be used based on analyte class, sample matrix, and data quality requirements. In contrast, performance specifications have been established for radiochemical analyses.

A blind performance evaluation program for all laboratories, both on-site and subcontracted commercial laboratories, provides continuous feedback on data quality. The necessity for subcontractor laboratories to participate in the performance evaluation program is a contractual requirement. Similarly, subcontract laboratories are contractually required to generate data which meet radiochemical performance specifications. The Fernald on-site laboratory must also fulfill these requirements. Laboratories with

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persistent problems or which generate data falling outside specified control limits are judged to be failing to generate comparable data.

In summary, although data used for environmental decision making purposes at Fernald are generated by multiple laboratories, comprehensive quality assurance and quality control programs have been formulated and implemented to ensure data comparability.

INTRODUCTION

Management of analytical laboratory services at a Department of Energy (DOE) site undergoing environmental restoration presents a variety of challenges. One of the major challenges is ensuring that sufficient analytical capacity is available to meet site customer schedule requirements as well as to meet performance criteria with regard to data quality objectives. Because of the complexity and lengthy duration of restoration activities at a DOE site, numerous analytical laboratories may be called upon to provide data during the entire cleanup phase. An implicit requirement for the use of multiple analytical laboratories is the criterion that data generated by those laboratories must be comparable. This paper outlines certain aspects of the program implemented at Fernald to assess data comparability.

Background

The Fernald site, formerly known as the Feed Materials Production Center, is a U.S. Department of Energy (DOE)-owned facility located about 17 miles northwest of Cincinnati, Ohio. From 1952 until 1989, the Fernald site provided high-purity uranium metal products to support United States defense programs. DOE is now conducting cleanup activities at the site under its Environmental Restoration and Waste Management Program. Environmental remedial actions at the Fernald site are being carried out in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA); and also in accordance with the Resource Conservation and Recovery Act of 1976 (RCRA), as amended by the Hazardous and Solid Waste Amendments Act of 1984 (HSWA). CERCLA response activities are being implemented at the Fernald site pursuant to the terms of an Amended Consent Agreement between DOE and the U. S. Environmental Protection Agency (USEPA), and RCRA activities are being conducted under the provisions of a Consent Decree with the State of Ohio. Thus, CERCLA and RCRA are two principal drivers associated with analytical support services. In 1992 DOE implemented an Environmental Restoration Management Contract or ERMC approach to the Fernald site, with the Fernald Environmental Restoration Management Corporation (FERMCO), a wholly owned subsidiary of Fluor Daniel, Inc., being awarded the ERMC contractor.

FEMP PROGRAMS REQUIRING ANALYTICAL DATA

Five broad functional programs require analytical data at the Fernald site: utilities operations and National Pollutant Discharge Elimination System (NPDES) operations, CERCLA characterization activities, RCRA characterization and monitoring activities, sitewide environmental monitoring, and CERCLA Treatability Studies (coordinated with DOE technology demonstration programs).

Utilities and NPDES analyses are performed on waste water and discharge water for a series of inorganic compounds. These include nitrates, nitrites, total uranium, total thorium, ammonia, fluoride, metals, and total dissolved solids.

Analyses associated with CERCLA activities often require a full suite of organic and inorganic analyses performed in accordance with EPA SW 846 or Contract Laboratory Program (CLP) protocols at high data quality levels. Radiochemical analyses associated with CERCLA activities may include strontium-90; technetium-99; americium-241; cesium-137; lead-210; polonium-210; actinium-227; neptunium-237; radium-226, 228; thorium-227, 228, 230, 232; uranium-234, 235/236, 238; and plutonium-238, 239/240, 241.

Analyses conducted for RCRA operations are performed to characterize drummed waste and construction waste and to determine if various substances and materials should be classified as RCRA hazardous. Organic and inorganic analyses are performed in accordance with SW 846 analytical protocols. Additionally, Toxic Characteristic Leaching Procedure (TCLP) analyses are routinely performed for specific organic compounds and metals.

Environmental monitoring programs at the Fernald site consist of periodic sampling and analysis of surface waters, ground waters, air, home owner wells, sediments, and selected biota to determine the impact of the site on the surrounding environment and to establish a baseline against which the progress of remediation efforts can be measured. The same types of organic, inorganic, and radiochemical analyses required for the CERCLA programs are required for these programs as well, although detection limits and data quality levels may be different between the CERCLA and environmental monitoring programs.

Bench-scale treatability studies are initiated to determine the optimum chemical, physical, and engineering parameters for conducting a specific type of remediation; the chemical and physical characteristics of products resulting from remediation; and the handling characteristics of remediation products. Pilot-scale technology demonstration programs delineate the feasibility of processes prior to field implementation.

Inorganic and organic data are currently being generated by seven laboratories---six commercial laboratories and the Fernald on-site laboratory. Radiochemical data are provided by six laboratories---five commercial laboratories and the Fernald on-site laboratory. Before final clean-up of the Fernald site occurs, numerous additional laboratories may well have provided analytical data for environmental programs.

COMPARABILITY

Comparability is one of the five PARCC (precision, accuracy, representativeness, completeness, and comparability) parameters used as indicators of data quality.(1) A typical definition of comparability is given below:

> "Comparability is a qualitative parameter expressing the confidence with which sample measurement data can be compared with measurement data for similar samples and sample conditions." (2)

However, such a definition is too generic to implement a practical program to assess data comparability for multiple laboratories. Accordingly, FERMCO has defined comparability (in the Fernald sitewide sampling and analysis QA plan discussed later in this paper) in terms which provide a quantitative statistical basis for assessing data comparability.

> "Comparability refers to one of five elements identified by the USEPA to describe data quality. It is an expression of the confidence with which one data set can be compared to another. Analytical data for the same analyte generated by the same analytical procedure (whether by the same laboratory at different times or by different laboratories) are comparable provided that specified acceptance criteria for quality control parameters such as detection limits, accuracy, precision, matrix spikes, etc. are met or exceeded. Data for the same analytes generated by different analytical procedures are also comparable provided that specified acceptance criteria for quality control elements such as those listed above are met or exceeded."

This definition of comparability has three advantages. First, it relates comparability to common analytical quality control parameters. This in turn has the benefit that common tools to assess data quality can be used to assess data comparability. Second, the definition implies that accurate and precise data are comparable; inaccurate and imprecise data are not. Thus, to the extent that data can be judged to be accurate and precise, data can also be judged to be comparable or incomparable. Each of the two advantages listed above provides a means of evaluating comparability for organic and inorganic data. Third, the definition opens the door for use of performance based methods by emphasizing the meeting of acceptance criteria for quality control parameters. The use of performance based methods for radiochemistry is an integral part of the analytical services program at Fernald as discussed below.

DATA COMPARABILITY ASSESSMENT PROGRAM

The program which FERMCO has implemented to address data comparability contains six essential elements: a quality assurance plan for environmental sampling and analysis, performance based methods for radiochemical analyses, contractual requirements for analytical subcontractor laboratories, performance evaluation, laboratory QA and QC audits, and data verification and validation. The first four of these elements are discussed in detail below.

Quality Assurance Plan

A quality assurance plan governing all environmental sampling and analysis activities was implemented at Fernald. The plan consolidates QA and QC requirements for a variety of environmental programs.

The functions of this QA plan are primarily three-fold: 1) to set minimum performance standards for sampling and analysis activities, 2) to direct that all Fernald environmental programs and activities follow these standards to ensure programmatic and temporal consistency, and 3) to allow data gathered under one cleanup program to be used by other cleanup programs.

One of the key elements in the Fernald QA (referred to as the Sitewide CERCLA Quality Assurance Project Plan [SCQ]) plan that significantly promotes comparability of current and future data are method selection tables for organic, inorganic, wet chemical, and historic Fernald site methods. The organic, inorganic, and wet chemical methods listed in the method selection tables are EPA or other standard methods commonly used for CERCLA and RCRA activities and commonly performed by the commercial analytical community. EPA methods may include 200-500 series methods (40CFR141), 600 series methods (40CFR136), SW 846 methods (40CFR261) and CLP-SOW methods. Other standard methods include those listed in "Standard Methods for the Analysis of Wastewater" (3), and those listed in American Society for Testing and Materials (ASTM) publications.

Because of the presence of radionuclides at the Fernald site, specific methods have been developed for radiochemical and chemical analysis of certain elements (e.g. uranium and thorium). Although these methods have a long history of use, they have not been promulgated nor have they been compiled as "standard methods" due to potential limited applicability. These methods are called historic Fernald site methods.

TABLE 1 gives an example of the Fernald site QA plan method selection tables. These tables specify which analytical methodologies and sample preparation procedures may be used at the Fernald site based upon analyte class, sample matrix, and data quality level. (Data quality levels at the Fernald site are called Analytical Support Levels, or ASL Levels. ASL Levels A, B, C, D are generally equivalent to EPA data quality levels I, II, III, and IV.) The primary intent of the method selection tables are to ensure uniformity and consistency of method selection and application. Such uniformity and consistency is an essential element toward the promotion of comparability.

Performance Based Radiochemistry Methods

Unlike inorganic and organic analyses, no single compilation of promulgated standard methods exists for radiochemistry determinations. Multiple sample preparation methods and multiple instrumental detection techniques are available commercially for many of the radionuclide analytes. Additionally, standard established quality assurance/quality control requirements and acceptance criteria have not been established for environmental radiochemistry analyses. Nonetheless, inter-laboratory

comparison studies in performance evaluation programs have demonstrated that accurate and comparable radiochemical data are attainable even though different analytical procedures are used.

To alleviate concerns over a potential lack of data comparability from multiple laboratories performing radiochemical analyses, FERMCO has adopted the approach of utilizing performance based methods for radiochemical analyses. FERMCO radiochemists (in conjunction with USEPA and commercial laboratory radiochemists) developed a set of performance-based criteria which cover a range of radiochemical analytes, matrices, and data quality levels (ASLs).

To establish such criteria, FERMCO formulated performance requirements for minimum detectable concentrations, tracer/chemical recovery, matrix spike recovery, method blank concentration, precision of duplicates, and accuracy of laboratory control samples. An example of such performance criteria is shown in Table 2. USEPA Region V has approved the use of these performance criteria, and they are routinely used in statements of work for subcontracted radiochemistry analyses. Contractual requirements for analytical services are discussed in more detail in the ensuing sections.

Contractual Requirements

As mentioned earlier, currently seven laboratories provide organic, inorganic, and wet chemical analytical data to the Fernald site; while six laboratories provide radiochemical data. Because the primary contaminants of concern at the Fernald site are radionuclides, this section will discuss radiochemical contractual requirements that directly affect data comparability.

Radiochemical analyses are performed by commercial laboratories through the use of Task Order Subcontracts. Qualified laboratories (the qualification process falls outside the scope of this discussion) bid to supply specific radioanalytical services which are defined in Task Orders. General-type requirements in the original statement of work as well as detailed specifications in each task order bearing upon data comparability must be met. The general requirements are delineated below:

1. **Subcontractor Quality Assurance Plan**

   The vendor shall have a Quality Assurance (QA) program which addresses the applicable requirements of the most recent version of the Fernald Sitewide CERCLA Quality Assurance Project Plan (SCQ) and ANSI/NQA-1. The SCQ must be a contract-specified attachment to the laboratory-specific QA plan and is the governing document in all matters relating to subcontractor QA programs. If there is any disagreement between a subcontractor QA program and the SCQ, the latter document shall govern.

2. **Preaward Verification of Analytical Capabilities**

In evaluating each subcontractor laboratory to be included on an approved list under the Radioanalytical Laboratory Services Task Order Subcontract (RLS-TOS), each one must submit a series of tables summarizing recent data from their laboratory for two matrices and each analyte of interest that demonstrates they can meet the FERMCO radiochemical analysis performance specifications. An example of the required summary tables (16 required) is shown in Tables 3A and 3B.

3. **Postaward Confirmation of Analytical Performance**

After all analyses have been completed for a specific task order, summary tables similar to those described above in Item #2 must be provided which demonstrates the extent to which the laboratory complied with the radiochemical analysis performance specifications designated in the SCQ. These data must be provided for all six Performance Parameters (ASL C or D) for each analyte/sample matrix combination included in the task order. The data must be provided in summary form. The Performance Parameters (if applicable) which must be addressed for each analyte/sample matrix combination are:

- Highest Allowable Minimum Detectable Concentration (HAMDC);
- Percent Overall Tracer/Chemical Recovery;
- Percent Matrix Spike Recovery;
- Method Blank Concentration;
- Laboratory Control Sample: Percent of Known Value; and
- Precision Requirements for Duplicate Samples (RER).

This information must be provided before work under each task order is considered complete.

4. **Participation in External QA Programs**

Subcontractor laboratories must participate in QA programs conducted by the DOE and the USEPA. The DOE's Environmental Measurements Laboratory (EML) conducts a Quality Assessment Program (DOE/EML-QAP) designed to evaluate the capabilities of laboratories to perform accurate environmental radiochemical analyses. FERMCO has established a quantitative scoring system, which includes specific pass/fail criteria, for evaluating each laboratory's performance in the DOE/EML-QAP. This system was used to initially qualify laboratories for providing radioanalytical services. In addition, this evaluation system also sets minimum performance criteria for

subsequent rounds of the DOE/EML-QAP which a laboratory must meet in order to remain qualified for bidding on task orders.

Laboratories must also participate in the USEPA's Environmental Measurements and Support Las Vegas Laboratory (EMSL-LV) Intercomparison Study evaluation program. A laboratory's performance in the EMSL-LV program is evaluated to determine if significant analytical problems exist. However, no pass/fail criteria have been established for this QA program.

5. **FERMCO Administered Performance Evaluations**

FERMCO conducts continuing performance evaluations by submitting quality control samples. Samples for ongoing performance evaluation are provided by FERMCO or a third party as part of a performance evaluation program.

Item 1 above ensures that all commercial laboratories utilize the same radiochemical QC elements, radiochemical performance specifications, and acceptance criteria for those specifications. Item 2 ensures that contractors can actually meet the performance specifications prior to performing any analyses for the Fernald site. Tables 3A and 3B are examples of proof of capability to meet radiochemical performance specifications (FERMCO audits verify data authenticity). Item 3 ensures that radiochemical data generated for the Fernald site in each task order meet the QC performance acceptance criteria. This item in particular contributes significantly toward ensuring data comparability. Item 4 helps ensure that well qualified contractor laboratories are selected initially and that these laboratories subsequently maintain an acceptable level of performance. Finally, Item 5 specifies that contractor laboratories (and the Fernald on-site laboratory) must participate in a FERMCO administered analytical performance evaluation program. As discussed in the following section, this program is another key element in assessing data comparability.

Performance Evaluation Program

The purpose of the FERMCO performance evaluation program is to assess comparability of data as well as the performance of multiple laboratories over a long period of time. As stated above, all commercial laboratories performing analyses for the Fernald site must participate in this program. The Fernald on-site laboratory is also included in this program.

Spiked samples (typically soils and water) are sent on a monthly basis to each contracted laboratory as well as to the Fernald on-site laboratory. The quantity of performance evaluation samples sent to individual laboratories is based upon the number of field samples sent to each laboratory for analysis. Identical sets of PE samples are sent to each participant in the program.

Basically, two sets of statistical parameters are calculated. The first is percent recovery defined as:

$$\text{Percent Recovery} = \frac{\text{Measured Concentration of Added Analyte Found}}{\text{Known Concentration of Analyte Added}} \times 100$$

The second is the deviation from the group mean which is defined as:

$$\text{Deviation from Mean} = \frac{|Xi - \bar{X}|}{S}$$

$|\ \ |$ = absolute value

Xi = value of individual result

$\bar{X}$ = group mean

S = standard deviation of the mean

Control charts are maintained for percent recovery where warning limits are set at the 95% confidence limit and control limits are set at the 99% confidence limit. Figure 1 shows a typical control chart for multiple laboratories based upon available data.

Finally, laboratories are ranked each month according to their performance. Rankings are based both upon percent recovery and average deviation from the mean. The closer a laboratory is to 100 percent recovery, the higher it is ranked. Thus, for a given analyte the laboratory with the absolute value of recovery closest to 100 is ranked number one, while the laboratory with the absolute value of recovery furthest from 100 is ranked lowest. Similar rankings are established for each analyte using the deviation from the mean. Table 4 shows an example of rankings of laboratories for the month of March, 1994. The overall rankings in Table 4 are based upon the combined % recovery and deviation from the mean rankings.

Through the use of statistical processes, control charts, and rankings, the performance evaluation data are used to identify trends, outliers, and problem areas. Laboratories with persistent problems or which consistently generate data falling outside control limits are judged to be failing to generate comparable data. Until corrective actions are taken to remedy problems to the satisfaction of FERMCO, no further samples will be sent to these laboratories.

CONCLUSIONS

Comparability of data is essential for environmental decision making at Fernald because multiple laboratories currently supply analytical data, and use of multiple laboratories will continue throughout the lengthy duration of the environmental restoration process. A definition of comparability that involves commonly used quality control parameters provides a basis for implementing a data comparability assessment program. The key elements of the program discussed above include a comprehensive QA plan for sampling and analysis activities, performance based methods for

radiochemistry analyses, contractual requirements for analytical subcontractor laboratories, and performance evaluation programs. Although the data comparability program is a relatively recent development at Fernald, all indications are that it is working well. Consequently, data being generated now and in the future will facilitate environmental decision making.

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TABLE 1
EXAMPLE OF FEMP SCQ METHOD SELECTION TABLES

		MATRICES AND METHODS			
		WATER & WASTEWATER		SOIL & SOLIDS	
ANALYTE OR CLASS OF ANALYTE	ASL	PREP METHOD(S)[1,2]	ANALYTICAL METHOD(S)	PREP METHOD(S)[1,2]	ANALYTICAL METHOD(S)
1a. VOCs	B	W	SW 846-8260	W	SW 846-8260
	C,D	W	CLP[8]	W	CLP[8]
1b. VOCs (Drinking Water)	B	W	EPA 524.2	N/A	N/A
2. Metals by GFAA	B	SW 846-3020 or 7060[6], 7740[6] or 7761[6]	SW 846-7000 series or 3500[4] series	SW 846-3050 or 7761[6]	SW 846-7000 series or 3500[4] series
	C,D	W	CLP[8]	W	CLP[8]
3. Metals by ICP	B	SW 846-3010 or 7760[7]	SW 846-6010 or 3500[4] series	SW 846-3050 or 7760[7]	SW 846-6010 or 3500[4] series
	C,D	W	CLP[8]	W	CLP[8]
4. Cyanide (Tot)	B	W	335.2[3]	W	335.2[3]
5. Cyanide (Low)	B	W	335.3[3]	W	335.3[3]
6. Alkalinity	B	W	310.1[3] or 2320B[4]	N/A	N/A
7. Oil & Grease	B	W	SW 846-9070	W	SW 846-9070 or 9071
8. Thorium, Low Level	B	W	EPM 1080[5], 3059[5], 3063[5]	W	EPM 1080[5], 3059[5], 3063[5]
9. Uranium, Low (ppm) Level	B	W	EPM 3002[5]	W	EPM 3002[5]
10. Uranium, High Level	B	W	EPM 1039[5]	W	EPM 1039[5]

(1) SW 846-1311 (TCLP) could be a prep; however, it is not necessary in all cases.
(2) "W" signifies that preparation is contained in the analytical method.
(3) Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020.
(4) Standard Methods for the Analysis of Water and Wastewater, 17th ed.
(5) Historic Fernald site method.
(6) 7060 contains the preparation for As, 7740 for Se, and 7761 for Ag.
(7) 7760 contains the preparation for Ag.
(8) USEPA Contract Laboratory Program Statement of Work, most recent.

TABLE 2

EXAMPLE OF RADIOCHEMICAL ANALYSIS PERFORMANCE SPECIFICATIONS FOR ANALYTICAL SUPPORT LEVELS C AND D

ANALYTE: U-234, U-235/236, U-238	SAMPLE MATRIX				
PERFORMANCE PARAMETERS	WATER	SOIL/SEDIMENT	AIR FILTERS(2)	FLY ASH	CONTAMINATED LIQUID(3)
Highest Allowable Minimum Detectable Concentration (HAMDC)(1)	0.2 pCi/L	0.1 pCi/g	4.0 pCi/Filter	0.2 pCi/g	0.5 pCi/L
Percent Overall Tracer/Chemical Recovery(6)	50-100%	45-100%	45-100%	45-100%	45-100%
Percent Matrix Spike Recovery(6)	50-100%	45-100%	45-100%	45-100%	45-100%
Method Blank Concentration	<HAMDC(4)	<HAMDC(4)	<HAMDC(4)	<HAMDC(4)	<HAMDC(4)
Laboratory Control Samples: Percent of Known Value(6)	85-115%	85-115%	85-115%	85-115%	85-115%
Precision Requirements for Duplicate Samples	RER≤2(5)	RER≤2(5)	RER≤2(5)	RER≤2(5)	RER≤2(5)

(1) $MDC = \frac{4.65\ SBLK}{K} + \frac{2.71}{TxK}$

Where SBLK is the standard deviation of the count rate of an appropriate method blank and, K is the correction factor that includes units conversion and typical values for the volume of weight of sample, decay correction factor, detector efficiency and the chemical recovers. T is the counting time of the sample.

(2) Glass Fiber 8" X 10".

(3) Two phase system containing 90% Water + 10% Organic liquid.

(4) Less than HAMDC or 5% of sample concentration whichever is greater.

(5) Relative Error Ratio, $RER = |C_1-C_2|/[(TPU_1)^2+TPU_2)^2]^{1/2}$ where C, and C_2 are measured concentrations for the sample and duplicate and TPU_1, and TPU_2 are the respective total propagated uncertainties. Measurements are acceptable if RER≤2. If RER is greater than 2 but less than or equal to 3, investigate the cause and take corrective actions if RER is consistently greater than 2. If RER >3, take corrective actions and reanalyze the batch of samples.

(6) Recoveries or percentages of known values which are 15% above or below the ranges listed are acceptable on an infrequent basis, i.e., less than 15% of the time. These occurrences must be investigated and explained. If more than 15% of the recoveries are outside the ranges listed, take corrective actions and reanalyze samples.

TABLE 3A

LABORATORY "A" DATA DEMONSTRATING CAPABILITY TO MEET FERMCO SCQ RADIOCHEMICAL ANALYSIS PERFORMANCE SPECIFICATIONS AT ASLs C/D

NEPTUNIUM - 237						
MATRIX	NUMBER OF SAMPLES	PERFORMANCE PARAMETER	SCQ REQUIREMENT	AVG. LAB RESULT	RANGE OF LAB RESULT	NUMBER OF OUTLIERS
WATER	12	HAMDC	0.5 pCi/L	0.2	0.11/0.40	0
	27	Tracer Recovery	50-100%	83.1	80.2/90.5	0
	15	MS Recovery	50-100%	90.1	67.4/95.6	0
	12	Blank Conc.	<HAMDC	0.01	-0.004/0.021	0
	15	LCS Recovery	85-115%	89.1	70.6/92.1	1
	12	MD RER	≤2	0.5	0.04/0.79	0
SOIL	12	HAMDC	0.2 pCi/g	0.1	0.07/0.17	0
	24	Tracer Recovery	45-100%	77.4	68.0/89.5	0
	15	MS Recovery	45-100%	97.4	94.0/99.4	0
	12	Blank Conc.	<HAMDC	0.01	-0.004/0.021	0
	15	LCS % Recovery	85-115%	89.1	70.6/92.1	1
	12	MD RER	≤2	0.9	0.62/1.4	0

TABLE 3B

LABORATORY "B" DATA DEMONSTRATING CAPABILITY TO MEET FERMCO SCQ RADIOCHEMICAL PERFORMANCE SPECIFICATIONS AT ASL B

THORIUM - 232						
MATRIX	NUMBER OF SAMPLES	PERFORMANCE PARAMETER	SCQ REQUIREMENT	AVG. LAB RESULT	RANGE OF LAB RESULT	NUMBER OF OUTLIERS
WATER	110	HAMDC	0.4 pCi/L	0.13 pCi/L	0.024/1.4 pCi/L	3
	110	Tacer Recovery	50-100%	86.9%	48.1/110%	4
	10	Blank Conc.	<HAMDC	0.077 pCi/L	0.019/0.18 pCi/L	0
	10	LCS Recovery	85-115%	94.2%	91.5/96.7%	0
SOIL	73	HAMDC	0.2 pCi/g	0.029 pCi/g	0.010/0.16 pCi/g	0
	73	Tacer Recovery	45-100%	77.1%	61.8/96.3%	0
	5	Blank Conc.	<HAMDC	7.9E-05 pCi/g	5.3E-05/1.2E-04 pCi/g	0
	5	LCS Recovery	85-115%	93.9%	91.5/98.0%	0

TABLE 4

OVERALL RANKING OF LABORATORIES PARTICIPATING IN THE FERMCO PERFORMANCE EVALUATION PROGRAM

FOR THE MONTH OF MARCH, 1994

LAB	METAL/ SOIL	VOA/ WATER	VOA/ SOIL	WET/ CHEM	SEMI-VOA/S	PEST/ SOIL	RAD/ SOIL	SUM OF RANKING	* AVERAGE RANKING	ABSOLUTE RANKING
D	2**	5	3	2	1	1	4	18	2.6	1
F	1	1	6	5	***	***	1	14	2.8	2
B	4	1	2	5	4	3	2	21	3.0	3
C	6	6	3	***	1	1	3	20	3.3	4
A	7	4	1	1	4	4	6	27	3.8	5
E	5	3	5	3	***	5	***	21	4.2	6
G	3	7	7	4	3	6	5	35	5.0	7

* = Sum of rankings divided by number of analyte groups analyzed.

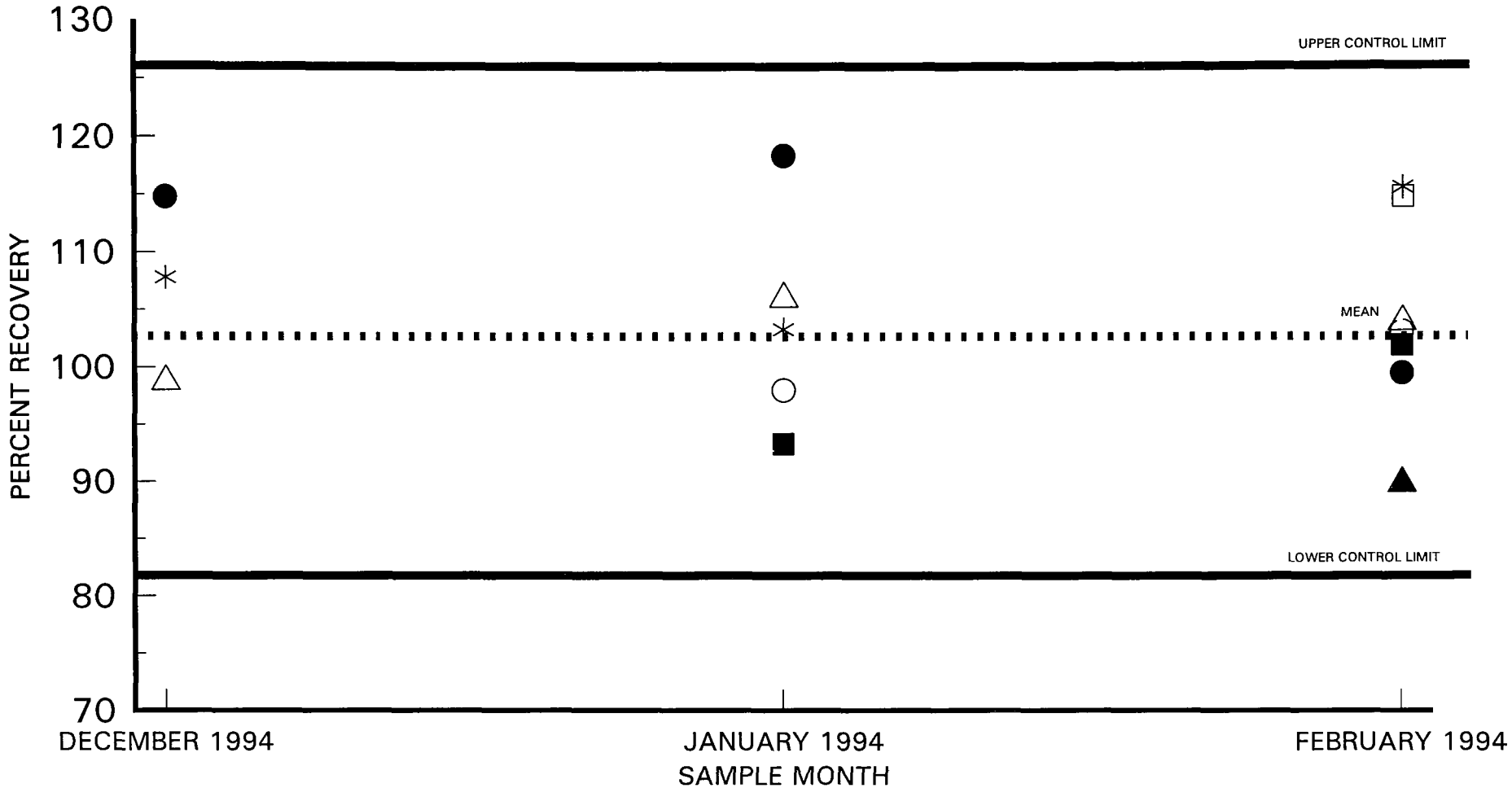
** = Ranking for a specific Analyte Class

*** = Laboratory did not participate in or submit results on this sample set.

FIGURE 1

ARSENIC

BY PERCENT RECOVERY



A ✳ B ○ C □ D △ E ▲ F ● G ■

95% CONFIDENCE LIMITS 87 - 121%
99% CONFIDENCE LIMITS 82 - 126%
MEAN 103.9% POINTS 13

UTILIZING STATISTICS IN SAMPLING TO MEET DATA QUALITY OBJECTIVES AT THE SAND CREEK SUPERFUND SITE

by: Erna Acheson, Remedial Project Manager (RPM)
Rick Edmonds, Quality Assurance Manager (QAM)

U.S. Environmental Protection Agency Region VIII
999 18th Street, Suite 500
Denver, Colorado 80202-2466

ABSTRACT

The 300 acre Sand Creek Superfund Site, located north of downtown Denver, Colorado is in a heavy industrial area. There are few residences within the vicinity of the Site but the population swells during the day to a few hundred people working in the area. The focus of this paper is to discuss the pesticide contaminated soils located at this Site.

Poor pesticide manufacturing practices during the 1960's and 1970's resulted in approximately 10,000 cubic yards of contaminated soil. Pesticides manufactured at this Site have been banned from production for over 10 years in part due to their persistence in the environment.

Years of investigations at this Site yielded a Record of Decision (ROD) for cleanup of 14,000 cubic yards of contaminated soils by soil washing. The cleanup cost estimate in the ROD was for 5 Million dollars. The volume of soil to be cleaned up detailed in the ROD was primarily based on only 17 soil samples. Subsequent to the ROD, a soil washing treatability study revealed that the cost of cleanup by this method would be 13 million dollars.

The goal in presenting this paper is to provide a "horror story beginning" with a "success story ending". The horror story begins with over double the cost estimate for cleanup and only 17 soil samples for data. The story end successfully through use of statistics, planning for meeting data quality objectives, and following "current" Superfund Accelerated Cleanup Model (SACM) guidance.

INTRODUCTION

The Sand Creek Superfund Site (Site) is located in Commerce City, Colorado, a suburb northeast of Denver, Colorado. The 300 acre Site has been the site of various industrial activities for more than 40 years. The Colorado Organic Chemical Company (COCC) manufactured pesticides and insecticides in the 1960s and 1970s which tainted the soil. Site inspections in the 1960's and 1970's by the Colorado Department of Health (CDH) revealed violations in the storage

and handling of pesticide products and waste. Subsequently, EPA conducted several investigations at the Site in the early 1980s. Sampling and analysis indicated the presence of chlorinated organic compounds, pesticides and metals. This information was used to place the Site on the National Priorities List (NPL) in 1982.

Several investigations were conducted to facilitate remediation of contaminated soil. These included a Remedial Investigation (1988), Feasibility Study (1989), Remedial Design (RD) (1993), and a pilot scale soil washing treatability study (1992). In addition, demolition and removal of selected COCC area buildings, tanks, rail cars and chemical waste plant residues occurred in 1991-1992. The Record of Decision (ROD) specified soil washing to remediate 14,000 cubic yards of contaminated soils. The cost estimate in the ROD to perform the washing of contamination from the soils was $5 million. Based on the results from the treatability study (1992), EPA determined that a more accurate cost estimate for soil washing was $13 million.

The expected site remediation costs were thus some $8 million greater than originally anticipated. The soils washing pilot tests also showed that soil washing would not reduce the concentrations of dieldrin and heptachlor to the action levels specified in the ROD. As a result of this treatability study, another sampling effort was conducted to better characterize the current extent of the contamination. This was done in order to reduce the area needing remediating and possibly modifying the action levels upward. Unbelievable as it may seem the original cleanup estimate of $5 million was based on the analysis of only 17 soil samples.

As a solution to this problem the EPA contractors were directed to prepare a proposal for a sampling program to better define the contamination problem; the draft proposal recommended the collection of 2820 soil samples. A desperate situation existed. The cleanup was to be completed within 1.5 years at a cost near the original estimate. This was a large number of samples for Remedial Design, that would take a great deal of time to complete and could disrupt the cleanup schedule (this is may be an appropriate number of samples for a Remedial Investigation, but not for a Remedial Design).

The focus of this paper is to provide a "horror story beginning" with a "success story ending." The horror story begins with over double the estimated cost for cleanup based on only 17 soil samples. The story ends with utilizing a sampling strategy / methodology that follows "current" Superfund Accelerated Cleanup Model (SACM) guidance.

CLEANUP GOALS

Chemicals of Concern were identified in the ROD: dieldrin; heptachlor; chlordane; DDT; 2,4-D; arsenic; and chromium. Based on data from the Sand Creek Remedial Investigation (RI; 1988) and OU5 Risk Assessment (RA; 1990), dieldrin and heptachlor were chosen as driver compounds for remediation of OU5 due to their carcinogenicity and concentrations. By treating dieldrin and heptachlor to action levels of 0.155 and 0.553 mg/kg, respectively an acceptable overall carcinogenic risk (for the occupational soil-ingestion pathway) of 2.7E-05 would be achieved for the site. The extent of contamination from other COCs was believed to generally coincide with dieldrin and heptachlor contamination. Therefore, the overall site risk for industrial workers would be lowered to at least the acceptable lifetime excess cancer riskrange of 1.0E-04 to 1.0E-06 by focusing on reducing dieldrin and heptachlor concentrations to the specified action levels.

SAMPLES

The jump from 17 samples to 2820 samples was clearly not reasonable. As stated earlier, 2820 samples for a Remedial Investigation may be warranted; but, this work was to be performed as part of the Remedial Design. Therefore, the QAM was contacted by the RPM to aid in reaching a reasonable sampling strategy.

The QAM and RPM, together with two other EPA scientists, planned a sampling strategy to utilizing statistics to reduced the number of required samples. Statistics as the basis for radom grid sampling performed during the initial sampling event. This initial phase of sampling consisted of collecting 10 grab samples and one composite sample from within a 50' by 50' grid of 10' by 10' cells. This random sampling was performed to determine the range of pesticide contamination within the cells and across the site. This sampling strategy provided the variability of heptachlor and dieldrin concentration levels in soils within the 50' by 50' grid, as well as between the cells.

The initial sampling was done to determine the variability of the soil across one "exposure unit" (EU). An EU was defined as one 50 X 50 feet square which is 5 feet deep. The EU's sampling depth horizons were 0 to 1 foot, 1 to 3 feet, and 3 to 5 feet. Seven one foot samples were taken by random (calculated location of random) for three separate EUs and pesticide levels measured for each sample. Additionally, a split of each seven foot sample EU was mixed together for a composite measurement of pesticides in each EU. Variability in levels of pesticides within each EU and between EUs was then calculated.

The initial goal was to arrive at an optimum amount of sampling in order to proceed with the final Remedial Design. It was decided that an additional goal of this initial sampling was to provide information on field immunoassay which would analyze for pesticides in the field. Unfortunately, the field immunoassay testing was not performed due to the lack of test kits available on the market today. Therefore the second phase of sampling, which would have evaluated the quality and usefulness of immunoassay field kits, was not carried out.
The number of samples required depended in part on the results of the initial sampling program. The final phase of sampling used recognized statistical methods with input from those persons familiar with pesticide contaminations. In order to determine which EUs to remediate, the team worked in conjunction with the toxicologist; the toxicologist's input in part was based on an evaluation of "hot spots".

Initially the COCC processing area was investigated by the same methodology as the adjacent railroad corridor. Because of several factors it was determined that the railroad corridor area needed to sampled under a different sampling stategy than the COCC property. These factors included risk determinations, cost of remediation, and difference in origin of contamination. The risk evaluation on the railroad corridor was determined by a child passing through the corridor scenario which is different than the on-site worker scenario utilized for the COCC facility risk evaluations. The cost of remediating the railroad corridor past the top foot of soil woud be excessive for there are three high pressure fuel product lines paralleling the tracks as well as a 72 inch sewer main serving metro Denver. In addition, the source of much of the railroad corridor contamination was from surface water drainage from the COCC processing area, which is considered a secondary residual waste. The type of pesicides found at the Site tend not to be very mobil. Therefore, the assumption was made that the higher levels of contamination would be found in the top foot of soil on the COCC property and that the COCC area would require more extensive sampling than the railroad corridor.

In addition to separating the Site into two distinct sampling areas, a more comprehensive list of chemicals were analyzed for in order to better define the apportionment of risk. The goal was to identify chemicals that contribute significantly to the overall human health risk at the Site so that a comprehensive list of cleanup levels would achieve site restoration goals.

SAMPLING METHOD

Soil samples were obtained for pesticide and metals analysis in soils for each cell. Samples obtained from the railroad corridor were collected by hand using a stainless steel bucket auger. The soil was then mixed or homogenized in a stainless

steel bowl and then transferred to sample jars, except for that portion of the sample to be analyzed for volatile organic compounds (VOC), which was transferred to a jar before homogenization. The samples were then placed in ice, labeled, and sent to a Contract Laboratory Program (CLP) laboratory for analysis. Samples obtained from the COCC area were collected by using a stainless steel split spoon sampler advanced with the aid of a truck mounted drill rig. A hand auger was used in cells inaccessible by the truck mounted rig. Samples collected for VOC analysis were collected from each depth interval at every third cell, from cells with cell numbers divisible by three. One blind field duplicate for each set of 20 samples was collected for VOC, metals, and pesticide analysis.

The sampling stategy utilized for the railroad corridor was to sample the top foot of soil in each grid. No deeper samples were obtained. There were some earlier samples that were taken from depths greater than the first foot of soil. These samples indicated lower levels of contamination than samples taken at the surface.

The sampling stategy utilized for the COCC area is called "a decision tree methodology" in which samples are obtained from three horizons: A-top, B-middle, and C-lower. Then, analysis was performed on all soil in the B-middle horizon. If the soil was found to be contaminated above the "action levels" then it was assumed that the A-top horizon was contaminated, and the C-lower horizon was analyzed to determine if the contamination continued past the B-middle horizon. However, if the B-middle soil was clean, then the A-top horizon was analyzed to determine if contamination was present. This methodology greatly reduced the number of samples requiring analyses.

Three horizons were sampled on the COC property. The A-top horizon is defined as the surface to one foot depth, the B-middle horizon is from one to three foot depth, and the C-bottom horizon from three to five foot depth. Samples taken at one time from one to three and three to five foot depths do not impact the cost as much as re-sampling at different times. The greatest cost savings are that the "decision tree methodology" allows for the reaonable assumption of where contamination would likely exist depending on the results of the B-middle horizon analysis. In this case there were 157 B-middle horizon samples analyzed, 97 A-top horizon samples analyzed and 58 C-bottom horizon samples analyzed. This methodology saved analyzing 159 samples. The cost savings from this methodology was approximately $330,000. In this day of limited resources and tight budgets, this savings should not be considered lightly.

As with any assumption, the assumptions made for this methodology were checked against the analytical findings. The

following tables indicate that in this case the assumptions made were reasonable. The A-top horizon has higher levels of contamination than B-middle and C-bottom horizons.

Additional field studies were undertaken in 1992 and 1993 as part of the RD and the results of the treatability study were impetus to preparing the ROD Amendmant (1993). The field sampling provided updated contaminant data and to fill in data gaps resulting from the focussed nature of earlier studies. In addition to reducing the area requiring remediation by over 25% EPA determined in 1993 that low temperature thermal treatment (LTTT) would be more cost-effective than soil washing in remediating tese soils. Unbelievable as it may seem the current estimate for cleanup is $3 million which is $2 Million less than original cost estimate. The agency goal for completion of the cleanup by LTTT is September 1994. The LTTT began in mid-May 1994.

Utilizing statistics to meet data quality objectives for the sampling effort at the Sand Creek Site was clearly successful. In addition the knowledge gained allowed the team to make a management decision for a more cost-effective approach to remediating the contaminated soils at the Site.

The additional field sampling satisfied the following objectives:

* Reduced the volume of soil needing remediation by approximately 25%.

* Provided a comprehensive and thorough knowledge of what areas require remediation, i.e. supplement a 1988 site-wide RI with more current and complete data.

* Reduced the number of samples to be analyzed through a phased sampling strategy and decision tree methodology.

* Reduced the time and costs from the initial plan (2820 samples) substantially.

* Provided data to re-evaluate contaminants so that more comprehensive health based cleanup levels could be determined.

The methodology used in this "success story" can readily be applied at other sites which at first glance may appear to require substantial sampling.

Savings realized from the initially proposed 2820 samples versus the 332 samples were substantial. Considering personnel costs, travel, oversight, equipment, supplies and analytical costs, the total savings was in the area of $500,000. Several months time was saved in the field sampling and several additional months in analytical work. It should

also be noted that several laboratories would have had to be involved if the initially proposed program had been carried out. The agency's goal regarding the time for cleanup also would not have been attained if the inital proposal was accepted.

Further cost-savings may have also been realized if the technology of immunoassay kits had been available for this study. This was initially investigated; however, the immunoassay is contaminant-specific and the pesticides that were of concern, e.g. heptachlor, dieldrin, etc. were not available at that time for the method. We encourage industry to develop the specific analyte capability for most pesticides; because, this could be a cost-savings tool for all of EPA in pesticide investigations. This would quickly identify "hot-spots" and provide a more timely characterization of where cleanup efforts should be concentrated.

Abstract

DEVELOPMENT OF A LABORATORY METHODS COMPARISON PROGRAM: A TOTAL QUALITY APPROACH TO RESOLVING A LABORATORY METHODS COMPARISON QUESTION

O. P. Bredt, T. Y. Hosaka, K. J. Kuhl-Klinger;Pacific Northwest Laboratory[1] (PNL), and K. N. Pool, A. D. Rice, C. Stacey, L. H. Taylor, W. I. Winters; Westinghouse Hanford Company.

Two primary laboratories, the Pacific Northwest Laboratory's, Analytical Chemistry Laboratory (ACL) and Westinghouse Hanford Company's Hanford Analytical Services (HAS) laboratory, analyze Hanford High-Level (radioactive) Tank Waste samples. Data from both laboratories feed into various Tank Waste Remediation programs where decisions on treatment, storage, and disposal will ultimately be made. The fact that both laboratories do not use the same procedures for preparation and analysis of tank material has led to questions regarding the comparability of analytical results between the two laboratories. To answer these questions of comparability, a collaborative was formed. This collaborative, called the Quality Assurance/Quality Control (QA/QC) Triad, includes participants from each laboratory and the Hanford sample-management office. The QA/QC Triad initiated a program that helped to answer the question of comparability and also provided insight on how analytical processes could be improved. This program, called the Sample Exchange/Evaluation (SEE) program, combines elements of both a performance evaluation and methods-comparison study (on real world samples). It provides the requisite information to make meaningful changes at the laboratory level and provides information to data users to ensure common understanding of results generated.

Keys to the SEE program success are attributed to the involvement of all the key players (QA/QC Triad) in the decision-making process, a "common sense" approach to resolving our common problem, and an emphasis on continuous improvement. Our poster will describe the process employed in developing this highly successful program, and will point to ways in which this program can be "cloned" at both commercial and other DOE analytical laboratories.

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ASSESSING DATA QUALITY FOR A FEDERAL ENVIRONMENTAL RESTORATION PROJECT: RATIONALIZING THE REQUIREMENTS OF MULTIPLE CLIENTS

Valerie R. Kiszka, Quality Assurance Coordinator, Environmental Restoration Division, and Tina M. Carlsen, Environmental Chemistry and Biology Group Leader, Environmental Restoration Division, Lawrence Livermore National Laboratory, 7000 East Avenue, L-619, Livermore, California 94550.

ABSTRACT

Most environmental restoration projects at federal facilities face the difficult task of melding the quality assurance (QA) requirements of multiple clients, as well as dealing with historical data that are often of unknown quality. At Lawrence Livermore National Laboratory (LLNL), we have successfully integrated the requirements of our multiple clients by carefully developing a QA program that efficiently meets our clients' needs. LLNL is operated by the University of California for the Department of Energy (DOE). The Site 300 Experimental Test Site is operated by LLNL in support of its national defense program. The responsibility for conducting environmental contaminant investigations and restoration at Site 300 is vested in the Site 300 Environmental Restoration Project (Site 300 ERP), which is part of LLNL's Environmental Restoration Division (ERD). LLNL Site 300 ERP must comply with the QA requirements of several clients, which include: the LLNL Environmental Protection Department, the DOE, the U.S. Environmental Protection Agency-Region IX (EPA), the California Regional Water Quality Control Board-Central Valley Region, and the California Department of Toxic Substances Control. We will present a hierarchy of QA documents prepared for the various clients, how they interact, and how they are implemented within the LLNL Site 300 ERP. This comprehensive QA program was used to determine the acceptability of historical data. The Site 300 ERP began soil and ground water investigations in 1982. However, we did not begin receiving analytical quality assurance/quality control (QA/QC) data until 1989; therefore, the pre-1989 data that were collected are of unknown quality. The U.S. EPA QAMS-005/80 defines data quality as the totality of features and characteristics of data that bears on its ability to satisfy a given purpose. In the current context, the characteristics of major importance are accuracy, precision, completeness, representativeness, and comparability. Using our established QA program, we determined the quality (as defined by EPA QAMS) of this historical data based on its comparability to the post-1989 data. By accepting this historical data, we were able to save a considerable amount of money in recharacterization costs.

INTRODUCTION

Environmental contaminant investigations of the Site 300 Experimental Test Site began in 1982 to investigate the impact to the site's soil, rock, and ground water by the operation of nine solid waste landfills, and to determine the extent of contamination of trichloroethene (TCE) from past waste handling practices. Ground water, soil, and rock chemistry and field measurement data were required to assess the extent of

contamination, understand the hydrogeologic characteristics of the site, determine the nature and location of possible sources of contamination, develop public health and ecological assessments, evaluate potential remedial action alternatives and engineering designs, and characterize baseline conditions.

In 1986, environmental investigations, routine environmental surveillance, and routine environmental monitoring were consolidated in the Environmental Protection Department (EPD) of Lawrence Livermore National Laboratory (LLNL). By 1987, all Site 300 soil, rock, and ground water investigations were performed by what is now the Site 300 ERP, which is a section of ERD within EPD. Also, by this time, a major effort was underway to consolidate and centralize all environmental chemical analytical data collected previously during various Site 300 activities. A centralized data management team was formed within ERD, and a centralized database on a DEC VAX mainframe computer was created.

The data management team collected all hard copy reports of analytical chemical data. Assisted by ERD chemists and geologists, this team verified all historical analytical reports, ensuring that proper sampling, handling, and analytical protocols were followed, and that proper documentation concerning the sample was available. After verification was complete, the data were entered into the centralized database. Analytical results failing such verification were excluded from the database or properly annotated. Samples were analyzed by both on-site LLNL laboratories and off-site commercial laboratories that were California state certified. Site 300 ERP started receiving QA/QC documentation from the off-site analytical laboratories in 1989. The QA data generated by on-site LLNL laboratories continue to be archived by them and are available for review by the Site 300 ERP QA chemists.

Prior to 1989, reports from off-site analytical laboratories contained minimal QA information. However, these reports did contain sufficient information required for data acceptance into the database. Reports always included LLNL sample identification, analytical laboratory identification, sample matrix, date sampled, date analyzed, and analytical results. Generally, the reports also included the analytical method, reporting detection limit, and certification by the laboratory manager. If the validity of a particular result was questioned, the laboratory was requested to provide all associated QC data for review by Site 300 ERP QA chemist.

From 1982 through 1989, field investigations were conducted under the guidance of the California Regional Water Quality Control Board (RWQCB)-Central Valley Region. Site 300 was placed on the National Priorities List on August 30, 1990, and guidance and oversight of the cleanup was transferred to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulations under EPA Region IX, the RWQCB, and the California Department of Toxic Substances Control (DTSC). In 1990, a formal manual of standard operating procedures (SOPs) and quality assurance project plan (QAPjP) were prepared for the Site 300 ERP. Both documents were revised in 1992. The Site 300 ERP's data must meet the specific quality criteria documented in the QAPjP to be considered meaningful to the data users.

Presently, the investigations at Site 300 require the sampling and analyses of more then 430 monitor wells for various parameters with the emphasis on volatile organic compounds (VOCs), inorganics, high explosive (HE) compounds, and radionuclides, using methods and procedures functionally equivalent to the methods and procedures used in the EPA Contract Laboratory Program (CLP) and the California DTSC Certified Laboratory Program. California state certified commercial laboratories are being utilized for the majority of analyses. However, on-site laboratories are used for QA/QC purposes to analyze collocated samples for HE compounds and for special radiochemistry analyses. Figure 1 details the environmental regulatory and QA/QC history of the Site 300 ERP.

DISCUSSION

Figure 2 depicts the document hierarchy that establishes the QA requirements governing the Site 300 ERP. The Department of Energy (DOE) initiated DOE Order 5700.6C in 1991 to improve the safety and reliability of the Department's programs, projects, and facilities. The 10 criteria of DOE Order 5700.6C direct organizations to develop, implement, and maintain a written quality assurance program. To comply with the DOE order, EPD within LLNL, developed a Quality Assurance Management Plan (QAMP) based on the 18 criteria of the American Society of Mechanical Engineers Nuclear Quality Assurance (ASME NQA-1) and satisfying the 16 elements of the Environmental Protection Agency Quality Assurance Management Staff (EPA QAMS). The EPD QAMP ensures that EPD management provides planning, organization, direction, control, and support to achieve EPD's objectives; that the line organizations achieve quality; and that overall performance is reviewed and evaluated using a thorough assessment program. The ERD developed the ERD Quality Assurance Plan (QAP), also based on NQA-1 and EPA QAMS, as required by the EPD QAMP. The ERD QAP establishes and presents the framework of requirements that shall be met in planning, performing, documenting, and verifying ERD quality-affecting activities. Since the Site 300 ERP is a part of ERD, it must comply with all the QA requirements of the QAP through the development of Quality Implementing Procedures (QIPs) and SOPs. The Site 300 ERP is also required by its Federal Facility Agreement (FFA) and EPA QAMS, to write a QAPjP that documents the policies, organization, objectives, functional activities, and specific QA/QC activities designed to achieve the data quality goals of the restoration project.

Along with the revision of the QAPjP in 1992 and the development of the ERD QAP in 1993, came many quality improvements and implementation of new quality affecting procedures. For example, 100% of the data generated by analytical laboratories is reviewed by the Site 300 QA chemist before being entered into the database. Figure 3 shows the flow of Site 300 project data. The QA chemist reviews the data for internal consistency, technical adequacy, and quality. The quality of the data is judged by the chemist's review of the QC data generated by the laboratory. The off-site commercial laboratories are contractually required to provide method blank, laboratory control sample, matrix spike, and matrix spike duplicate results with every analysis. Calibration information is made available upon the request of the QA chemist. If problems are found, the QA chemist can qualify the data by assigning CLP-like data qualifier flags that are entered into the database. All data are flagged in the database with the appropriate analytical level (I-V). Periodic statistical analyses are performed on all the data in the database to identify outliers. When outliers are flagged, the QA chemist investigates the

possibility of data entry or analytical laboratory errors. Electronic validation/verification procedures are being developed to expedite the review of data by the QA chemist.

The Site 300 ERP QAPjP requires that 10% of all samples collected be collocated. Five percent are sent blind to the primary laboratories and 5% are sent to the QA/QC laboratories to assess interlaboratory and intralaboratory precision. The QAPjP also specifies that Site 300 ERP will conduct performance checks twice a year and a systems audit annually. Currently, the off-site analytical laboratories are receiving blind VOC and metals performance check samples on a quarterly basis.

Before an off-site laboratory is awarded an analytical contract, they must be California state certified, and their QA program and operating procedures are evaluated for technical adequacy. On-site LLNL laboratories must be evaluated by the EPD QA Office and placed on a Qualified Suppliers List before work can begin. The EPD QAMP requires that off-site analytical laboratories also be subjected to audits before a contract can be awarded. The auditors verify that the laboratory is in compliance with its internal procedures and QA program, and that all DOE and EPD requirements are met.

The Site 300 ERP QA program is frequently assessed and/or audited by DOE, EPD, and through ERD's self assessment program. The Site 300 ERP monitors the QA program by submitting QA reports to Site 300 ERP management at least annually. These QA reports may summarize inter- and intralaboratory precision, performance check sample results, qualified data, outliers, any audit findings, completeness, accuracy of laboratory control samples and matrix spikes, and progress toward future quality goals.

While the majority of the data collected prior to 1989 was not reviewed by the QA chemist for compliance with matrix spike, matrix spike duplicate, and laboratory control sample precision and accuracy acceptance limits, the data in most cases were analyzed by California state certified laboratories using standard analytical methods. Since the laboratories were certified by the state and had met the strict state criteria, we assumed that the analytical laboratory chemists had already reviewed the data for quality and technical adequacy.

By melding all the Site 300 ERP clients' QA requirements and our own QA/QC procedures, the Site 300 restoration project data produced since 1989 are legally reproducible, defensible, and of known quality. The pre-1989 data were then visually compared to the usable current data, looking for variances and anomalous trends. Figure 4 contains a graph of four monitoring wells that have been sampled and analyzed for TCE since 1982. The graph demonstrates the natural variability of TCE within the ground water. On the basis of this examination and comparison, the Site 300 ERP has determined that the majority of the pre-1989 data is internally consistent with the post-1991 data. Historical data were accepted and used together with more recent data of known quality for delineation of the nature and extent of contamination at Site 300 and for use in the baseline quantitative risk assessment.

CONCLUSION

The Site 300 ERP has successfully implemented all of its clients' QA requirements and is continually striving to improve the quality of the project's data and the availability of the data to the user. By showing the historical data to be equivalent to the more recent data and therefore acceptable, the Site 300 ERP was not required to duplicate their previous site characterization effort and consequently saved the DOE a considerable amount of money.

Figure 1. Environmental regulatory and QA/QC history of LLNL Site 300 Environmental Restoration Project.

Date	Event	Lead agency
1982	Site 300 seeks informal guidance from the California RWQCB after discovering soil and ground water contamination.	California RWQCB
1982-1989	Field investigations under the guidance of California RWQCB.	California RWQCB
1988	Started to receive QA/QC monthly from the California state certified analytical laboratories for all VOC analyses.	
March 1989	RCRA[a] 3008(h) Order: required LLNL to investigate all releases of hazardous waste or hazardous constituents at the site and to determine if corrective actions under RCRA were required.	EPA IX
April 1989	Draft Cleanup and Abatement Order: required LLNL to continue environmental restoration efforts already underway.	California RWQCB
July 1989	RCRA 3004(u) Corrective Action Order: required LLNL to comply with provisions of RCRA 3008(h) Order.	EPA IX
July 1989	Site 300 proposed for inclusion on National Priorities List.	EPA IX
1990	Started to receive QA/QC with individual analytical reports. Standard Operating Procedures (SOPs) and Quality Assurance Project Plan (QAPjP) developed.	
August 1990	Site 300 placed on NPL; guidance and oversight of Site 300 cleanup transferred to CERCLA[b] regulations.	EPA IX, RWQCB, DTSC
October 1990	RCRA 3008(h) negotiations suspended in favor of a CERCLA Federal Facility Agreement (FFA).	EPA IX
October 1990	Draft Letter of Agreement issued to cover Site 300 environmental restoration until FFA is signed.	EPA IX
October 1990	Letter of Agreement signed by U.S. DOE and U.S. EPA.	EPA IX
1991	Began receiving QA/QC data electronically by special request. EPD QAMP implemented.	
1992	Began assigning data qualifier flags and analytical levels to analytical data. SOPs and QAPjP revised and approved by regulatory agencies.	
June 1992	Federal Facility Agreement signed by U.S. DOE, EPA, DTSC, and RWQCB-Central Valley.	EPA IX
January 1994	ERD QAP approved.	
Present	ERD working with analytical laboratories to develop electronic QA/QC data transfer protocol.	

a RCRA = Resource Conservation and Recovery Act.

b CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act.

Figure 2. The Lawrence Livermore National Laboratory's Environmental Protection Department's Quality Assurance Document Hierarchy.

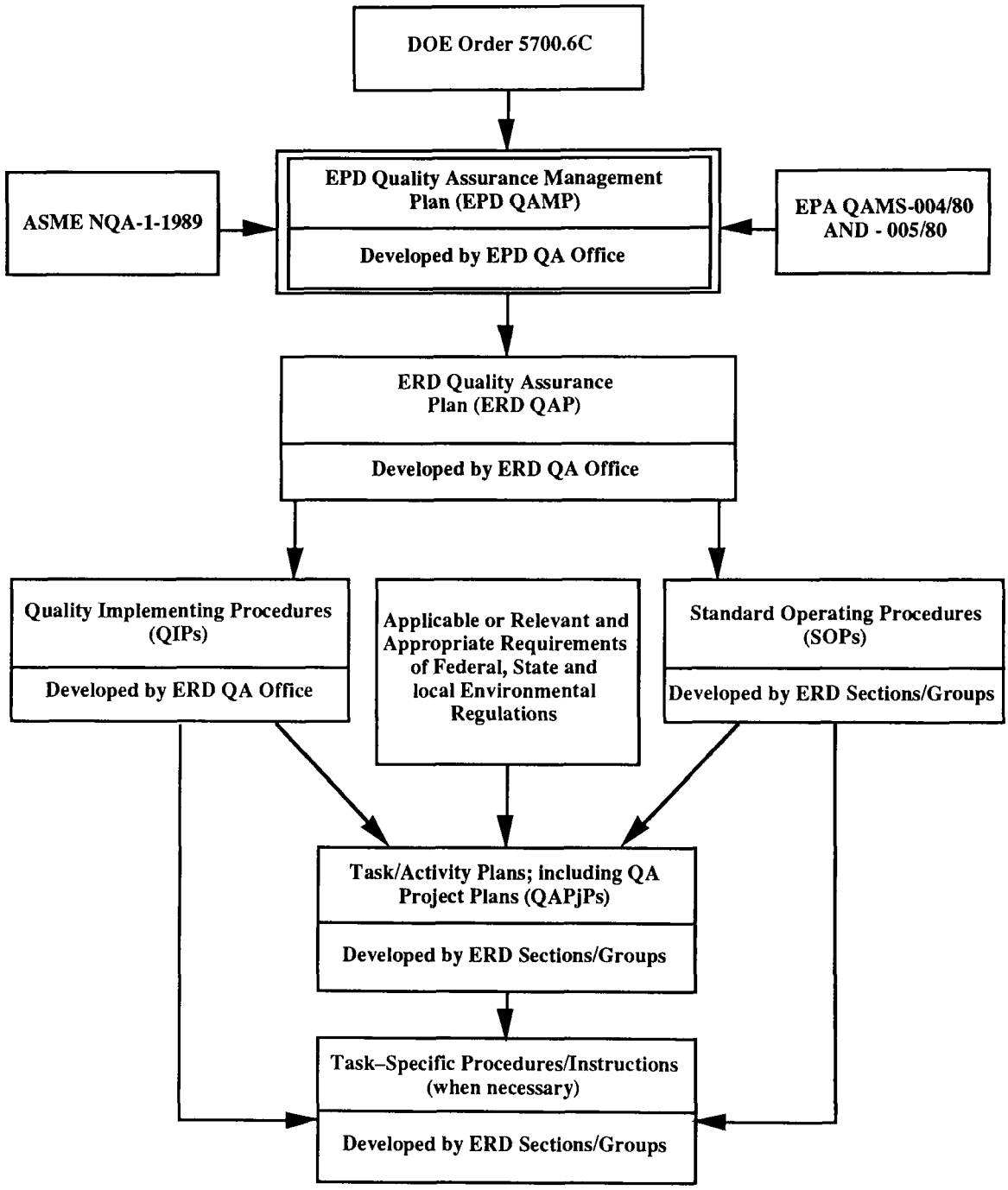


Figure 3. Flow of LLNL Site 300 Environmental Restoration Project data.

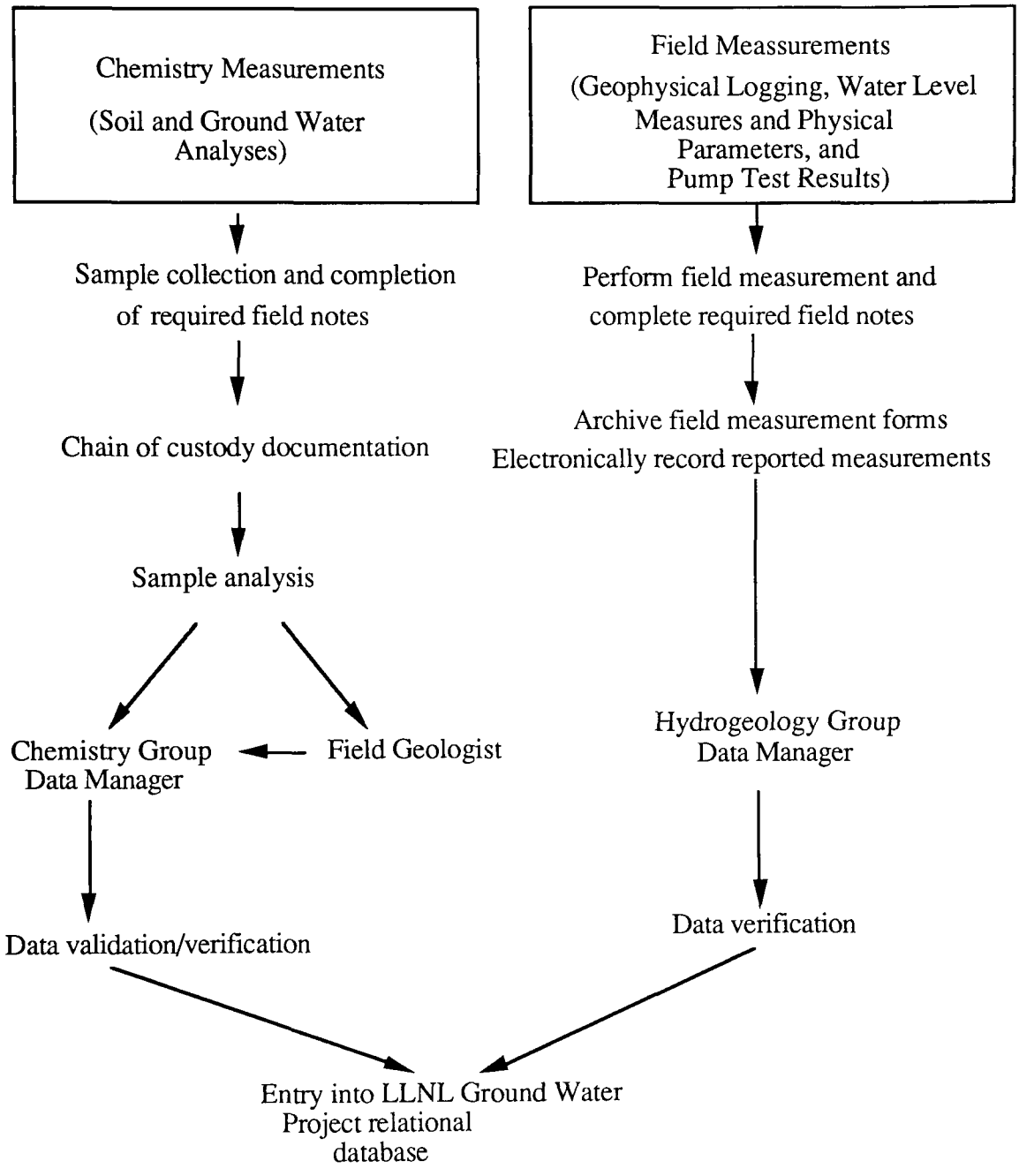
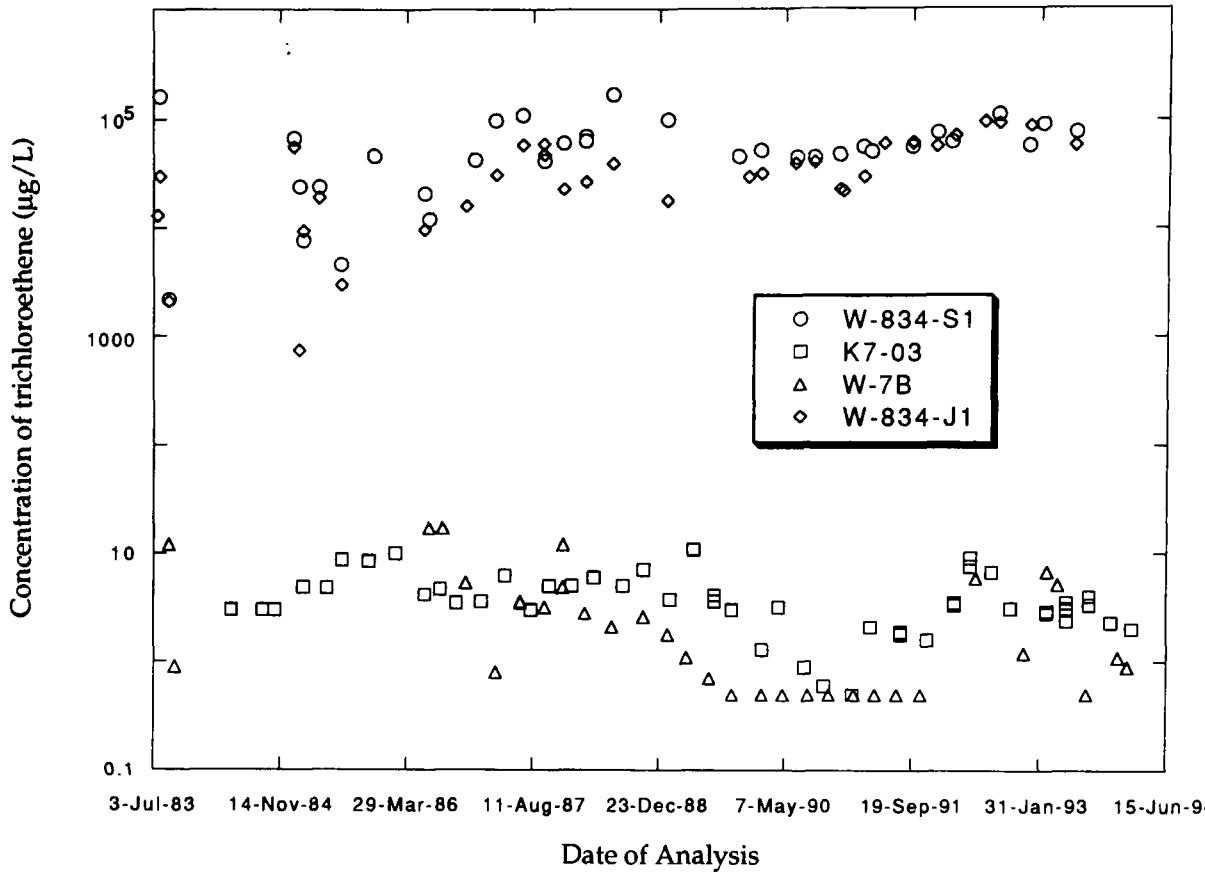


Figure 4. Time trend graph of trichloroethene concentrations in four monitoring wells located at Site 300.



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EXPLORATORY DATA ANALYSIS USING EPA'S CONTRACT LABORATORY PROGRAM DATA

Peter Novick, Muhannad Kanaan, Roger Litow, M. V. Chacko, DynCorp Viar, Inc., 300 North Lee Street, Alexandria, Virginia 22314-2695
David Eng, U S EPA Analytical Operations Branch, Hazardous Site Evaluation Division, 1235 Jefferson Davis Highway (52046), Arlington, VA 22202

The EPA regulates and manages one of the largest environmental analytical data repositories in the nation. All data in electronic media submitted to the EPA under the national Contract Laboratory Program (CLP) is stored in this repository - the CLP Analytical Results Database (CARD). The database contains analytical results for over three hundred thousand samples collected over a seven year period. This vast database is an ideal source of data for exploratory searches catering to numerous interests whether they be studies on instrumental performance, quality control parameters, analytical methods, spiking compounds, or even searches for possible trends or patterns across multiple analytical protocols and databases. Exploratory data analysis (EDA), when appropriately controlled and carefully balanced by classical statistical methods, has contributed to scientific progress.

This paper discusses the prospects of conducting such an exploratory data analysis experiment using CARD. In our search for a non-trivial subject of interest, we decided to search for possible trends or patterns that would suggest an effect on the quantitation and recovery of certain matrix spiking compounds due to the presence of inorganic elements. Although prior studies have established that a correlation can exist, our initial searches for the same in CARD did not suggest this. As indicated by other studies, the analytical and environmental effects of these elements is related to several other factors, including the pH of the environment, the soil matrix, as well as the metal species and anions present and their concentrations. This was complicated further by the fact that the database did not contain some of the information necessary to ascertain the state of these factors.

We proceeded to take control of some of these factors in our further probing of the data. Resistant methods were applied to pay less attention to outliers. The inorganic analytes were segregated based on their chemical properties; and the organic sample spike recoveries were examined at three different pH ranges. We began to see interesting patterns. The next step is to establish a resistant fit that may include the bulk of the data, and if one is found, to separate this fit from the data, leaving behind a resistant residual. These residuals can warn of important systematic aspects of data behavior crucial to further explorations, aiding us in confirmatory data analysis that would assess the reproducibility of the observed trends.

Finally, the data behavior can be displayed via a variety of visual/graphical representation techniques that would enable the viewer to grasp the unexpected results as well as the more familiar features of the data as determined by the EDA experiment.

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COST AND QUALITY EFFECTIVENESS OF OBJECTIVE-BASED AND STATISTICALLY-BASED QUALITY CONTROL FOR VOLATILE ORGANIC COMPOUNDS ANALYSES OF GASES

J. T. Bennett, Scientific Specialist, Engineering Research and Applications Department (ERAD), C. A. Crowder, Senior Scientist, ERAD, S. J. Sailer, Senior Scientist, ERAD, and M. J. Connolly, Scientific Specialist, Environmental Restoration and Waste Management Department, Idaho National Engineering Laboratory, EG&G Idaho, Inc., P.O. Box 1625, Idaho Falls, Idaho 83415-4107

ABSTRACT

Gas samples from selected drums of radioactive waste at the U.S. Department of Energy (DOE) Idaho National Engineering Laboratory are being characterized for 29 volatile organic compounds (e.g., acetone, bromoform, tetrachloroethylene) to determine the feasibility of storing the waste in DOE's Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. Quality requirements for the gas chromatography and gas chromatography/mass spectrometry chemical methods used to analyze the waste are specified in the Quality Assurance Program Plan for the WIPP Experimental Waste Characterization Program. This document was prepared by DOE with input and review by U.S. Environmental Protection Agency. Quality requirements consist of both objective criteria (i.e., data quality objectives, DQOs) and statistical criteria (i.e., process control). The DQOs apply to routine sample analyses, while the statistical criteria serve to determine and monitor precision and accuracy (P&A) of the analysis methods and are also used to assign upper confidence limits to measurement results close to action levels.

After over two years and more than 1000 sample analyses there are two general conclusions concerning the two approaches to quality control:
(1) Objective criteria (e.g., ± 25% precision, ± 30% accuracy) based on customer needs and the usually prescribed criteria for similar EPA-approved methods are consistently attained during routine analyses.
(2) Statistical criteria based on short term method performance are almost an order of magnitude more stringent than objective criteria and are difficult to satisfy following the same routine laboratory procedures which satisfy the objective criteria. Statistical P&A criteria are initially established from 30 replicate analyses of a standard sample over a period of several days. System performance is then tested semiannually by analysis of seven replicates whose results are compared to the results of the initial 30 replicates. The inability to obtain statistically equivalent data sets at the 95% confidence level for the majority of analytes arises primarily from short term (i.e., few days to few weeks) precision being more definitive than long term (i.e., few weeks to few months) excersions in accuracy even though the accuracy is always well within the DQOs.

A more cost effective and representative approach to establishing statistical method performances criteria would be either to utilize a moving average of P&A from control samples over a several month time

period or to determine within sample variation by one-way analysis of variance of several months replicate sample analysis results or both. Confidence intervals for results near action levels could also be determined by replicate analysis of the sample in question.

INTRODUCTION

Analytical chemistry laboratories conducting repeated chemical measurements of environmental, industrial, and waste samples must utilize standardized and formalized quality control (QC) and quality assurance (QA) procedures to continuously control and evaluate the results from their analysis activities. In most laboratories these QA/QC procedures are derived from a combination of objective-based and statistically-based criteria. Objective-based criteria are usually measurement control limits that are designed to provide data of acceptable quality and agreed to by both the laboratory and the customer prior to analyses being conducted. These objective criteria are often referred to as data quality objectives (DQOs) and are established considering two primary factors:

(1) Customer's intended use of the data
(2) Capabilities and limitations of the chemical analysis method

Statistically-based criteria are also employed as measurement control limits, but compared to DQOs these criteria are less arbitrary and based more on actual analysis method performance. The control limits in this case are established and periodically revised from the measured performance of the analysis system (e.g., repeated measurements of a sample to establish precision control limits). This statistically-derived form of QA/QC is also referred to as statistical process control (SPC).

For an analytical chemistry laboratory to consistently produce analysis results which are of acceptable quality, strict adherence to standardized QA/QC procedures is essential; however, cost effectiveness and quality effectiveness of a laboratory's QA/QC procedures can vary substantially depending on the specific manner in which the procedures are implemented and maintained. At the U.S. Department of Energy (DOE) Idaho National Engineering Laboratory (INEL) a program is underway to determine the feasibility of storing radioactive waste in DOE's Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. One aspect of this program is to chemically analyze gas samples taken from selected drums of radioactive waste currently stored at INEL. The QA/QC requirements for these chemical analyses are a combination of objective and statistical criteria and are described in detail in the Quality Assurance Program Plan for the WIPP Experimental Waste Characterization Program (USDOE, 1991). Volatile organic compounds are one of the types of compounds being analyzed for, and this paper summarizes and evaluates the quality effectiveness and cost effectiveness of the QA/QC procedures for such analyses conducted between February 1992 and March 1994.

QUALITY REQUIREMENTS

The QA/QC requirements for volatile organic compound (VOC) analyses for the WIPP Experimental Waste Characterization Program vary depending on the chemical analysis methods, which for this investigation were as follows:

- WIPP Method 430.1: Modified Method TO-14 for the Determination of Volatile Organic Compounds in Waste Container Headspace Using SUMMA® Passivated Canister Sampling and Gas Chromatographic/Mass Spectrometric Analysis
- WIPP Method 440.1: Gas Chromatography-Flame Ionization Detector Determination of Alcohols and Ketones in Waste Container Headspace Collected Using SUMMA® Passivated Canisters

WIPP Method 430.1 is a gas chromatographic technique with mass spectrometric detection (GC/MS) using mass flow controller for gas injection. This method is derived from U.S. Environmental Protection Agency (EPA) Ambient Air Method TO14 (USEPA, 1988a and 1988b). WIPP Method 440.1 is a gas chromatographic technique with flame ionization detection (GC-FID) using a sample loop for direct gas injection. The principal VOCs, which these methods are designed to identify and measure, are listed in Table 1.

As previously stated the QC requirements are a combination of objective criteria and statistical criteria. The objective-based QC apply to routine sample analyses, while the statistically-based QC serves to determine and monitor precision and accuracy (P&A) of the analysis methods and is also used to assign upper confidence limits to measurement results close to action levels.

Objective-Based Quality Control

The objective-based quality control procedures, which will also be referred to as data quality objectives (DQOs), are primarily numeric control limits for QC measurements. These QC measurements and associated evaluations are required during all phases of analysis system calibration and sample analyses and are summarized in Tables 2 and 3. The specific numeric values of the control limits were chosen to satisfy DOE's data usability needs and also considering the inherent capabilities and limitations of the analysis techniques. The DQOs listed in Tables 2 and 3 are very similar in type and magnitude to those generally used for similar published and commonly used analysis techniques, such as EPA SW-846 Method 8240 (USEPA, 1990).

Brief descriptions of DQOs and explanations of how their indicators listed in Tables 2 and 3 are calculated are provided in the following subsections:

- Precision
- Accuracy
- Completeness

Table 1. VOC analysis Target Compound List (TCL) and Program Required Quantitation Limit (PRQL).

Volatile Organic Compounds	CAS Number	PRQL[a] (ppmv)
1. Acetone	67-64-1	100
2. Benzene	71-43-2	1
3. Bromoform	75-25-2	1
4. 1-Butanol	71-36-3	100
5. 2-Butanone	78-93-3	100
6. Carbon tetrachloride	56-23-5	1
7. Chlorobenzene	108-90-7	1
8. Chloroform	67-66-3	1
9. Cyclohexane	110-82-7	1
10. 1,1-Dichloroethane	75-34-3	1
11. 1,2-Dichloroethane	107-06-2	1
12. 1,1-Dichloroethene	75-35-4	1
13. cis-1,2-Dichloroethene	156-59-2	1
14. Ethyl benzene	100-41-4	1
15. Ethyl ether	60-29-7	1
16. Methanol	67-56-1	100
17. Methylene chloride	75-09-2	1
18. 4-Methyl-2-pentanone	108-10-1	100
19. 1,1,2,2-Tetrachloroethane	79-34-5	1
20. Tetrachloroethene	127-18-4	1
21. Toluene	108-88-3	1
22. 1,1,1-Trichloroethane	71-55-6	1
23. Trichloroethene	79-01-6	1
24. 1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1
25. 1,3,5-Trimethylbenzene	108-67-8	1
26. 1,2,4-Trimethylbenzene	95-63-6	1
27. m-Xylene[b]	108-38-3	1
28. o-Xylene[b]	95-47-6	1
29. p-Xylene[b]	106-42-3	1

[a] Values based on delivering 10 mL to the analytical system.
[b] These xylene isomers cannot be resolved by the analytical methods employed in this program.

Table 2. Calibration requirements for VOC analyses.

Method	Procedure	Frequency of Procedure	Acceptance Criteria
430.1 (GC/MS)	Bromofluoro-benzene (BFB) tune	Every 12 hours	Within specified key ion abundance ranges
430.1 (GC/MS)	5-pt initial calibration	Initially and as needed	Percent relative standard deviation (RSD) for all compounds <35%
430.1 (GC/MS)	Continuing calibration	Every 12 hours	Relative percent differences (RPD) for all compounds within 30% of initial calibration
440.1 (GC-FID)	3-pt initial calibration	Initially and as needed	RSD all compounds <30%
440.1 (GC-FID)	Continuing calibration	Every 12 hours	RPD for all compounds within 30% of initial calibration, retention time within 3 standard deviations of initial calibration

Precision: Precision is a measurement of the random error in an analytical measurement process (i.e., the degree of agreement between independent measurements determined by the analysis of replicate samples).

When calculated for duplicate sample analyses, precision is expressed as the relative percent difference (RPD), which is calculated as

$$RPD(\%) = \frac{|S - D|}{(S + D)/2} \times 100$$

where

S = first sample value (original)
D = second sample value (duplicate)

When precision is calculated for three or more replicate determinations, the relative standard deviation (RSD), also known as the coefficient of variation (CV) expressed in units of percentage, is used. This is an expression of the spread of the data relative to the mean value, $\bar{X}$, of the determinations. The specific formulas used for calculation of the RSD are

Table 3. VOC analysis data quality objectives.

Compound	Precision (RSD or RPD)	Accuracy		Completeness (C)
		Recovery (R)	Detection (MDL)	
Method 430.1 (GC/MS) Benzene Bromoform Carbon tetrachloride Chlorobenzene Chloroform Cyclohexane 1,1-Dichloroethane 1,2-Dichloroethane 1,1-Dichloroethene cis-1,2-Dichloroethene Ethyl benzene Ethyl ether Methylene chloride 1,1,2,2-Tetrachloroethane Tetrachloroethene Toluene 1,1,1-Trichloroethane Trichloroethene 1,1,2,-Trichloro-1,2,2-trifluoroethane 1,3,5-Trimethylbenzene 1,2,4-Trimethylbenzene m-Xylene o-Xylene p-Xylene	≤25%	70-130%	8 ng or less	90%
Method 440.1 (GC-FID) Acetone 1-Butanol 2-Butanone Methanol 4-Methyl-2-pentanone	≤25%	70-130%	50 ng or less	90%

RSD = Relative standard deviation
RPD = Relative percent difference
MDL = Method detection limit (total number of nanograms delivered to the analytical system per sample)

$$\bar{X} = \frac{\sum_{i=1}^{n} x_i}{n} \quad \text{and} \quad s = \left[\frac{\sum_{i=1}^{n} (x_i - \bar{X})^2}{n-1} \right]^{1/2}$$

$$RSD(\%) = CV = \frac{s}{\bar{X}} \times 100$$

where

x_i = result value for the i_{th} measurement
n = total number of measurements
s = standard deviation, expresses the variability of data about the mean, $\bar{X}$

Accuracy: Accuracy (bias) is a measurement of the extent to which a measured value of a quantity (parameter or analyte) agrees with the accepted value of that quantity. Accuracy is assessed by the analysis of samples of known concentration (e.g., laboratory control samples, calibration samples, field reference standards, or additional QC samples) for the analyte of concern, or by spiking samples with a known quantity of the analyte of concern before analysis. In both instances, accuracy is quantified by calculating the percent recovery (R) of the known quantity (true value, TV) of analyte. The general equation used for this calculation is

$$R(\%) = \frac{\text{Measured Value} \quad \text{Background Value}}{\text{True Value of Sample or Spike}} \times 100$$

Method detection limits (MDLs) are determined for each analyte for each method. These MDLs are determined by (a) conducting replicate analyses of standards at quantities approximately one to five times the estimated MDL, (b) determining the standard deviation, s, of the replicate measurements, and (c) calculating the MDL from

$$MDL = t_{(n \quad 1,\ 1-\alpha \quad 0.99)} \times s$$

where

n = the number of replicate analyses

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = The t distribution value appropriate to a 99% confidence level (one-tailed) and standard deviation estimate with n - 1 degrees of freedom

The MDL calculated in this manner represents the minimum amount of a substance that can be measured and reported with 99% confidence that the analyte quantity is greater than zero.

Completeness: Completeness (C) of the reported data (expressed as a percentage) is calculated as

$$C(\%) = \frac{V}{T} \times 100$$

where

V = number of measurements judged to be valid (meets all QA/QC requirements)

T = total number of measurements expected (based upon number of samples submitted for analysis)

Statistically-Based Quality Control

A summary of the program's required approach to statistically evaluating analysis method performance is shown in Figure 1. Initially, precision and accuracy are assessed using analysis method performance data from analysis of 30 laboratory reference standards (i.e., initial P&A data set). Thereafter, precision and accuracy data for each analysis method is continuously monitored and evaluated by analysis of at least seven replicates every six months (i.e., continuing P&A data set). Corrective actions must be taken if consecutive data sets are not statistically equivalent.

Analysis of Precision: The F test is used to determine if the precisions obtained from different data sets are statistically the same. Comparison of data sets is done at the 95% confidence level (two-tailed). A calculated F value is determined by taking the ratio of the two data set variances:

$$F_{v1,v2} = s_1^2/s_2^2$$

where

v_1 = number of degrees of freedom for data set 1
v_2 = number of degrees of freedom for data set 2
s_1 = standard deviation of data set 1
s_2 = standard deviation of data set 2

When calculating F values, s_1 and s_2 are chosen so that s_1 is greater than s_2; therefore, s_1^2/s_2^2 is always greater than one. The calculated F value is then compared to the critical F_c value found in tables of critical F values. The F_c value is at the 95% confidence level with the degrees of freedom (v_1v_2) such that v_1 is degrees of freedom for the numerator and v_2 is the degrees of freedom of the denominator. The precisions obtained from two data sets are statistically equivalent if the calculated F value is less than the critical F_c value.

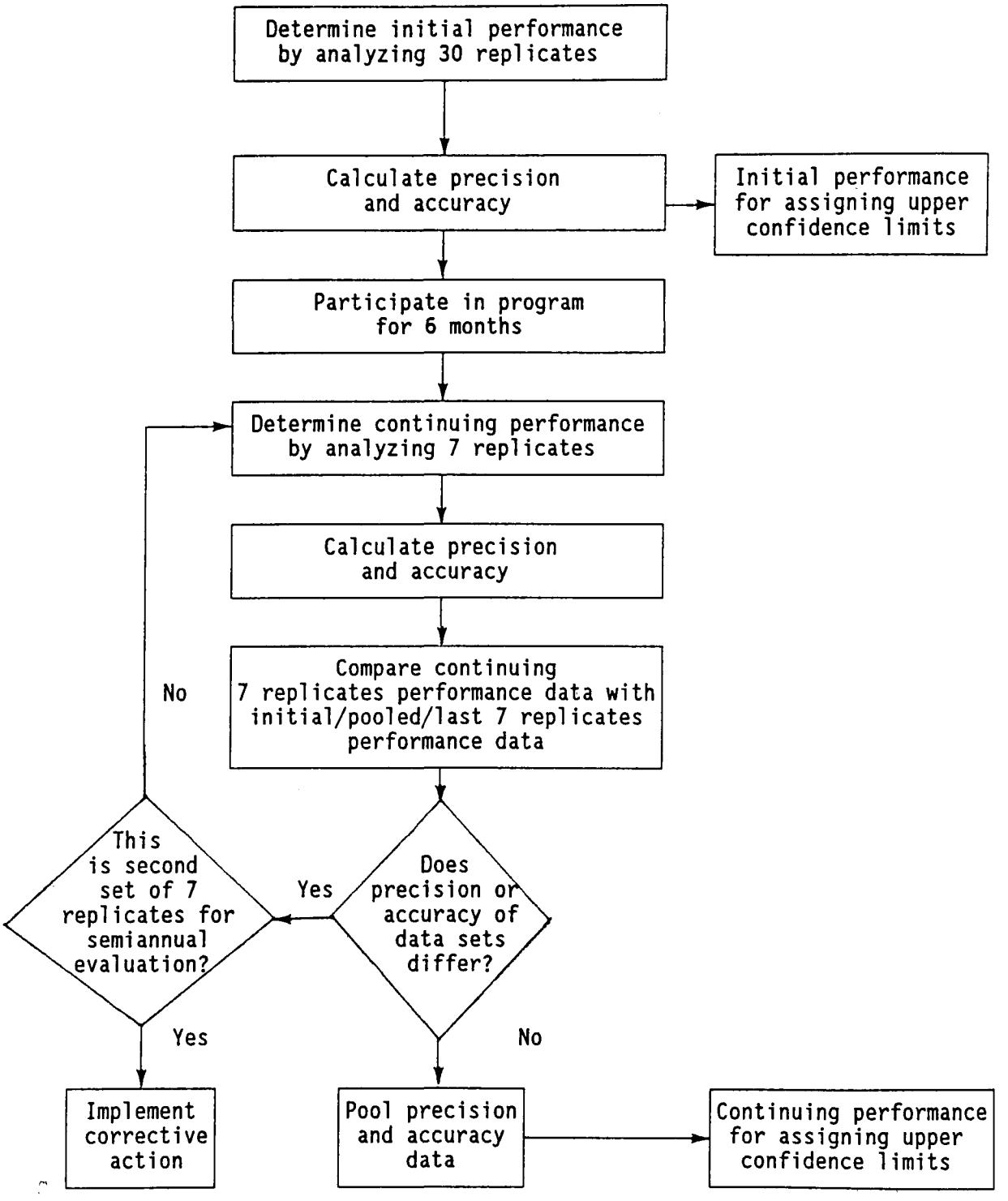

Figure 1. Statistical analysis of method performance data.

from two data sets are statistically equivalent if the calculated F value is less than the critical F_c value.

Analysis of Accuracy: The accuracy obtained from two data sets is evaluated at the 95% confidence level (two-tailed) by comparing the data set averages using the t-statistic. If the standard deviations of two data sets are statistically equivalent by the F-test, a pooled estimate of the standard deviation is calculated as follows:

$$s^2 = [(n_1 - 1)s_1^2 + (n_2 - 1)\ s_2^2]/(n_1 + n_2 - 2)$$

where

n_1 = number of samples in data set 1

n_2 = number of samples in data set 2

The t value is given by

$$t_v = (\bar{X}_1 - \bar{X}_2)/[s(1/n_1 + 1/n_2)^{1/2}]$$

where

v = number of degrees of freedom $(n_1 + n_2 - 2)$

$\bar{X}_1$ = mean concentration of data set 1

$\bar{X}_2$ = mean concentration of data set 2

If the standard deviations of the two data sets are significantly different, the t value is given by

$$t_v = (\bar{X}_1 - \bar{X}_2)/\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^{1/2}$$

with the degrees of freedom, v, given as

$$v = \left[\frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{(s_1^2/n_1)^2}{n_1 + 1} + \frac{(s_2^2/n_2)^2}{n_2 + 1}}\right] - 2$$

For either case, the mean concentrations of the two data sets are not significantly different if the t value obtained is less than the critical value of t_c. If the mean concentrations do not differ significantly, then the accuracies for the two data sets do not differ.

RESULTS AND DISCUSSION

During routine analysis of samples between February 1992 and March 1994, associated quality control (QC) measurements were over 99% compliant with program data quality objectives (DQOs). This near zero defects performance was due primarily to two factors: (1) representativeness and reasonableness of QC measurement acceptance criteria and (2) good laboratory practice. The general manner in which analysis method QC procedures are applied also contributes to avoiding DQO deficiencies. For example, QC requirements for analysis method calibration must be satisfied before conducting sample analyses, and this phased approach greatly reduces the probability the noncompliant QC measurements as the analysis process proceeds.

Based on laboratory control sample (LCS) analysis results during routine sample analyses, average precision and accuracy (P&A) for the 29 compounds of interest was relative standard deviation (RSD) precision of 7.5% (7.0% for Method 430.1, 9.7% for Method 440.1) and recovery (R) accuracy of 97.8% (98.2% for Method 430.1, 97.8% for Method 440.1). These average values are well within the corresponding program DQOs of 25% RSD and 70-130% R. Even if individual compounds are considered, the compounds with largest deviations from the ideal results (i.e., maximum RSD: 15.2% for 1-butanol, minimum R: 85.3% for 1,3,5-trimethylbenzene, maximum R: 106.1% for 1,2-dichloroethane) are still well within the program's DQOs.

The described sample analysis performance was achieved during normal laboratory operations, and instances where work had to be repeated to satisfy QC requirements were very infrequent (i.e., less than 3% of total analysis time). Since analysis costs averaged $800 per sample, the cost for rework (i.e., price of nonconformance) was about $24 per sample. For the time period considered, close to 1,000 samples were analyzed, so total analysis costs were about $800,000 of which the cost for rework to satisfy QC requirements was at most $24,000.

In contrast to program DQOs being rather simply and inexpensively satisfied through good laboratory practices, satisfaction of program statistically-based QC requirements proved to be both difficult, if not impossible, and expensive. Summaries of statistical test results are provided in Tables 4 and 5.

As is the case for the LCS analysis results, average P&A results for the statistical test results are all well within program DQOs. Additionally, the statistical test results show:

(1) average precision for each data set is generally much better (i.e., smaller RSD) than that compiled from all LCS analyses
(2) magnitude of dat set precisionis directly related to the length of time for conducting data set analyses
(3) data set precision approaches overall LCS analysis precision for data set analysis time intervals of about six months or more

Table 4. Method 430.1 (GC/MS) statistical test results for VOC analyses.

Data Set Identification Number	Analysis Time Period (dates)	(days)	Replicate Analyses (number)	Average Precision (% RSD)	Average Accuracy (% R)	Statistical Test Results for Compounds Statistically Equivalent (%): Data Set Compared To (ID)	Precision	Accuracy	Precision & Accuracy
1	02/18/92 - 02/24/92	7	30	3.62	99.2	NA			
2	10/05/92 - 10/05/92	1	7	2.69	105.6	1	78	30	17
3	10/05/92 - 10/23/92	19	7	4.30	97.2	2	96	48	43
4	10/05/92 - 04/15/93	30	30	5.54	99.8	NA			
5	05/15/93 - 06/18/93	34	7	3.86	98.7	4	61	61	39
6	06/22/93 - 08/10/93	49	7	2.03	99.5	5	61	74	39
7	12/22/92 - 08/10/93	231	30	5.45	99.6	NA			
8	11/17/93 - 03/18/94	121	7	4.92	92.4	7	69	17	13
9	02/23/93 - 03/18/94	388	30	5.55	97.1	NA			

NA = Not applicable. New initial (i.e., 30 replicate analyses) data set.

Table 5. Method 440.1 (GC/FID) statistical test results for VOC analyses.

Data Set Identification Number	Analysis Time Period (dates)	(days)	Replicate Analyses (number)	Average Precision (% RSD)	Average Accuracy (% R)	Statistical Test Results for Compounds: Data Set Compared To (ID)	Statistically Equivalent (%): Precision	Accuracy	Precision & Accuracy
1	03/11/92 - 03/17/92	7	30	1.40	99.5	NA			
2	09/14/92 - 09/14/92	1	7	0.91	101.7	1	100	20	20
3	09/18/92 - 09/18/92	1	7	0.92	101.4	2	100	100	100
4	03/04/93 - 04/26/93	53	30	7.25	94.1	NA			
5	06/30/93 - 08/10/93	41	7	6.13	84.1	4	80	40	40
6	08/11/93 - 10/06/93	56	7	4.45	90.1	5	100	20	20
7	04/09/93 - 10/06/93	180	30	7.80	86.7	NA			
8	01/20/94 - 03/10/94	49	7	3.21	96.4	7	60	20	20
9	04/22/93 - 03/10/94	322	30	11.86	89.8	NA			

NA = Not applicable. New initial (i.e., 30 replicate analyses) data set.

In five comparison between data sets, however, statistical equivalency between two data sets at the 95% confidence level was never satisfied for all 29 compounds. Examination of the statistical test results indicate the inability to obtain statistical equivalent data sets was due mainly to data set precision being more stringent than differences in accuracy between data sets. Apparently, P&A data generated from replicate analyses over short time intervals as specified by the program are not representative of actual method performance during routine sample analyses. This also means the accuracy of sample confidence limits estimated from such P&A data is questionable.

In conducting the statistical tests, data sets 1-4 were compiled by replicate reference standards analyses conducted independently of routine sample analyses. This required at least 60 analyses with costs of about $48,000 for analyses and $6,000 for data compilation and evaluation. For the time period considered the statistical tests cost was about 15% of total laboratory costs. In early 1993 it was concluded that data sets analyzed over short period of time (i.e., few days to few weeks) were not providing representative P&A data, so subsequent data sets were compiled from LCSs analyzed during routine sample analyses. Using LCS analysis results for the statistical tests greatly reduced costs for the tests to less than 2% of total laboratory costs; however, the data sets were still not statistically equivalent. Without incurring substantial additional expense to implement extremely stringent QC procedures (i.e., about 10 times more restrictive than current DQOs), it is unlikely the statistical tests as specified by the program could ever be satisfied and the data representative of routine analysis method performance.

A more practical approach to obtaining representative P&A data would be a moving average of LCS analysis results; this would also be the most cost effective approach since LCS analyses are required as part of routine sample analyses. Since the primary purpose of the P&A data is for assigning upper confidence limits to selected sample analysis results, replicate analyses of the sample in question would be a much more direct and representative way to obtain that information. Another potential technique for obtaining representative precision information is one-way analysis of variance (one-way ANOVA). By subjecting all replicate sample and replicate LCS analysis results to one-way ANOVA, representative analysis precision would be provided by the one-way ANOVA error sum of squares term (i.e., variation within individual samples).

CONCLUSIONS

Comparisons of objective-based and statistically-based quality control (QC) measurement results from volatile organic compounds analyses of gases revealed some distinct differences. In general for the two year time period and the gas chromatography and gas chromatography/mass spectrometry analysis techniques considered, objective-based QC was effective and inexpensive while statistically-based QC was ineffective and expensive.

More specifically, key observations and differences between the two approaches are as follows:

Objective-Based Quality Control

- Effective - over 99% compliant with QC specifications
- Inexpensive - less than 3% of total analysis costs
- Representative - measurement QC limits consistent with analysis method capabilities
- Workable - measurement QC limits easily and consistently satisfied during routine laboratory operations

Statistically-Based Quality Control

- Ineffective never fully compliant with program QC requirements
- Expensive - up to 15% of total analysis costs
- Unrepresentative - short period (days) precision and accuracy (P&A) data not representative of long period (months) analysis method performance
- Unworkable statistical equivalency of P&A data between data sets from replicate analyses not demonstrable at 95% confidence level

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A CASE STUDY COMPARISON OF A HTW DATA EVALUATION PROCEDURE USING EPA SW-846 AND ARMY CORPS OF ENGINEERS ENGINEERING PROTOCOL AND THE EPA CLP FUNCTIONAL GUIDELINES METHOD OF DATA EVALUATION

Ajmal M. Ilias, Chemist and George J. Medina, Chemist, U.S. Army Corps of Engineers, 1491 N.W. Graham Ave. Troutdale, Oregon, 97060-9503

ABSTRACT

Historically, EPA functional guidelines have been used for data evaluation of environmental studies with mixed reviews from the analyst and regulators. The CLP methods and functional guidelines have been effective for certain matrices and projects; however, it has come under scrutiny as being, excessively voluminous with documentation and not cost effective. There is a need for a comprehensive, yet practical data evaluation procedures, particularly for complex matrices, that is also cost effective. Using EPA SW-846 methods and quality control protocols, the Corps of Engineers has established a quality assurance program that is comprised of the evaluation of ten - percent quality assurance splits by an impartial referee laboratory (inter-laboratory) for the evaluation of precision, accuracy, reproducibility, comparability and completeness (PARCC). A case study of a remedial action with specific EPA clean-up goals that uses the CLP and SW-846 data evaluation procedures in conjunction with Corps of Engineers guidelines, is presented and discussed.

INTRODUCTION

The contract laboratory program (CLP) and SW-846, for the majority of analytical methods, have common functional data evaluation elements, such as dealing with laboratory blanks, detection limits, surrogate recoveries, matrix spike (MS), matrix spike duplicate (MSD) recoveries and relative percent differences (RPDs) obtained either from duplicate analysis or from the MS and MSD recoveries. In spite of the above mentioned controls, the following elements are not completely covered by either system; (a) confidence, (b) reliability, (c) comparability and (d) completeness. Both systems have stringent guidelines about data precision and accuracy but are monitored or approached differently. CLP has established guidelines for accuracy, which is obtained from surrogate and MS/MSD recoveries. Precision is obtained from the analysis of duplicate samples or calculated from the MS and MSD recoveries. In the case of SW-846, laboratories are suppose to establish their own acceptance criteria through a series of experimental analysis for each method of interest and matrices. In the case of CLP, accuracy and precision of the laboratories vary from laboratory to laboratory and the method does not articulate specific evaluation criteria. In addition to differences in precision and accuracy by both systems, there are quite a few variability in protocols for the determination of detection limits, the number of targeted analytes covered, the standards to be used and the execution of the initial and continuing calibration, holding

times and sample preservation. Because of this ambiguity, there is a tendency, on the part of the scientific community and environmental laboratory staff, to use the interchangeable guidelines of CLP and EPA SW-846.

In the interest of expediency, only notable difference that impact data evaluation will be addressed. The Army Corps of Engineers approach is to require the use EPA SW-846 Methods and criteria by laboratories performing analytical work. Ten percent of the samples are pulled in triplicate, with blind duplicate splits (intra-laboratory), called quality control (QC) samples being submitted to the primary laboratory and the remaining split, called the quality assurance (QA) sample being sent to an impartial referee laboratory (inter-laboratory). Data obtained in this manner is legally defensible with a high degree of confidence derived from PARCC evaluation and assessment. Data from eleven ground water studies from Ft. Lewis Logistics Center, Washington, are chosen to demonstrate the effective use of data evaluation procedures using CLP protocol and EPA SW-846 in conjunction with the Army Corps of Engineers QC and QA approach.

EXPERIMENT AND DATA EVALUATION

An ongoing ground water monitoring study, Fort Lewis Logistics Center, Deep Aquifer Study, is chosen to demonstrate the effectiveness of the two systems of data evaluation. Eleven groundwater samples including one blind duplicate, three project trip blanks and one project rinsate were collected by an architectural engineering firm (AE) for the project laboratory. One QA sample with a trip and rinsate blank were collected by the same AE firm at the same time for the QA laboratory to evaluate and compare against the project blind duplicate data generated by the project laboratory, a sub-contractor of the AE.

The analytical methods used are Methods For Chemical Analysis Of Water and Waste (1), Test Method For Evaluating Solid Waste (2), and Method For The Determination Of Organic Compounds In Drinking Water (3).

All samples were analyzed for volatile organics (VOC) by EPA Method 524.2 or 8260, semi-volatile organics (BNA) by EPA Method 8270, chlorinated pesticides/PCB by EPA Method 8080, twenty-three total and dissolved metals using EPA Method 6000/7000 series and cyanide by EPA Method 9010. Trip blanks were analyzed for VOC only. The data evaluation procedures used CLP functional guidelines and SW-846 method required guidelines along with Corps of Engineers inter and intra data comparison procedures, which are detailed in Table 1. Inter and intra data comparisons of VOC in Table 2 and total metals in Table 3 are presented. The data comparisons of other methods are not presented since no disagreements between the data of the two laboratories were found. Because of limited space, data of trip and rinsate blanks are not shown but are discussed later in the data evaluation comparison in Table 1. The Corps of Engineers collects and analyzes ten percent of all samples or at least one duplicate or sequential samples, whichever is greater for each matrix, for the comparison and evaluation of the project

laboratory's data. In this case study, the QA data were evaluated by the Corps of Engineers, similar to project data evaluation presented in the left column of Table I. After evaluation, the QA data were compared with project blind duplicate data. Tables 2 and 3 evaluate and compare the QA and the project data to assess comparability, completeness and confidence.

Table 1. Comparison of Data Evaluation Procedures

	Evaluated by Corps of Engineers	Evaluated by Architectural Engineering Firm
QC Items Covered	Use of SW-846 Method required QC and Corps of Engineers inter and intra laboratory data comparisons approach.	EPA CLP Statement of Work for organic (No. OLM01) and inorganics multimedia document and (OLM02.1) 1991.
a. Surrogates:	Surrogate recoveries in BNA and pesticides/PCB were within laboratory established (LE) or method required QC limits and were accepted. The surrogate recoveries in VOC samples LC-35D, -41D, -41F, -21C, -41E, -67D, -26D, -35DR, -21ER, LC-26DMSD, -41D and -41F (after dilution) were above LE or method required QC limits. Of these out of control recoveries, the data of re-run samples LC-21CR, LC-41ER and LC-67DR were acceptable as one of the two surrogate were marginally out side the QC limits and are acceptable. The surrogate recoveries in all trip, rinsate and laboratory blanks of EPA Method 524.1 were within method required QC limits and are acceptable.	All field BNA and associated control samples of surrogate recoveries were within special QC criteria. No surrogate recoveries of chlorinated pesticides/PCBs were mentioned. Surrogate recoveries for volatile organic analysis exceeded criteria in samples LC-35-D, LC-41D, LC-41F, LC-21C, LC-41E, LC-67D and LC-26D. Re-analysis of the samples revealed the same high surrogate recoveries exceeding criteria. Samples LC-21C and LC-41E were re-analyzed at a 1:10 and 1:20 dilution, respectively, due to high analyte concentrations. Surrogate recoveries of these dilutions were also high. Sample LC-26D had high surrogate recovery but was not re-analyzed in accordance with the CLP protocol. All surrogate results with recoveries out of specification were qualified as estimated (J). LC-21C re-analyses results were not qualified as only one surrogate slightly exceeded the QC limit.

	Evaluated by Corps of Engineers	Evaluated by Architectural Engineering Firm
b. Matrix Spike (MS) and Matrix Spike Duplicates (MSD) Recoveries:	Six out of ten MS and MSD of Method 524.1 were above upper QC limits. VOC data are questionable due to surrogate, MS and MSD recovery failures. Three out of twenty-two MS and MSD of Method 8270 were above QC limits; data were not affected as no targeted analytes, with the exception of (bis 2-Ethylhexyl) phthalate, detected in one sample. MS and MSD of pesticides/PCB's were within QC limits and are acceptable. MS recoveries of about one-half of the metals were outside QC limits. Data are accepted based on acceptable post-digestion and laboratory control recoveries.	Sample LC-26D was analyzed as a volatile organic compound MS/MSD. Six out of ten spike recoveries exceeded the method QC limits. All percent RPDs were within specified criteria except for chlorobenzene. Based on the result of MS/MSD and surrogate analyses, field sample with surrogate recoveries out of specification were qualified as estimated (J). All volatile organics analyses are acceptable. Three out of twenty-two BNA spike recoveries exceeded method QC limits. The N-nitro di-n-propylamine recovery was fourteen percent, but was outside the advisory QC limits. Field sample data was not qualified on the basis of MS/MSD criteria in accordance with the functional guidelines. All BNA data are acceptable. Pesticides and PCBs MS/MSD results met all QC criteria and indicated acceptable precision and accuracy. Samples LC-26D and T-9E were analyzed as total metals matrix spike samples. Samples LC-41E and T-9E were analyzed as dissolved metals matrix spikes. LC-35D and LC-47D were analyzed as total and dissolved mercury matrix spikes, respectively. QC criteria for metals is 75-125 percent. In accordance with data validation guidelines, arsenic, beryllium, cadmium, antimony, manganese and vanadium results greater than the IDL for total metals were assigned estimated (J) qualifiers. Thallium total metals results were qualified as usable (R) for all non-detected values. For the dissolved metals, cadmium, thallium and antimony non-

detected values were qualified as unusable (R) due to low recoveries. Manganese sample results below the IDL and positive detects were qualified as estimated (UJ) for both total and dissolved samples. Mercury dissolved and total analytical results below the IDL were also qualified as estimated (UJ). Cyanide percent recoveries were not reported.

	Evaluated by Corps of Engineers	Evaluated by Architectural Engineering Firm
c. Laboratory Duplicate Analysis:	The relative percent differences (RPDs) of VOCs, BNAs and pesticides/PCB's were within QC limits except one out of five VOCs and six out of ten BNAs which were above QC limits. BNA data were not affected as no targeted analytes except phthalates were detected. The RPD of beryllium, barium, iron, zinc, aluminum, antimony, cadmium and copper ranged from 31 through 200-percent, indicating large analytical variation. Data of these metals should be considered estimates.	RPDs of organics were discussed along with MS/MSD recoveries. Inorganic duplicates analyses discussed as follows. Duplicate sample analyses was performed on samples LC-26D (total) and T-9E (total and dissolved). Applying the control limits of +/- 20 percent relative percent difference (RPD) for sample 5XCRDL, zinc, cadmium and iron results in sample T-9E (total) were outside criteria. An estimated qualifier J was assigned to zinc, cadmium and iron results for the total metals only.
d. Blind Duplicates:	Blind duplicate data are shown in Tables 2 and 3. All data agree except for methylene chloride and toluene in Table 2, due to varying degree of laboratory contamination. Blind duplicate data of other methods are shown in Corps of Engineers unpublished chemical quality assurance report (4). All blind duplicate results were found within a factor of three to each other and were considered comparable.	Blind duplicate results were not presented.
e. Laboratory Blanks:	VOC laboratory blanks were contaminated with methylene chloride, toluene and BNA. Blanks were contaminated with 1-methylbenzene. Data of these analytes are not applicable for site evaluation. Laboratory blanks of all other methods were free of targeted analytes.	Methylene chloride and toluene were detected in VOC blank. Other laboratory blanks were free from targeted analytes.

	Evaluated by Corps of Engineers	Evaluated by Architectural Engineering Firm
f. Trip Blanks:	Up to ten VOC analytes, ranging in concentration from detection through 3.24 ppb were detected.	Not discussed/Not included with data evaluation.
g. Rinsate Blanks:	Seven VOCs, ranging in concentration from 0.9 through 2.04 ppb were found. 30 ppb of methylbenzene was found in the BNA rinsate and up to 858 ppm of four alkali and alkaline earth metals were found in the filtered and unfiltered rinsates. Data of these analytes should be considered with caution.	Not discussed/Not included in the data evaluation.
h. Holding Times:	Discussed	Discussed
I. Detection limits, tuning and mass calibration	All met method requirements and are acceptable	Not included in data evaluation package or not discussed
j. Initial and Continuing Calibration:	Not discussed in this project. Inadvertently left out.	Discussed in detail for VOC and BNA methods. No discussion of initial or continuing calibrations were found for chlorinated pesticides/PCB, metals or cyanide.
k. ICP Interference Check:	Not discussed	Interference check sampler (ICS) were run at the beginning and end of each sample analysis. Sodium and potassium analysis did not include an ICS at the end of the sample run. All reported recoveries were within 20 % of the true value. All laboratory control sample results were within 80-120 % recovery.
l. Overall Evaluation of the Project Laboratory's Data:	Project data were accepted except for the following. I. Ten VOC analytes found in the trip blanks are identical in	No data were rejected. All data were used with some sort of qualifier.

concentration to that found in most samples except for trichloroethene (TCE) and cis-dichloroethene (cis-DCE) in samples LC-41D and LC-41F. The analytes found in the trip blanks should be treated with caution.

II. Seven VOC analytes were found in the rinsate blanks; data of these analytes should be viewed with caution.

III. The data of methylene chloride and methylbenzene should be discarded due to their presence in all laboratory blanks.

IV. Certain metals were found at higher levels in the filtered samples than the unfiltered samples. Recommend rechecking for possible switch between filtered and unfiltered samples.

V. Data of beryllium, barium, iron, zinc, aluminum, antimony, cadmium and copper should be considered estimates due to the high degree of analytical variability.

Table 2: COMPARISON OF PROJECT BLIND DUPLICATE AND QA RESULTS

Project: Ft. Lewis Logistics Center, Deep Aquifer Study Matrix: Water Prefix: LC-41
Project Laboratory: Hittman Ebasco QA Laboratory: CAS, Inc.

Method: Volatile Organics (EPA 524.2) Units: ug/L (ppb)

Analytes Detected	Project Lab -D Initial	Project Lab -D Re-analysis	Project Lab -F Initial	Project Lab -F Re-analysis	Detection Limits	QA Lab -F	QA Lab Detection Limits
Methylene Chloride	2.28	13.8	2.13	27.2	0.10-2.00	ND	2.0
cis-1,2-Dichloroethene	22.4	21.4	19.8	20.0	0.10-2.00	16	0.1
Benzene	0.4 J	ND	ND	ND	0.10-2.00	ND	0.1
Trichloroethene	137	155	119	145	0.10-2.00	130	0.1
Toluene	ND	1.89	0.24	ND	0.10-2.00	ND	0.1
Ethylbenzene	ND	0.51 J	ND	ND	0.10-2.00	0.2	0.1
Total Xylenes	ND	0.58 J	ND	ND	0.10-2.00	ND	0.3
1,1,1-Trichloroethane	ND	ND	0.68	ND	0.10-2.00	0.6	0.1
Trans-1,2-Dichloroethene	ND	ND	ND	ND	0.10-2.00	0.2	0.1
Chloroform	ND	ND	ND	ND	0.10-2.00	0.1	0.1
Tentatively Identified Compounds							
Hexane	0.4	ND	50	ND		ND	
Methylcyclopentane	ND	ND	8	ND		ND	

J = Estimated concentration
ND = None detected

SUMMARY: The project blind duplicate and QA data agree for all targeted analytes except for methylene chloride, toluene and 1,1,1-trichloroethane. Data discrepancies for methylene chloride and toluene are probably due to laboratory contamination of the project laboratory. The 1,1,1-trichloroethane discrepancy is due to analytical variations of the project laboratory, as it was found in one out of four trials at close to that reported by the QA laboratory. Data comparisons at close to or below detection limits are not significant.

Table 3: COMPARISON OF PROJECT BLIND DUPLICATE AND QA RESULTS

Project: Ft. Lewis Logistics Center, Deep Aquifer Study Matrix: Water Prefix: LC-41
Project Laboratory: Hittman Ebasco QA Laboratory: CAS, Inc.

Method: Dissolved Metals (EPA 6000/7000 Series) Units: ug/L (ppb)

Analytes Detected	Project Lab -D	Project Lab -F	Detection Limits	QA Lab -F	Detection Limits
Arsenic	ND	ND	97.0	80	50
Antimony	ND	ND	3.0	ND	3
Arsenic	1.3	1.3	--	ND	1
Barium	19.4	17.8	--	ND	5
Beryllium	ND	ND	0.2	ND	0.2
Cadmium	ND	ND	0.1	0.7	0.1
Calcium	9500	9480	--	11,900	50
Chromium	ND	ND	2.2	ND	5
Cobalt	ND	ND	8.7	ND	10
Copper	ND	ND	11.0	ND	10
Iron	ND	ND	13.0	140	20
Lead	ND	ND	3.0	4	2
Magnesium	5010	4970	--	6240	10
Manganese	ND	ND	3.4	6	5
Mercury	ND	ND	0.2	ND	0.5
Nickel	ND	ND	22.0	ND	20
Potassium	978	1170	--	ND	2000
Selenium	ND	ND	3.3	ND	5
Silver	ND	ND	2.8	ND	10
Sodium	9050	ND	--	5900	100
Thallium	ND	ND	1.0	ND	5
Vanadium	ND	ND	4.0	ND	4
Zinc	27.9	15.6	--	140	10

-- = Not reported
ND = None detected

SUMMARY: The project blind duplicate and QA data agree within a factor of three to each other or their detection limits except for zinc. A higher zinc level was found in the QA filtered samples than the unfiltered samples, where no zinc was detected at 10 ppb. This anomaly could be due, in part, to field filtration procedures, sample bottles used or a sample switch that may have occurred during sample labeling or loading into auto-sampler in the laboratory. Iron data discrepancies could not be resolved analytically. Both laboratories had acceptable internal QC data

RESULTS AND DISCUSSIONS:

An advantage to the CLP data evaluation procedure is the thoroughness of the review and validation of data by going back to the raw data. The CLP evaluates, at a minimum, ten percent of all raw data. Recalculation of data serves as a check to assure data validity. Unlike the Corps of Engineers, the CLP procedure evaluates the initial and continuing calibration of GC/MS analyses and reviews and confirms that GC/MS tuning parameters are within the specified acceptance criteria. Similarly, the CLP validates that matrix interference checks have been used when EPA Method 6010 metals are reported, where the Corps of Engineers does not. This effort on the part of CLP assures that false positives, due to positive matrix interference, are not reported.

The Corps of Engineers QA report preparation comprises review and evaluation of all internal QC data. There is no re-calculation of raw data since contractually three levels of review are required. Both the CLP and SW-846 Corps of Engineers analytical programs emphasize demonstration of precision and accuracy. However, it is the opinion of the authors that reproducibility, comparability and completeness is not emphasized sufficiently by the CLP program. In addition to the mandated demonstration of accuracy and precision, the Corps of Engineers requires ten percent inter and intra laboratory data comparison. This requirement is key to meeting the extended requirements of aforementioned PARCC.

The trip and rinsate blanks data checks for potential cross contamination during sample shipment/storage and collection, respectively. Up to ten VOC and about one and a half dozen of the targeted analytes were detected in the trip and rinsate blanks (this data is not provided in this paper). Because the CLP data evaluation process does not address trip/rinsate blanks sufficiently, erroneous false positives can skew the data assessment. Unaccountable cross contamination can impact engineering decisions in a negative way.

Data reproducibility and comparability are shown in Tables 2 and 3. In about ten detected analytes of VOCs (Table 2), data of methylene chloride, toluene and 1,1,1-Trichloroethane did not agree due, in part, to the project laboratory's varying degree of laboratory cross contamination and variation of data close to the detection limits. All twenty-three metals in Table 3 agree within a factor of three to each other or their detection limits except for the data of inorganic zinc. These data disagreements or anomalies could be due, in part, to cross contamination encountered in the field, sample switching (total/dissolved), sample mis-labeling, or incomplete filtration of dissolved samples. Two out of three project and QA samples were compared to the data of the dissolved samples portion present in this table. CLP data evaluation procedure often do not account for these types of anomalies. Overall, Corps of Engineers data evaluation coupled with internal QC elements of SW-846 provide data that would meet PARCC requirements.

ACKNOWLEDGMENTS:

The authors are grateful to Mr. Timothy Seeman, Director, U.S. Army Corps of Engineers, North Pacific Division Laboratory.

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12

Contract Management Strategies for Overseeing Laboratory Analysis - Special Analytical Services

Sean J. Kolb, DynCorp Viar, Alexandria, Virginia 22314

ABSTRACT

The Special Analytical Services (SAS) program has provided CLP data users access to non-routine analytical services since 1982. These services are based on technical requirements developed by the data user and have been obtained by subcontracting with commercial environmental testing laboratories through the USEPA's Sample Management Office contractor. In several instances, the subcontractor community may be unable to provide the services as requested by the Regional client. These situations can lead to unusable data that can cause delays in Superfund site remediation activities. Since 1990, numerous modifications have been made to the contract management system used by the SMO contractor in managing these activities. This paper will outline the overall SAS program and will examine six separate case studies of highly visible SAS projects. These case studies will include a summary of the scope of each project and the issues involved. The issues in these case studies include the data users need for fast turnarounds and/or low detection limits, method/laboratory performance problems, complex sample matrices, and data reporting requirements for the projects. These case studies will also review the problem-solving approaches used by the Region, SMO contractors and laboratory subcontractor for addressing these issues, and how the results of these projects have been applied to the continuous improvement of the SAS program. These results of these case studies show that there are common characteristics and strategies for successfully managing and obtaining these types of services.

CREATION OF A SITE-SPECIFIC SOIL LABORATORY CONTROL SAMPLE FOR THE IDAHO NATIONAL ENGINEERING LABORATORY

S. J. Sailer, J. M. Connolly, T. R. Meachum, EG&G Idaho, Inc., Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415; R. B. Chessmore, RUST Geotech, Inc., P.O. Box 14000, Grand Junction, Colorado 81502-5504

ABSTRACT

Natural soil matrix quality control (QC) materials are needed to evaluate analytical method performance in support of Environmental Management (EM) projects. Commercially available materials are usually synthetically prepared and may not adequately mimic the specific chemical and physical characteristics of actual field samples. The use of site-specific natural soils as QC materials ensures that analytical method performance will be comparable between the QC materials and the site's routine field samples. The Idaho National Engineering Laboratory (INEL) has developed a site-specific soil material for use as a laboratory control sample (LCS) which will be provided to laboratories supporting EM projects as a quality improvement tool.

The LCS was created from residual samples of radioactively contaminated soil collected as part of characterization activities at the INEL during 1990. Data from the original analyses of the residual samples provided baseline information to develop a formulation scheme for the LCS. Certain metal analyte concentrations were enhanced to desired levels through the addition of natural mineral source materials.

This paper discusses the protocols used for the preparation, verification of homogeneity , and characterization of this material. Characterization of the material was limited to the 23 metal target analytes of the Contract Laboratory Program (CLP) and 10 radionuclides historically detected at the INEL. Metal analyte concentrations were characterized using the CLP methods that are routinely used on INEL field samples. Radionuclide characterization utilized total dissolution procedures with the determinative method selected by the participating laboratories.

Analyte concentration control limits for the LCS material were statistically derived from the characterization data, and will be updated as the material is used. Results of the characterization and control limit determination are presented, along with lessons learned during the preparation and characterization processes.

AUDIT STANDARDS FOR FIELD SAMPLING AND FIELD MEASUREMENT

Bob Newberry and Dave Bottrell, Office of Environmental Restoration and Waste Management, EM-563
Michael Johnson, United States Department of Energy, Environmental Measurements Laboratory, New York, NY 10014.

ABSTRACT

A well established and supported audit program is critical to the success of the characterization, remediation and post-closure monitoring activities at DOE facilities. The Office of Environmental Restoration and Waste Management (EM), Laboratory Management Division (EM-563), is responsible for assuring that all EM operations are effectively performing the environmental sampling and field measurement services required. In support of this goal EM-563, along with the Department of Energy's, Environmental Measurements Laboratory, (EML), has developed a series of audit standards. These standards provide detailed questions related to various Quality Assurance (QA), operational and technical aspects of the operation of many of the most commonly used field sampling and field measurement equipment and procedures. In support of these audit standards these is a companion guide is being developed that explains the technical reason for the question, the intended response and typical problems and limitations associated with using the specific field sampling or field measurement devise.

The standards cover field sampling for liquid, soil, sediment, sludge, air, surface and vegetation matrices. The standards address devises such as COLIWASAs, direct emersion samplers, lysimeters, scoops, augers, corers, triers, split spoon samplers, various types of dredges, filters, impingers, canisters, traps and various types of equipment for soil gas sampling. The standards for field measurement cover the same matrices as the sampling equipment and address devises such as oxygen meters, portable combustible gas indicators, portable Flame Ionization Detectors (FIDs), portable Photoionization Detectors (PIDs), calorimetric indicator tubes, electrodes, enzyme test kits, portable Dissolved Oxygen (D.O.) meters, spectrophotometers and X-ray fluorescence equipment. Also covered are field radiation measurements using devises such as proportional counters, G-M counters, semiconductor detectors, solid scintillation and liquid scintillation detectors.

These audit standards are being designed for assessments of DOE/EM contractors. They can also serve as guidance for an internal assessment program at any facility performing field sampling and field measurement activities.

QUALITY ASSURANCE FOR THE EPA REGION V ESAT FIELD ANALYTICAL SUPPORT PROGRAM

Lewis Kranz and Dennis Miller, Lockheed Environmental Services Assistance Team, Region V, Chicago, IL 60605 and *Jay Thakkar,* USEPA, Regional Project Officer, CRL Region V, Chicago, IL 60605

Abstract

To achieve the goal of properly documenting the quality of the analysis data generated, an effective mobile laboratory program for on-site field analyses requires a quality assurance/quality control program containing not only standard operating procedures (SOPs) for sample preparation and analysis, but also for sample tracking, data management, data validation, data communication and other logistical support. The QA/QC program must be both flexible and stringent to accommodate variable reporting timeframes for appropriately reviewed data for both short term (one to two weeks) projects and long term (three to ten weeks) projects involving analyses of generally site specific target compounds (i.e. VOCs, PAHs, PCBs, pesticides, etc.) in multiple matrices. The QA/QC program must include uniform procedures and checklists easily utilized by different analysts performing different analyses.

Environmental Services Assistance Team (ESAT) chemists utilize EPA Region V Central Regional Laboratory mobile laboratory equipment and instrumentation to support field screening analysis needs of Superfund sites. A quality assurance program has been developed and implemented which effectively documents the complete field laboratory process tracking from sample receipt to the approval of the final deliverable. The overall sophisticated QA process allows for stepwise checks and balances through interlocking SOPs encompassing sample tracking, extraction, analysis, data handling, rapid field data review, timely field data reporting and final QC data approval. An examination of the ESAT field QA preparation, review and approval processes demonstrates that field screening analyses in the laboratory can provide data equivalent to that of a static laboratory. Effective utilization of definitive operational procedures and appropriate quality control measures for an on-site mobile laboratory program can provide the associated documentation of laboratory processes necessary to ensure the defensibility of field screening data for litigation purposes.

Introduction

Lockheed utilizes the EPA Region V ESAT Field Analytical Support Program (FASP) mobile laboratories to provide on-site, real-time analysis of soils, sediments, soil gas, waters, oils and wipes for selected organic and inorganic analytes. Field operations primarily support Superfund activities and may include field screening analyses for site characterization, cleanup, monitoring and spill response. Sample analyses are conducted using modified static laboratory protocols which can accommodate turnaround of analytical results within 24 hours of sample receipt. FASP analyses are conducted within a quality assurance program which maintains quality control through a progression of checks and balances administered throughout the field operations. The chain-of-custody established during field sampling is maintained by in-laboratory chain-of-custody processes throughout the entire analytical sequence from sample receipt to the submission of hardcopy data package to the data user.

The mobile laboratories are maintained in a "road-ready" status and have the capability to rapidly move on-site and be utilized for multiple analyte analysis of a large number of samples in either a short or extended timeframe. The field screening routinely analyses routinely performed in the mobile laboratories include volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and selected metals by x-ray fluorescence (XRF). The site specific target compounds or elements of interest and the required detection limits are determined prior to mobilization to the site. Table 1 gives a representative list of sites where FASP mobile laboratories have been utilized for field screening analyses.

Program Development

The FASP laboratories have primarily been utilized at Superfund sites but the analysis services are also available to NPDES and RCRA projects.

1. Laboratory Personnel

FASP mobile laboratory personnel are degreed chemists experienced in sample preparation and GC or GC/MS analysis. The FASP chemists perform routine "CLP type" sample analyses at the Region V Central Regional Laboratory and review/validate CLP and PRP data packages when they are not in the field. When new technology, new instrumentation or new analysis procedures are incorporated into existing FASP SOPs, the field chemists are thoroughly trained and must demonstrate proficiency before being allowed to utilize the "new methods"

for sample analysis. Training and proficiency evaluation are appropriately documented. Immunoassay test kit use is being incorporated into the PAH and PCB analysis SOPs. Two FASP chemists were trained and certified by Ensys to utilize their immunoassay test kits for SW-846 field screening methods 4020 and 4035 for PCBs and PAHs, respectively

A minimum of 2 chemists (for safety considerations) are used to staff the laboratory during any effort, but 3 chemists may be required when multiple analyses are being conducted.

In addition to the laboratory personnel, an available in-office member of FASP is made the Project Lead for any site the FASP laboratory is servicing. This Project Lead provides an in-office contact, coordinates and organizes the analytical data as received from the FASP laboratory into a final report and ensures proper document archiving.

Additionally, the ESAT QA/QC Coordinator is involved in the preplanning of the site project and serves as a check and balance in the review/approval of individual data sets and approval/release of the hardcopy site data set package. To aid in the planning, a questionnaire (see Figure 1) requesting basic information of the site, the analytes of interest, report deliverables and the intended usage of FASP is supplied to ESAT in preparation of on-site operations.

2. Standard Operating Procedures (SOPs)

FASP SOPs have been written for both sample analysis and data quality control (data reporting, logbooks) procedures. A typical analysis SOP includes sample preparation procedures, calibration and analysis procedures, and quality assurance/ quality control (QA/QC) requirements for sample preparation and analysis. Operational procedures identify chain-of-custody policies, sample tracking requirements, report deliverables and data handling protocols. The FASP SOPs currently in use are listed in Table 2.

A FASP mobile laboratory is normally utilized to simultaneously perform field screening analysis for more than one analyte type and thus organizational systems are required to direct specific samples for the proper analyte analysis and report the corresponding sample data in both a daily and comprehensive final manner. Therefore, suitable QA/QC steps with realistic turnaround times have been incorporated into a complete monitoring process which progresses from sample receipt through calibration and analysis to data reporting and data package review.

To achieve this goal, field samples received under chain-of-

custody by the mobile laboratory are logged into a computerized program designed to track individual samples as they proceed progressively through the preparation, analysis and reporting. Table 3 is an example of sample tracking at a recent site where VOA analyses were performed. The samples are entered by their assigned sample ID number along with the date of receipt, analysis parameter and matrix type. Additionally, samples requiring extraction are entered into a site specific extraction logbook and are assigned an unique GC autosampler vial number.

All samples, whether requiring extraction or direct analysis, are analyzed using the sample ID being entered into the instrument run log. The instrument run log is retained in the site logbook and is utilized as a monitoring tool for documentation of the sample trail.

An overall data reporting system was developed using daily data file names for sample tracking and incorporates information derived from the sample receipt date, sample site and analytical parameter. This system is utilized to segregate and compile the individual daily data set packages. The daily list of samples has the corresponding file name assigned permits sorting and listing by ascending sample ID order. This list provides a convenient method for compiling, assembling and reviewing the sample data for subsequent levels of QC review. These data set packages are normally released to the data user in the field within twenty-four hours after sample receipt. This tracking system is updated daily and allows for a check and balance monitoring of incoming samples and outgoing analysis results to ensure that received samples are analyzed and reported within the targeted turnaround time.

Using the established tracking systems, a reviewer can quickly inspect the documentation to ascertain the exact status of any samples received, where a sample is in the analytical process, what level of QC review has been conducted and when/if the data set package has been reported.

3. Deliverables

Due to the timely reporting of the FASP sample analysis data, the FASP reporting deliverables are tailored to efficiently present the analytical results without raw data. The analytical data is summarized in a data set report which consists of a narrative identifying samples, describing analytical problems or anomalies, listing matrix spike recoveries and includes a discussion of the calibrations, the associated blank results and the analytical results listed in tabular form.

The daily analytical data packages are compiled and assembled in the following order: the narrative describing analytical problems or anomalies associated with the samples and/or QC, the blank results, the sample results, QC data package checklist and matrix spike recoveries accompanied by a completed chain-of-custody transfer form.

The final FASP deliverable, prior to dissemination of any information, is reviewed and scrutinized by the two field chemists and the QA/QC Coordinator. This review is aided by the use of a checklist (Figure 2) which identifies the major elements of the data set report and the specific areas of QC focus. Completion of the QC checklist provides documentation that a three tier check encompassing all the pertinent data information has been completed and assembled. The QC checklist is utilized in the data report assembly and data review process, but it is not part of the final data set report.

4. QA/QC Review Process

The samples, calibrations, blanks and spikes are analyzed during the course of a daily analytical run and the corresponding data set is compiled and the appropriate data reporting forms are completed. A narrative detailing the specifics of the analytical results and associated QC is produced on-site by the chemist (designated as QC1) conducting the analysis. The data set package is assembled in the order specified in the appropriate SOP by QC1 chemist using the QC checklist. The entire data set package then undergoes an in-field review by another on-site chemist (QC2). The data set package is either (1) approved by QC2 and the narrative is signed by QC2 and it is then released to the data user as a daily field report or (2) the data set package is returned to QC1 for corrections and the process is repeated until an acceptable data report is signed by QC2. The original field daily report is placed in an individual folder with all the associated supporting raw data as a unique data set package. The daily data set packages generated during field operations are returned to the ESAT home office for a final review by the QA/QC coordinator (QC3). After all of the daily data set packages are approved by the QA/QC Coordinator, each data set package is collated in chronological order to prepare the final data set site report. A case narrative summarizing all of the analytical problems or anomalies associated with the site samples and/or QC is written and the final site report and a chain-of-custody transfer form bearing the appropriate release approvals are delivered to the Lockheed ESAT Team Manager for his review and approval. Flowchart 1 illustrates the routing of samples and analysis under chain-of-custody procedure. The final site report is produced within five days of the conclusion of FASP on-site support activities.

5. Archiving

The raw data and supporting documentation for a FASP operation is archived by site name and date of activity. The hardcopy data set packages are packed into file boxes in chronological order with a copy of the final report and all computer files generated during the effort. In the instances where multiple analyses were conducted during the effort, the data set packages are grouped by analysis type and arranged in chronological order.

6. Audits

The ESAT QA/QC Coordinator has conducted several on-site audits of the mobile laboratory during field operations. The audits have been identified QA/QC areas requiring improvements or modification. The audits also helped highlight deficiencies in extraction and analysis procedures which are being addressed through method development.

The use of PE samples as QC blinds is also utilized to assess the accuracy of the FASP field screening methods. In other cases, representative field samples or extracts were brought back to the CRL for GC/MS analysis to more appropriately qualify field screening results. Modifications are made to analysis procedures when severe matrix problems arise. For example, most Continental Steel soil samples contained significant amounts of petroleum type hydrocarbons which complicated PAH analysis using a GC/FID system. To minimize the number of false positive analytical results, a dual column confirmation procedure was implemented for the dirty samples and a larger extract volume was employed. The SOP changes were documented and appropriately higher detection limits were utilized for reporting non-detects.

7. Method development

FASP flexibility and adaptability has been demonstrated at sites requiring the measurement of analytes not found on the SOP target compound list. For our last field project, precision, accuracy and method detection limit studies were performed for acetone, tetrahydrofuran and methyl ethyl ketone so that these compounds could be incorporated into the site-specific target compound list. Chromatographic parameters were optimized to achieve adequate compound resolution and calibration levels were identified to meet site measurement needs. The generic FASP VOC analysis SOP modifications were documented and the on-site field screening analyses were made using the modified SOPs. Empore disc solid phase extraction (SPE) procedures are being developed and validated for water samples containing PAHs and PCBs because the FASP

liquid/liquid extraction procedures are cumbersome, time consuming and generally have lower analyte recoveries than the SPE procedures.

Conclusions

The sample results reported in FASP data packages generated from on-site field analysis are reviewed 100%. The data review process entails three levels of data scrutiny, approval and a positive release system for the final reported results. Chain-of- custody is maintained throughout the operation from sample receipt to final data set package delivery. The level of documentation of the entire analytical and reporting process coupled with the levels of review assures the capacity of legally defensible data.

TABLE 1

SITES WHERE FASP HAS BEEN UTILIZED

SITE	LOCATION	ANALYTES
Scrap Processing	Medford, Wisconsin	VOAs, PAHs, PCBs, Pb
Evergreen Manor	Roscoe, Illinois	Chlorinated VOAs in soil gas and groundwater
Rockford Groundwater	Rockford, Illinois	Chlorinated VOAs in groundwater
Allied Paper	Kalamazoo, Michigan	PCBs in soil & paper waste
Conrail Rail Yard	Elkhart, Indiana	Chlorinated VOAs
Prestolite Battery	Vincennes, Indiana	Chlorinated VOAs
Continental Steel	Kokomo, Indiana	VOAs, PAHs, PCBs
Circle Smelting	Beckmeyer, Illinois	Pb, Cu, Zn and Fe in sediments by field portable XRF
Galen Myers Dump	Osceola, Indiana	VOAs, PAHs
Maumee River Basin	Toledo, Ohio	VOAs, PAHs, PCBs
Brooklyn Park Dump	Brooklyn Park, MN	Geoprobe collection of soil screening samples
Tomah Armory	Tomah, Wisconsin	Geoprobe collection of groundwater screening samples
Tomah Fairgrounds		
Belvidere Landfill	Belvidere, Illinois	Geoprobe collection of groundwater screening samples

TABLE 2

ESAT REGION V STANDARD OPERATING PROCEDURES LIST
Updated May 11, 1994

SOP NUMBER	SOP NAME	METHOD SOP TITLES
022	FSOILGAS-02	FASP SOIL GAS METHOD
023	FSP-CAL-00	FASP CALIBRATION STANDARDS PREPARATION
024	FSP-PAH-03	FASP POLYAROMATIC HYDROCARBON METHOD
025	FASP-PCB-03	FASP POLYCHLORINATED BIPHENYLS METHOD
026	FSP-VOA-03	FASP VOLATILE ORGANIC ANALYSIS METHOD
027	FSP-XRF-00	FASP X-RAY FLUORESCENCE ANALYSIS METHOD
030	FSPPESTC-00	FASP CHLORINATED PESTICIDE ANALYSIS METHOD
SOP NUMBER	**SOP NAME**	**QA ADMINSTRATION SOP TITLES**
021	FSLOGBOK-00	FASP LOGBOOK MAINTENANCE
008	CASENARR-00	CASE NARRATIVE GENERATION PROCESS
012	CUSTRANS-00	DATA SET CUSTODY (COC) TRANSFER FORM
016	DATASET-00	DATA SET PACKAGE ASSEMBLY
017	DISTSLOG-00	SOP DISTRIBUTION RECORDKEEPING LOG
028	FSPCHLST-00	FASP DATA SET CHECKLIST
029	FASP-HND-00	FASP SAMPLE AND DATA SET PACKAGE HANDLING
031	GEN-APP-00	SOP GENERATION AND APPROVAL PROCESS
038	LABAUDIT-00	LABORATORY ANAYLSIS AUDITS

TABLE 3

LOCKHEED FASP MOBILE LABORATORY
DOUGLAS ROAD LANDFILL, IN
APRIL 21, 1994

RECEIPT DATE	SAMPLE ID	TARGET ANALYTE VOA	MATRIX	VOA DATA REPORT FILE	QC2 CHECK
04/11/94	DRLGG0820	X	WATER	DRLVOA.V11	X
04/11/94	DRLGG0835	X	WATER	DRLVOA.V11	X
04/11/94	DRLGG0850	X	WATER	DRLVOA.V11	X
04/11/94	DRLRW0100	X	WATER	DRLVOA.V11	X
04/11/94	DRLRW0200	X	WATER	DRLVOA.V11	X
04/12/94	DRLGG0624	X	WATER	DRLVOA.V11	X
04/12/94	DRLGG0624D	X	WATER	DRLVOA.V11	X
04/12/94	DRLRW0400	X	WATER	DRLVOA.V11	X
04/12/94	DRLGG0724	X	WATER	DRLVOA.V11	X
04/12/94	DRLRW0300	X	WATER	DRLVOA.V11	X
04/12/94	DRLRW0500	X	WATER	DRLVOA.V11	X
04/12/94	DRLRW0700	X	WATER	DRLVOA.V11	X
04/12/94	DRLGG0221	X	WATER	DRLVOA.V12	X
04/12/94	DRLRW0321	X	WATER	DRLVOA.V12	X
04/12/94	DRLRW0421	X	WATER	DRLVOA.V12	X
04/12/94	DRLRW0521	X	WATER	DRLVOA.V11	X
04/13/94	DRLRW0600	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG0118	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG0121	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG0921	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG1021	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG0118D	X	WATER	DRLVOA.V12	X
04/13/94	DRLMWE011	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG1224	X	WATER	DRLVOA.V12	X
04/13/94	DRLGG1321	X	WATER	DRLVOA.V13	X
04/13/94	DRLGG1421	X	WATER	DRLVOA.V13	X
04/14/94	DRLRW0502	X	WATER	DRLVOA.V13	X
04/18/94	DRLGG1521	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG1624	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG1624D	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG1724	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG0236	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG0251	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG2518	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG2624	X	WATER	DRLVOA.V21	X
04/18/94	DRLGG1918	X	WATER	DRLVOA.V21	X

FIGURE 1

ESAT/FASP USAGE QUESTIONNAIRE

Requestor _____

Mailing Address or Mail Code _____

Phone Number _____

Projected date(s) when services are needed _____
(3-weeks is the maximum amount of time for a single project)

Name of site _____

Location of site (State and nearest city) _____

Brief site history (contaminants & concentrations) _____

_____

_____

_____

What are your data quality objectives? _____

_____

Matrix(ces) and Estimated Sample Number
Soil _____
Water _____
Sediment _____

Target analytes _____

Requested turn-around time for: field analysis results _____
final deliverables at project completion _____

Form of final deliverables _____

Will CLP/CRL confirmation be required? _____
If yes, at what frequency? _____

Do you require technical assistance in other areas (SAS analyses, data validation)? _____
Briefly describe _____

_____

_____

Please return completed form to:

Jay Thakkar
ESAT Regional Project Officer
Central Regional Laboratory
536 South Clark Street
Chicago, Illinois 60605
Mail Code: SL-10C

FIGURE 2

FASP ANALYTICAL CHECKLIST FOR DATA SET PACKAGES

FASP Method:_____ **TID #**_____

Site Name:_____ **Charge Number**_____

Analyst/Date (QC1):_____
Task Lead/Date (QC2):_____
QA Personnel/Date (QC3):_____

		Approvals QC1	QC2	QC3
I	MATRIX (CONTROL)/MATRIX SPIKE DUPLICATE			
1.	The associated samples are properly listed	___	___	___
2.	The header form is correct	___	___	___
3.	Sample QC data matches the quantitation reports	___	___	___
4.	Target analyte and concentrations are listed on MS/MSD form	___	___	___
5.	MS/MSD recoveries and RPDs are correctly reported	___	___	___
II	METHOD BLANK			
1.	The Method Blank Summary is correct	___	___	___
2.	The associated samples are properly listed	___	___	___
3.	The header form is correct	___	___	___
III	INITIAL CALIBRATION			
1.	The initial calibration is present	___	___	___
2.	The initial calibration is within method criteria	___	___	___
3.	External calibration checks are reported	___	___	___
IV	CONTINUING CALIBRATION			
1.	Continuing calibration ran at proper intervals	___	___	___
2.	Each continuing calibration is listed on a form	___	___	___
3.	The concentration and analytes are listed on the continuing calibration form	___	___	___
4.	The %D's are reported	___	___	___
5.	Continuing calibrations that do not meet criteria are discussed in the case narrative	___	___	___
V	FINAL CALIBRATION			
1.	Results of the final calibration are listed on a form	___	___	___
2.	The %D's are reported	___	___	___
3.	If final calibration does not meet criteria samples are "J" flagged and outlier is discussed in the case narrative	___	___	___

FIGURE 2

FASP ANALYTICAL CHECKLIST FOR DATA SET PACKAGES

	Approvals QC1	QC2	QC3
VI SAMPLE RESULTS			
1. A report form is present for all samples/blanks	___	___	___
2. "D" flags and appropriate dilution factors are present for all diluted samples	___	___	___
3. All reported results are properly rounded	___	___	___
4. All MDLs are properly listed	___	___	___
5. The "F" flag is reported for all samples/blanks	___	___	___
VII QUANTITATION REPORTS			
1. Quant reports/chromatograms for all standards	___	___	___
2. Quant reports/chromatograms are present for all samples, blanks and spikes	___	___	___
3. Samples are quanted <u>after</u> calibrations	___	___	___
VIII MISCELLANEOUS			
1. Copies of all extraction records are present	___	___	___
2. Copies of all run logs are present	___	___	___
IX CASE NARRATIVE (Form ESAT-5-007.0 - Case Narrative)			
1. Method, Date, Author are on narrative	___	___	___
2. The narrative is consistent with the facts	___	___	___
3. The narrative has correct spelling	___	___	___
4. The rhetoric of the narrative is correct	___	___	___
X DATA CUSTODY			
1. The data set has been placed in storage	___	___	___

XI COMMENTS

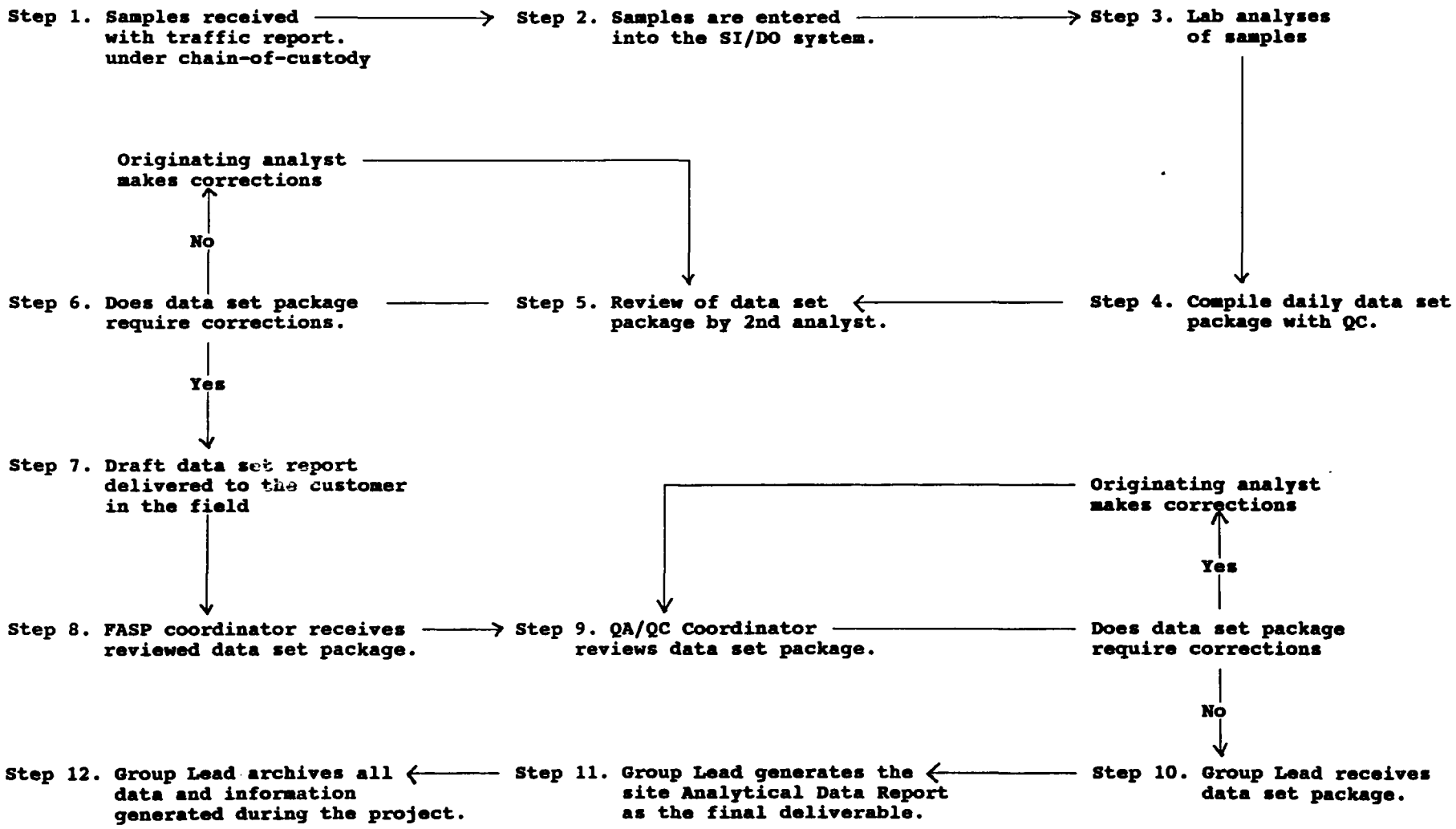
_____
_____
_____
_____
_____
_____
_____
_____
_____
_____

Data Package approved for release: Yes No (Circle) Date_____

Returned for correction of deficiencies: Yes No (Circle) Date_____

FLOWCHART 1

SAMPLE/DATA ROUTING CHAIN-OF-CUSTODY FLOWCHART



The Quantification of Data Quality with Explicit Examples from Organic, Inorganic and Radiochemical Methods

A.D. Sauter, PAR Enterprises, Inc., 217 Garfield Drive,
Henderson, Nevada 89014

ABSTRACT

Knowledge of the quality of sets of environmental data is essential for interpreting test results. While there are those that claim to hold the holy grail of data quality calculations, we show in this paper that data quality calculations can not be described by any one approach. Rather, we demonstrate that environmental data quality must be calculated using different metrics to provide the necessary alternate perspectives on various data features. Using GC, GC/MS, ICP and Gamma Ray Spectrometry environmental data, we show how alternate data quality calculations compliment each other and how they provide insight on given test sets. We also demonstrate how our approach whose essence arises, from exploratory data analysis techniques can be utilized to train junior personnel and others to easily provide environmental data quality insight with off-the-shelf software products.

RAPID SITE ASSESSMENT USING THE QTM SERVICE
A QUALITY ASSURANCE PERSPECTIVE

M. Catherine Eldridge, Environmental Chemist/Analyst, Bruce E. Lane, Technical Analyst, and Loren E. Minnich, Technical Manager/Analyst, DynCorp Viar, Inc., 300 North Lee Street, Alexandria, Virginia 22314-2695

ABSTRACT

In the initial phase of site assessment, it is crucial to identify any further action that may be required to mitigate threats to the environment and to human health. Loss of time and effort due to questionable analytical results may have potentially serious legal and financial consequences for the regulatory and/or enforcement communities. A service which promotes efficiency in collecting samples, laboratory analysis, obtaining data, and making decisions while assuring high levels of quality is essential. The Quick Turnaround Method (QTM) Service provides this necessary degree of quality assurance (QA) while fulfilling the requirements for rapid analysis, reporting, and decision making.

The QTM Service is a powerful tool in screening, monitoring, and performing hazardous waste site assessment activities, providing full organic analyses of twenty volatile organic compounds, fifteen polynuclear aromatic hydrocarbons, fourteen phenolic compounds, nineteen organochlorine pesticides, seven aroclors and toxaphene. Under routine conditions, laboratories providing analytical services for the QTM Service are required to analyze and report analytical results, in an electronic format, within 48 hours (depending upon batch size) from the time of sample receipt. Delivery of the complete, Contract Laboratory Program (CLP) format hardcopy data packages is accomplished within seven (7) days.

To ensure that the laboratories participating in the program are able to meet the requirements of the QTM Service, each of the laboratories successfully performed a stringent prequalification phase. This phase of QA consisted of the analysis of multiple performance evaluation samples by the laboratories and the demonstration of their capabilities through the completion of an on-site laboratory evaluation. When quality laboratory services are linked with the QTM analytical methods, which are designed to permit effective and rapid extractions and instrumental analyses with rigorous quality control (QC) requirements, the user is provided with analytical results of high quality. Additionally, when integrated with the QTM Software systems, incorporating several automated data review functions, the user is able to receive that data, with a variety of validation reports, in a very short period of time.

Through providing analytical results of known and documented quality within 48 to 72 hours (depending upon batch size) with rigorous levels of QA/QC, the QTM Service is a useful tool within the Superfund Program. As the analytical results are available to users rapidly, and are of high quality, the results can be applied to direct sampling efforts and/or be used to monitor the effectiveness of treatability operations, cleanups, and removals with a high level of confidence and efficiency.

INTRODUCTION

In an effort to increase the productivity of the Superfund Program, the United States Environmental Protection Agency (EPA) initiated the Superfund Accelerated Cleanup Model (SACM). SACM was conceived to make hazardous waste cleanups more timely and efficient by focusing on the initial phases of the process, including rapid site assessment, remediation, and removal. As a result, services that support SACM must provide a faster and more efficient process for obtaining defensible, high quality analytical data to support decisions during all phases of the SACM process.

In response to the SACM initiative, the Quick Turnaround Method (QTM) Service was designed to meet a specialized need for keeping site work underway during site characterization studies, treatability studies, and site cleanup. The QTM Service was developed to provide analyses of large numbers of samples in short periods of time. This was made possible by streamlining analytical methods to enable a laboratory to perform many analyses in a rapid turnaround period. Additionally, the QTM Service was created to report analytical results electronically and incorporate automated data review and report generation features to increase the speed of data reporting and validation.

To compliment the efficiency of the QTM analytical procedures and reporting functions, stringent quality control (QC) and quality assurance (QA) activities were implemented. Rigorous QC measures were incorporated into the analytical methods to ensure that the results being reported by the laboratories were of the highest technical quality. The data reporting software applied an automated QA module which aided the laboratory and the user in identifying possible contractual and/or performance issues. Additionally, to assist the user with the data validation and decision-making processes, the software included an automated data validation module.

Once the initial versions of the QTM analytical procedures and software were completed, a pilot program was implemented to serve as a working prototype to evaluate the service. QA of a similar scope to the analytical methods was included in the pilot program to ensure the use of highly qualified laboratories. This function consisted of each QTM candidate laboratory completing multiple performance evaluation sample analyses and an on-site laboratory evaluation. After the placement of contract awards, data deliverables submitted by the laboratories were

routinely assessed for contract compliance and overall laboratory performance throughout the lifetime of the pilot program.

The implementation of the pilot program provided the EPA with a mechanism which would satisfy the Superfund Program's immediate needs for a fast turnaround analytical screening service that included considerable QC and QA measures in the same timeframe. Additionally, the pilot program gave the EPA the opportunity to evaluate and modify the analytical requirements and software systems and ensure that the service continued to provide data of known and documented quality to the various EPA clients.

DynCorp Viar, Inc. worked closely with the EPA on the QTM pilot program by dedicating a team experienced in laboratory procurement, software development, and analytical chemistry. Our role in the pilot program included procuring laboratory services, assisting in the development of automated systems, and monitoring laboratory performance throughout its duration.

THE PILOT PROGRAM

LABORATORY SERVICES

With the initiation of SACM, the U.S. EPA Analytical Operations Branch (EPA AOB) conducted a survey of the EPA Regions to determine the need for a CLP analytical screening service to support the Superfund Program's remedial, removal, and site assessment activities. Based on the results, EPA AOB and the EPA Regions began the development of quick turnaround methods and procedures that would satisfy their needs. During the summer of 1991, the first procurement of analytical laboratory services for the QTM Service pilot program began. The scope of the project offered the EPA Regions full organic analysis for a variety of matrices, including water, soil/solid, oil/oily, and wipe samples, within 48 hours (depending upon batch size) from the time of sample receipt at the laboratory. Under routine conditions, the analytical results would be transmitted directly from the laboratory to the EPA user in an electronic format with complete CLP hardcopy data deliverables being submitted within seven (7) days.

In September 1991, the pilot program was implemented with two laboratories providing a total capacity of up to 9600 fractional analyses over an eighteen month period. The results of the pilot program enabled EPA AOB to test the analytical methods with true environmental samples and identify whether these methods would be adequate to meet EPA Regional needs. Technical comparisons between the QTM results and those of similar EPA methods used for other projects within the CLP provided EPA AOB with additional method performance and comparison information useful in evaluating whether the technical requirements would be achieved. The QTM Regional and Laboratory Software were also enhanced to include valuable QA procedures. The software modules were designed to assemble the analytical results in the

appropriate CLP format, enabling the laboratory to check the data for noncompliance, and reprocess the data, if necessary, prior to submission to the EPA mainframe system. Software was also developed to process the results through an automated data review program which enabled EPA clients to obtain customized, validated reports directly from the laboratory results.

In September 1992, the scope of the QTM pilot program was expanded to enable the EPA AOB to refine the analytical methods, complete testing of software systems, and stress-test both aspects to determine any weak points in the QTM Service. To facilitate this expansion and ensure continued QA, the following processes were developed:

Specific analytical and data deliverable criteria were developed to assess the abilities of potential QTM laboratories prior to field sample analysis. This included the incorporation of a two-step laboratory prequalification period designed to assess a laboratory's ability to meet not only the analytical requirements of the project, but also their ability to deliver compliant electronic and hardcopy data deliverables within the timeframe required. Three laboratories participated in this validation process. In Part 1 of this process, the laboratories completed the analysis of laboratory-spiked samples within an extended (14 day) period of time. This set of analyses was intended to gauge each laboratory's ability to perform and meet all of the technical requirements of the analytical methods. Upon completion of those analyses and obtaining feedback regarding their performance, the laboratories began the analysis of similar samples under real-time conditions (Part 2). This phase was intended to measure each laboratory's ability to meet both the analytical and electronic data transfer requirements of the QTM Service.

The analytical data submitted by the laboratories for Part 1 underwent a detailed technical review process. The review, performed by a QA chemist dedicated to the QTM pilot program, consisted of a manual review of all data reporting forms and associated raw data for accuracy, consistency, and verification of calculations. Chromatogram data were checked for compliance with analytical and contractual requirements. The results were reported to each laboratory prior to preceding with Step 2 of the validation phase so that procedural adjustments could be made accordingly.

Upon each laboratory's completion of Part 2, the results were reviewed to determine whether each laboratory successfully transmitted the electronic data deliverables within the required timeframe and if the analytical results were compliant with all contractual and technical requirements of the project. As the analyses for Part 2 were performed on samples similar to those employed for Part 1, and to accelerate the prequalification phase, a streamlined data review process was used, focusing primarily on the issues raised previously and the results of the Contract Compliance Screening (CCS) module of the QTM Software. Again, the results were provided to each laboratory prior to the

performance of on-site laboratory evaluations so that all issues could be resolved at that time.

The final step in the QA process was to verify the analytical capabilities and instrumentation of each of the candidate QTM laboratories. To achieve this, a detailed on-site evaluation was performed. Through completion of the on-site evaluations, it was confirmed that each of the laboratories had the capabilities, analytical instrumentation, computer hardware, and expertise required to meet all the analytical and data deliverable requirements and successfully participate in the QTM pilot program.

Through the two-step analytical prequalification phase and the on-site evaluations, each of the three candidate laboratories successfully demonstrated their ability to adequately perform the analyses as required for the QTM Service and were subcontracted to supply the EPA with the necessary laboratory capacity.

In June 1993, after the completion of the procurement process, the QTM pilot program was expanded with three laboratories providing analytical services for a total capacity of up to 7500 fractional analyses over a one (1) year period. Field samples from a number of EPA Regions were scheduled with each of the laboratories and the Service continued routinely. To ensure that overall laboratory performance remained at the high levels expected within the CLP, on-going technical data review activities were completed. This form of QA monitoring assisted the EPA in gauging not only laboratory performance but method and software performance as well. The data obtained from the reviews was also used to further advance the method and electronic facets of the Service.

ANALYTICAL METHODS

The QTM Service offers full organic analyses using gas chromatography (GC) for the following fractions: volatile organic compounds (VOAs) using heated headspace sampler instrumentation with GC/photoionization detector (PID) and GC/electrolytic conductivity detector (ELCD); polynuclear aromatic hydrocarbons (PAHs) using solvent or solid phase extraction (SPE), with GC/flame ionization detector (FID); phenols (PHENs) using solvent or SPE, with GC/FID or GC/PID; and organochlorine pesticides (PESTs) and polychlorinated biphenyls (PCBs) using solvent or SPE, with GC/electron capture detector (ECD)[1]. Table 1 provides an overview of the QTM analytical methods.

In order for the instrumental analyses to be rapid and effective, a 24-hour analytical sequence is used. It consists of two (2) types: an initial calibration analytical sequence and a daily calibration check analytical sequence. The analytical sequences consist of the following requirements:

Table 1. QTM Analytical Methods Overview

Fractions:	**VOA**	**PAH**	**PHEN**	**PEST**	**PCB**
No. Compounds:[1]	21	16	16	20	8
CRQLs (unadjusted):[1]					
- water (μg/L)	20	20	50	0.1	1-5
- soil/solid (μg/kg)	40	330	830	1.7	17-83
oil[2] (μg/L) (miscible)	400	--	--	--	--
oil[2] (μg/kg) (non-miscible)	400	20,000	830	100	1000-5000
Sample Size:					
water (mL)	2	100	100	100	100
- soil/solid (g)	1	6	6	6	6
- oil[2] (μL) (miscible)	100	--	--	--	--
- oil[2] (g) (non-miscible)	6	1	6	1	1
Sampling Volume:					
- water samples	40 mL	1/2 gal	1/2 gal	1/2 gal	1/2 gal
soil/solid samples	120 mL	6 oz	6 oz	6 oz	6 oz
high concentration (water or solid)	6 oz	6 oz	6 oz	6 oz	6 oz

1 Target Compound Lists and Contract Required Quantitation Limits (CRQLs) listed in the draft QTM SOW, 2/93.

2 Miscible: methanol miscible/aqueous miscible oil samples. Nonmiscible: methanol non-miscible and methanol miscible/aqueous non-miscible oil samples.

Initial Calibration Analytical Sequence[1]

- Three-point Initial Calibration (high standard proceeded by mid and low standards);
- Instrument Blank;
- Laboratory Control Sample(s);
- Method Blank(s);
- Field Sample(s);
- Instrument Blank(s); and
- Performance Verification Standard(s).

Daily Calibration Analytical Sequence

- Instrument Blank;
- Calibration Check Standard (mid standard);
- Method Blank(s);
- Laboratory Control Sample(s);
- Field Sample(s);
- Instrument Blank(s); and
- Performance Verification Standard(s).

The QC requirements of the QTM analytical methods are structured to provide consistent results of known and documented quality. Data reviewers are able to determine the quality of data, as well as the applicability to each sampling activity. The minimum QC requirements of the QTM Service are outlined in Table 2.

ELECTRONIC DATA TRANSFER CAPABILITY

In order to provide real-time computer-reviewed and computer-validated electronic summary data directly to the EPA Regions, a QTM electronic data delivery and reporting system is used, consisting of two components; the QTM Laboratory Software and the QTM Regional Software. Data are entered into the QTM Laboratory Software, checked for format, contractual requirements, data reviewed and evaluated, and transmitted. Data receipt is accomplished by downloading the validated electronic summary data from a user-secured mailbox on the EPA mainframe using the QTM Regional Software . This secured mailbox is necessary to ensure that the integrity of the data retrieved by the user is not compromised. In addition to downloading data, the QTM Regional Software can produce reports that generate the analytical data package, automated data review results, CCS results, and other information that are helpful in the data review process at the EPA Regional level. Figure 1 illustrates the flow of electronic data deliverables from the QTM laboratory to the EPA user.

Under the program, the laboratories are required to transmit data to the EPA Regions in electronic format 48-hours after the validated time of sample receipt (VTSR) of the last sample in the batch. (If more than three fractional analyses were requested, data must be transmitted within 72-hours after VTSR of the last sample in the batch.) By using

Table 2. Minimum Quality Control Requirements of the QTM Analytical Methods

QC	Frequency	Purpose
Initial Calibration	Initial 3-point and when CCS or PVS criteria not met	Analysis of three different concentration standards at the beginning of the sequence and whenever QC criteria not met. The initial calibration assesses the instrument's linearity, generates calibration factors for sample quantitation, and establishes target compound identification windows.
Calibration Check Standard	Start of 24-hour sequence	Analysis of the calibration check standard (CCS) is to determine whether the initial calibration is still valid, to ensure linearity of the curve, and to evaluate the system for retention time shifting.
Method Blank	Per matrix	Analysis of the method blank is to evaluate the level of laboratory background contamination. The method blank is subjected to the entire analytical procedure.
Laboratory Control Sample	Per matrix	Analysis of the Laboratory Control Sample (LCS) is to demonstrate that the analytical system is in control. The LCS is subjected to the entire analytical procedure to assess the instrument's capability of producing consistent data.
Instrument Blank	At least two per sequence	Analysis of the instrument blank is to evaluate instrument cross-contamination.
Performance Verification Standard	At least one per sequence	Analysis of the Performance Verification Standard (PVS) is to ensure that instrument stability and sensitivity was maintained during sample analyses.
System Monitor Compound	Spiked into each field sample	System Monitor Compound (SMC) is added to every field sample and QC sample to assess analytical efficiency by evaluating target compound retention time shift and recoveries.

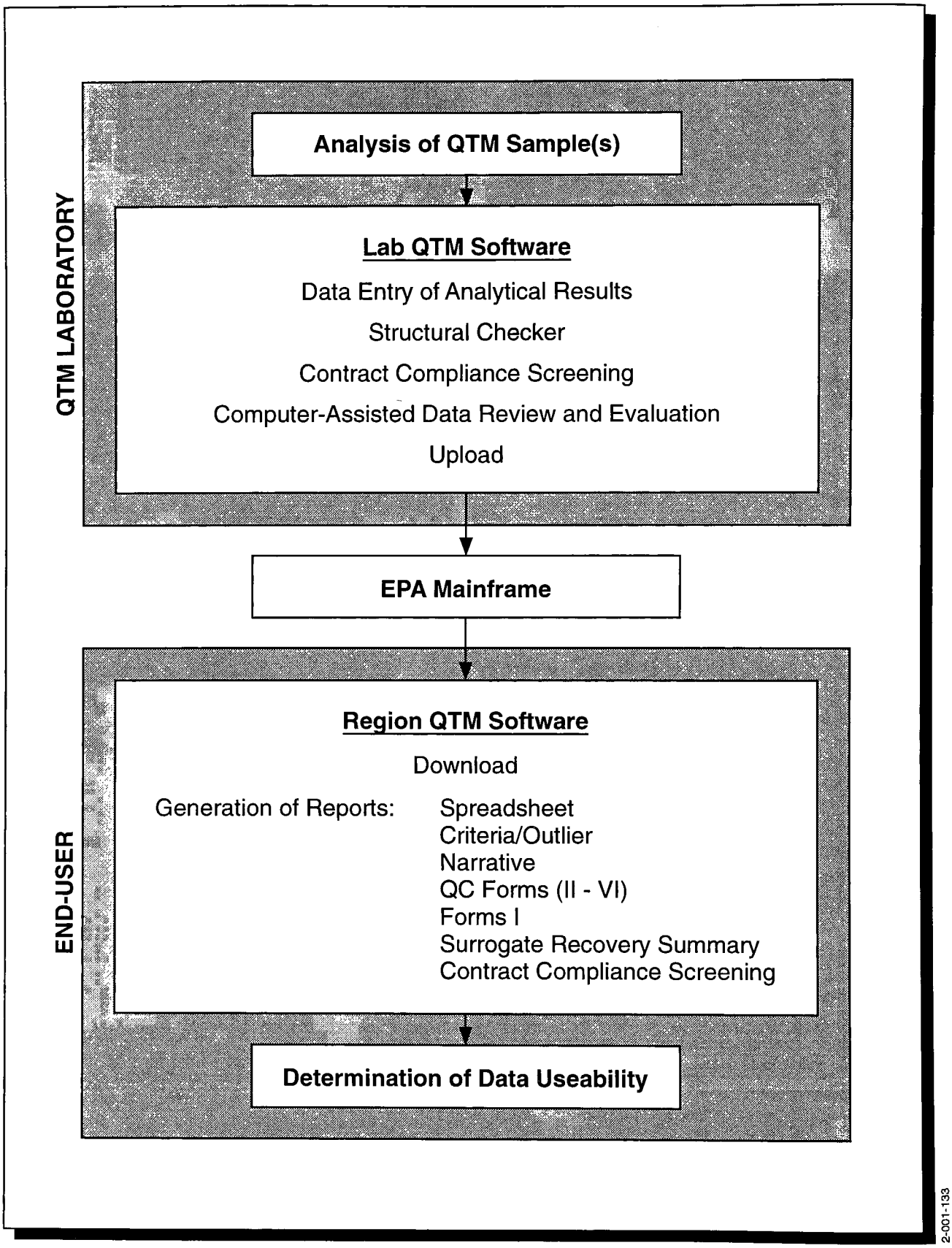


Figure 1. QTM Electronic Data Deliverable Process

the QTM Laboratory Software, the laboratory can transmit the data quickly and efficiently. The QTM Laboratory Software contains the following five (5) components[2]:

Component I. Data Entry Software allows entry of required analytical data and performance information. In order to further advance the efficiency of the electronic reporting, the laboratories are encouraged to develop in-house software that can produce data in the required format directly from their instrumentation.

Component II. Structural Checker ensures that the final data product submitted by the laboratory can be loaded into the CLP Analytical Results Database (CARD) and be adequately evaluated by other automated systems such as CCS and Computer-Assisted Data Review and Evaluation (CADRE). This ensures that certain variables are in the correct positions and in the required format. If errors are encountered, an error report is generated, the transmission process is stopped, and the laboratory must make the appropriate corrections and reprocess the data. This cycle continues until the data passes this phase of the transmission process, thereby ensuring that the data being delivered is structurally and contractually compliant.

Component III. CADRE occurs at the laboratory level prior to submission. CADRE is based on the Draft of the National Functional Guidelines for QTM Data Review[3], dated May 1993, which is concerned with QC performance regarding aspects that are within the laboratory's control. The QC criteria used to evaluate the data includes: initial calibration; calibration check standard; performance verification standard; laboratory control sample; system monitor compound; laboratory blanks; analytical sequence; and quantitative results verification. CADRE is blind to the laboratory, but the results are saved and transmitted to the EPA Region along with the required electronic data package information. This feature saves data processing time at the EPA Region.

Component IV. CCS ensures that data analysis procedures occurred according to the specifications of the contract. This feature produces a report for the laboratory so that they can correct any identified defects prior to data submission to the EPA mainframe.

Component V. Data Transmission is the final data processing phase. This part of the software sends a copy of the laboratory's analytical results data package plus CADRE results to the EPA mainframe via standard telephone lines. As soon as the data transmission process is complete, the data are available for EPA user access.

Once the data are uploaded to the EPA mainframe by the QTM laboratory, the EPA user, with a valid system password, can retrieve the analytical results to an IBM AT, 386 or compatible personal computer through the use of the QTM Regional Software. The software also features view or hardcopy options for generating QTM electronically-produced reports[4].

These reports include:

Data Spreadsheet. A CADRE-generated report that includes a compilation of sample result information based on Form QIs with CADRE-assigned data review final qualifiers.

Criteria/Outlier Report. A CADRE-generated report that includes analyte concentration, CADRE-assigned data review qualifiers, qualification parameters, and associated criteria. This report can be used in assisting with site decisions or determining samples for reanalysis.

Batch Narrative. A report detailing documentation provided by the laboratory of any QC, sample shipment, and/or analytical problems encountered in processing and analyzing the samples reported in the data package. The laboratory also lists the samples analyzed and describes the associated sample matrices.

Form QIs. The data reporting forms that include tabulated analytical results and retention time information.

Quality Control Forms. The data reporting forms (II through VI) that include tabulated analytical results of the initial calibration, calibration check standard, LCS, and PVS, and a summary of the date and time of analyses.

Contract Compliance Screening Results. A report that identifies contract compliance discrepancies by fraction, field sample, code, and criterion.

Surrogate Recovery Summary Report. A report that includes a summary of the System Monitor Compound (SMC) recoveries for all field and QC samples.

When these electronic data review processes and automated reports are used in conjunction with the hardcopy data deliverables (including mass spectra and other raw data) and manual data review and validation processes, the user is provided with an efficient and comprehensive approach to ensuring a high level of confidence and usability of the data generated under the QTM Service.

STATUS/SUMMARY

Over the past several years the QTM Service has continued to develop and expand, adding more laboratory capacity and EPA Regional users. To date, four (4) subcontracted environmental laboratories and five (5) EPA Regions have participated in recruitment and analysis of approximately 5,500 samples within the QTM Service. Multiple special method studies and software development initiatives have been completed, each with the intent of making a stronger, more efficient program. At the foundation of all the development and enhancements of the QTM Service has been the focus on the production of high quality, defensible data. This function

has been aided, in large part, by the depth of QC in the analytical methods, the QA mechanisms within the software systems, and the overall mission of quality throughout the QTM Service.

REFERENCES

1 U.S. EPA/Analytical Operations Branch. February 1993 (Draft). *USEPA Contract Laboratory Program Draft Statement of Work for Quick Turnaround Analysis.*

2 U.S. EPA/Analytical Operations Branch. Fall 1991. *Quick Turnaround Method Regional Training Manual.*

3 U.S. EPA/Analytical Operations Branch. May 1993 (Draft). *National Functional Guidelines for Quick Turnaround Method Data Review.*

4 U.S. EPA/Analytical Operations Branch. June 1993 (Draft). *User's and Sampler's Guide to the Quick Turnaround Method (QTM) Analytical Service.*

Studies of Method Detection Limits in Solid Waste Analysis

David E. Kimbrough*, Public Health Chemist, and Janice Wakakuwa, Supervising Chemist, California Department of Toxic Substances Control, Southern California Laboratory, 1449 W. Temple Street, Los Angeles California 90026-5698.

Abstract

A two part study is presented to assess the applicability of the USEPA's Method Detection Limit (MDL) to analysis of solid materials. The first part compares MDLs calculated for arsenic, cadmium, molybdenum, selenium, and thallium in soil with the actual method performance on real spiked soils with these analytes at concentrations above and below the calculated MDL. The MDL method is examined both for its empirical suitability for solid waste analysis and whether it is the proper theoretical tool for solid matrices. The criteria are the precision and accuracy of results. The results show that the MDL method produces accurate and precise results only in interference free conditions.

This investigation was extended to an inter-laboratory study which included the same five soils used above and five other soils spiked with PCBs. 160 accredited environmental laboratories participated in this study. The applicability of the MDL was assessed by measuring the number of qualitative and quantitative errors produced by the these laboratories. The results indicate that approximately two thirds of the reported MDLs produced significant errors.

HOW THE REGION II RCRA QUALITY ASSURANCE OUTREACH PROGRAM HAS ASSISTED INDUSTRY TO MINIMIZE RCRA COMPLIANCE COSTS

L. Lazarus, U.S. Environmental Protection Agency, Region II, Edison, New Jersey 08837; P. Flax, U.S. Environmental Protection Agency, Region II, New York, New York 10278; and T. Ippolitto, U.S. Environmental Protection Agency, Region II, New York, New York 10278.

ABSTRACT

The goal of the EPA Region II RCRA quality assurance outreach program is to help the regulated community understand how to comply with RCRA requirements and minimize RCRA compliance costs.
The FY'93 outreach program consisted of the following seminars:

First Quarter FY'93 Outreach Efforts

1. Organic Data Validation. This five day course was offered October 19-23, 1992 at Westchester County College in Valhalla, New York. This course, which is scheduled several times each year, illustrates how federal, state and local government agencies can cooperate to assist the regulated community comply with environmental regulations in a cost effective manner. Members of the Region II Environmental Services Division's QA staff provided guidance in developing the curriculum used for this course, which is based on the Region II Organic Data Validation Training Manual. Westchester County College is a local government agency. The New York State Department of Environmental Conservation (NYSDEC) allows individuals to demonstrate their proficiency at validating data by successfully completing the data validation training course.

2. Conference on Quality Assurance in Environmental Monitoring. This conference was sponsored by Westchester County College and the New York Water Environment Association - Lower Hudson Chapter on November 18, 1992 in Yorktown Heights, New York. The conference was hosted by the IBM T. J. Watson Research Center, and was open to the public. Topics presented included quality assurance concepts, data quality objectives, ground water monitoring, data validation, quality assurance requirements in New York State, data management, sampling heterogeneous media, and data assessment. The Region II QA staff were involved in developing the agenda for this conference as well as presenting some of the sessions. On November 19, 1992 a modified version of this presentation was offered for the New York State Department of Environmental Conservation in Latham, New York.

Third Quarter FY'93 Outreach Efforts

1. April 19-23, 1993 Twenty five scientists and engineers attended Westchester County College's inorganic data validation training course in White Plains, NY. The NYSDEC recently recognized individuals who pass the inorganic data validation final examination as acceptable to perform data validation for the Division of Hazardous Waste.

2. April 27-29, 1993 Twenty nine individuals attended the EPA Region II Monitoring Management Branch's " How to write/review a RCRA quality assurance project plan training course" in Edison, New Jersey.

3. May 11, 1993 The TCLP training manual was finalized. The manual was edited by an engineer from IBM's T. J. Watson Research Center. IBM donated his time to the outreach project. State agencies with RCRA primary enforcement responsibility provided written copies of their TCLP policies. Partnerships of federal and state agencies, with private industry, produced more effective, and less expensive, outreach seminars.

4. June 7-11, 1993 Twenty eight scientists and engineers attended Westchester County College's organic data validation training course in White Plains, New York.

5. June 7-8, 1993 130 individuals representing, state agencies, environmental laboratories, generators, and TSDFs attended the RCRA Toxicity Characteristic Leaching Procedure: Implementation and Compliance (TCLP) seminar in Albany. On June 8, 1993, 119 individuals attended the TCLP seminar in Rochester.

6. June 14, 1993 100 individuals attended the TCLP seminar in San Juan, PR. On June 15-16, 1993, fifty seven individuals attended the how to write/review a RCRA quality assurance project plan training course in San Juan, PR.

7. June 21-23, 1993 110 individuals attended the Princeton, NJ TCLP seminar on June 21; 88 people attended the seminar in Edison, New Jersey on June 22; and 101 people attended the seminar in New York City on June 23.

Fourth Quarter FY'93 Outreach Efforts

1. The TCLP seminar was offered twice at the Waste Testing and Quality Assurance Symposium in Alexandria, VA. The Region II organic, inorganic, dioxin, and TCLP data validation protocols, and the Region II TCLP and CERCLA quality assurance manuals, were uploaded onto OSWER's CLU IN computer bulletin board system. This saves copying and mailing costs, and allows the

regulated community to obtain copies of requested documents immediately.

2. The October 21, 1993 Conference on Quality Assurance in Environmental Monitoring was organized. The conference was sponsored by Westchester County College and the New York Water Environment Association, and was held in Yorktown Heights, New York. The conference was hosted by the IBM T. J. Watson Research Center. The goal of the conference was to teach regulators and the regulated community how to reduce monitoring costs. Conference topics included demonstrating EPA quality assurance software, auditing environmental laboratories, selecting monitoring well construction materials, and utilizing immunoassay analyses.

FY'94 Outreach Efforts

We are arranging a series of QA monitoring conferences, TCLP seminars, and quality assurance project plan training courses to reduce the cost of environmental monitoring in the RCRA program.

Discussion

The USEPA Region II RCRA quality assurance outreach program assists the regulated community to minimize costs when complying with RCRA regulations. There are four types of training courses offered by the outreach program:

I. One day symposia on quality assurance in environmental monitoring. These symposia offer two concurrent sessions on monitoring and compliance issues. Conference attendees receive EPA quality assurance training software on various topics, such as data quality objectives (DQO), QA/QC principles, and preparation of quality assurance project plans. A typical conference agenda is attached.

II. One day toxicity characteristic leaching procedure (TCLP) training courses. These courses illustrate how to use the DQO process to generate valid data. The courses also demonstrate how to reduce hazardous waste generator costs by explaining when TCLP data are inapplicable, and how to obtain corrective action management unit (CAMU) variances from the Land Ban regulations.

The following synopsis describes four inappropriate uses of TCLP, and how to obtain a CAMU variance:

A. Invalid Risk Assessments

The TCLP model assesses risk to ground water when potentially hazardous toxicity characteristic (TC) waste is co-disposed with garbage into sanitary landfills. The TCLP model does not assess risk when potentially TC waste is disposed in any other matrix. Waste which is hazardous because it exhibits the toxicity characteristic for mercury may be solidified by adding cement and water to the waste in a tank. In this example, the resultant concrete in not hazardous, and will be disposed at the facility where it was generated. The waste concrete is not hazardous because the concentration of mercury in the concrete's TCLP extract is not a risk to ground water beneath a sanitary landfill. However, because this concrete is non-hazardous, it may emplaced where it was generated (at a non-hazardous disposal site). We do not know if the concrete poses a risk to the ground water at the non-hazardous disposal site. The resultant concrete may only be emplaced where it was generated if it does not exhibit the toxicity characteristic for mercury, unless a CAMU is obtained. The TCLP model discloses no information about potential risks to groundwater at the disposal site where the mercury immobilized in concrete is emplaced. EPA is designing site specific risk assessment models, but these will not be promulgated for several years.

When determining whether to use the TCLP for risk assessment, it is important to remember that TCLP simulates worst case management of hazardous waste in a landfill. Much caution must be used before TCLP data are used in risk assessment because the TCLP conditions rarely reflect actual site conditions. EPA's Science Advisory Board Report outlines many limitations of using TCLP for risk assessment at industrial sites. The Science Advisory Board recommends developing leach tests which emulate site conditions.

EPA's 1991 Science Advisory Board report on Leachability Phenomena concluded that:

1. Many of the proposed uses of the EP and TCLP test have been inappropriate because the waste management scenarios of concern were not within the range of conditions used in the development of the tests themselves. In most cases of inappropriate use of the EP or TCLP tests, the justification given was that it was necessary to cite "standard" or "approved" methods. Even if it is acknowledged that the tests cannot be applied without significant change in test protocol itself, the need to use a previously "approved" test has been cited. (page 3)

2. A variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching should be developed and used to assess the potential release of contaminants from sources of concern. In scientific terms, no "universal" test procedure is likely to be developed that will always produce credible and relevant data for input to all decision making exercises. (pages 7-8)

3. Leach test conditions appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential. The best way to estimate the extent of contaminant release from a waste matrix of interest is to have a test that reflects realistic field conditions. (page 13)

4. To facilitate the evaluation of risk implications of environmental releases, the EPA should coordinate the development of leach tests and the development of models in which the release terms are used. (page 17)

In addition, the TCLP test cannot predict the potential for toxic chemicals to leach from oily waste, through soil, to contaminate ground water. This applies to both sanitary landfills and industrial sites. EPA and the American Society of Testing and Materials (ASTM) have formed a workgroup to develop a site specific risk assessment model for oily waste. At a minimum, the model will incorporate physical and chemical characteristics of the oily waste and the soil. However, this model is not expected to be approved by EPA for several years. Until EPA approves this site specific model for oily waste risk assessments, oily waste site assessments should be based on total constituent analysis, not TCLP extract analysis.

B. <u>Unnecessary Hazardous Waste Determinations</u>:

1. Generator's knowledge of waste (e.g. chocolate ice cream).
2. Exempt waste (e.g. household garbage).
3. Material is not a solid waste (e.g. clean sand, laundry detergent).
4. Generator's testing of waste (total constituent analysis is available).
5. The solid waste is a listed hazardous waste.

C. <u>Unnecessary Land Ban Determinations</u>:

1. Some Land Disposal Restrictions (LDRs) are for total constituent instead of TCLP extract concentrations.
2. Generator's testing of waste (total constituent analysis is available).
3. Pure liquid waste samples (waste is TCLP extract; waste would fail paint filter test).

D. Determination of Corrective Action Clean-up Levels and Clean Closures

Corrective action clean up levels and clean closures are site specific. They are not based on toxicity characteristic regulatory action levels.

E. LDR Variances: CAMUs are Designed to Reduce the Cost of On-Site Remediation

Corrective action management unit (CAMU) regulations are enumerated in 40CFR260.10 and 40CFR270.2. CAMU is an area within a facility designated by the EPA Regional Administrator for implementing CERCLA or RCRA corrective action requirements. A CAMU may only be used for the management of remediation wastes pursuant to corrective action requirements at a facility.

Placement of hazardous remediation waste into a CAMU will not automatically trigger LDRs. This variance from the LDRs can result in substantial cost reductions. CAMU boundaries are not confined to where contamination exists at the site; CAMU boundaries are based on where remediation waste will be managed.

Limitations and Conditions Applicable to CAMU Designations

1. The CAMU shall facilitate the implementation of reliable, effective, protective, and cost-effective remedies;
2. Waste management activities associated with the CAMU shall not create unacceptable risks to humans or to the environment resulting from exposure to hazardous wastes or hazardous constituents;
3. The CAMU may only include uncontaminated areas of the facility if the incorporated area is more protective than management of such wastes at contaminated areas of the facility;
4. Areas within the CAMU, where wastes remain in place after closure of the CAMU, shall be managed and contained so as to minimize future releases to the extent practicable;
5. The CAMU shall expedite the timing of remedial activity implementation, when appropriate and practicable;
6. The CAMU shall enable the use, when appropriate, of treatment technologies (including innovative technologies) to enhance the long-term effectiveness of remedial actions by reducing the toxicity, mobility, or volume of wastes that will remain in place after closure of the CAMU; and
7. The CAMU shall, to the extent practicable, minimize the land area of the facility upon which wastes will remain in place after closure of the CAMU.

III. Five day organic and five day inorganic data validation training courses at Westchester County College.

The EPA Region II CERCLA QA manual defines data validation as "a systematic process for reviewing a body of data against a set of criteria to provide assurance that the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verifying, certifying, and reviewing." Data validation reduces false negatives, false positives, and misquantitation in reported data. Misquantitation includes both laboratory arithmetic errors, and data qualified as estimated or presumptively present because of analytical problems. Agendas for both data validation courses are attached.

IV. The three day course in preparing and evaluating RCRA quality assurance project plans has been condensed into a one day workshop on generating scientifally valid and legally defensible data. A typical agenda is attached.

Outreach Activities on OSWER's CLU-IN Computer Bulletin Board System

Administrator's Update #5, issued on September 24, 1993, discussed cost-saving measures the government can take to reduce useless expenditures, such as increased utilization of electronic reporting and communication. In order to comply with Update 5, we have uploaded our TCLP manual, CERCLA quality assurance manual, and data validation protocols onto the OSWER CLU-IN computer bulletin board system. When people call Region II for copies of these protocols or documents, we tell them how to download the files from the CLU-IN bulletin board system. This saves copying and mailing costs, and people obtain copies of these documents immediately.

Proposed 1995 RCRA Outreach Activities

In 1995, we plan the following additional outreach activities:

1. Modify EPA's QASPER 4.0 quality assurance project plan preparation software to properly identify and characterize some types of hazardous waste. Assisting hazardous waste generators identify and characterize their waste in a cost effective manner is a fundamental objective of the Region II RCRA QA outreach program.

2. OSWER's CLU-IN computer bulletin board system will be reconfigured in the near future. In 1995, the Region II RCRA Outreach program will have an easily accessible category of the bulletin board system devoted to increasing compliance and reducing costs.

Course Itinerary for Generating Scientifically Valid and Legally Defensible Data Workshop at 1994 Waste Testing and Quality Assurance Symposium

How to Use Proper QA/QC Procedures, and the DQO process, to Generate Scientifically Valid and Legally Defensible Data

Leon Lazarus and Dr. Margo Hunt, USEPA Region II, Environmental Services Division.

This course is designed for project managers who are responsible for sampling potentially hazardous waste. The course consists of lectures, hands on computer training, and brief discussions on quality assurance project plan training materials which will be disseminated.

As buzz words, Quality Assurance (QA), and Quality Control (QC), seem to leave most individuals in the dark as to their meaning, their difference, and their significance. A brief introduction to both QA and QC will clarify the subject and give you insights into their importance at EPA. Also to be discussed is the Data Quality Objectives (DQO) process recommended by EPA. Most individuals recognize that the evolution of a project is a multistep process which entails several individuals that must function together. The DQO process is a systematic planning tool for ensuring that the type, quantity, and quality of data collected will correspond to the decision to be made, and the importance of making the right decision. For example, a very low detection limit is needed if drinking water is sampled for volatile organic compounds whereas soils on a Superfund site would not need such low detection limits since contaminant regulatory action levels are much higher.

Appropriate QA/QC procedures are also delineated in the DQO process. Proper containers, preservatives, and holding times are essential if the data generated are assumed to be valid. For example, if sampling equipment or containers are not cleaned properly, samples may show the presence of contaminants that originated from the equipment or containers themselves. If monitoring wells are not properly constructed and evacuated, the resultant sample data may be too high or too low, even if the lab analyzed the sample perfectly. If proper chain of custody procedures are not followed, data will not be considered valid in court.

Course Outline

8:00 am Quality Assurance Concepts

9:00 am Hazardous Waste Field Sampling Computer Based Training hands-on demonstration

10:30 am Coffee Break

10:45 am Data Quality Objectives

11:30 am Data Quality Objectives Computer Based Training hands-on demonstration

12:30 pm Additional Quality Assurance Materials (provided on 3 1/2 inch computer disks):

1. New York State Department of Environmental Conservation RCRA QA Manual
2. USEPA Region V RCRA QA Project Plan Preparation Guidance
3. Data Quality Objectives and Sampling Design, from USEPA Region II TCLP Manual
4. USEPA QASPER 4.0 DQO based Project Plan Preparation Software
5. USEPA Region II SOP for Writing SOPs.

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Organic Data Validation

Course # XAP-555
November 15-19, 1993
8:30 a.m. to 4:30 p.m.

Tuition: $1,100, includes all course materials, continental breakfast, and lunch daily.

This 35 hour course in the Performance of Data Validation Techniques For Organic Analyses As Required By The Superfund Program includes a four hour final examination. Techniques will include reviews of both CLP and non-CLP generated data and the data will be reviewed for both validity and usability. A certificate will be issued by the College to those passing the examination. Holders of this certificate are recognized by the NYS Department of Environmental Conservation as acceptable to perform Organic data validation for ENCON's Division of Hazardous Waste.

Recommended Prerequisite: B.A. or B.S. in Science or Engineering and at least 6 mos. experience in the chemical analysis of environmental samples; or college level instrumentation course in analytical chemistry (GC or GC/MS).

Participants should bring a scientific calculator.

The instructor for the course will be John H. Samuelian, Ph.D. Dr. Samuelian is a certified organic data validator and has over five years experience in data validation in federal and state Superfund programs. He participated in the development of the first training manual and has peer reviewed the current training manual. He is currently serving as program manager for EA Engineering, Science and Technology's data validation program.

Topics will include:

Intro to Sampling Analysis Plans and Data Quality Objectives (SAPs & DQOs)
Intro to Contract Laboratory Procedure Analysis (CLP)
Intro to Data Package
Intro to Validation
Holding Times
Blanks
Calibration
Internal Standards
Contact Required Quantitation Limits (CRQLs)
Data Calculations
Surrogates
Special ID
Field Duplicates
Matric Spike/Matrix Spike Duplicates
Pest Holding Times
Pest Surrogate Times
Pest MS/MSD
Pest Blanks
Pest Calibration
Pest Analytical Sequence
Pest Cleanup Verification
Pest ID
Pest Calculations
CLP Contract

Inorganic Data Validation

Course # XAP506
April 19-23, 1993
8:30 a.m. to 4:30 p.m.

Tuition: $1,100, includes all course materials, continental breakfast, and lunch daily.

This 35 hour course in the Performance of Data Validation Techniques For Inorganic Analyses As Required By The Superfund Program includes a four hour final examination. Techniques will include reviews of both CLP and non-CLP generated data and the data will be reviewed for both validity and usability. A certificate will be issued by the College to those passing the examination. Holders of this certificate are recognized by the NYS Department of Environmental Conservation as acceptable to perform inorganic data validation for ENCON's Division of Hazardous Waste.

A B.A. or B.S. in Science or Engineering, plus one year of College Chemistry are minimum requirements for registration.

Participants should bring a scientific calculator.

The instructor for the course will be Dale S. Boshart. Mr. Boshart is currently a Team Manager with Lockheed Engineering, Managing Region III ESAT Project in support of USEPA's commitment to the Superfund program. He was formerly associated with Roy F. Winston Corporation, ESAT, USEPA Region II as senior Inorganic Data Reviewer.

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Course # _____ Organic Data Validation ▪ November 15-19, 1993 ▪ Course fee: $1,100 ▪ Limit 25

Registrations must be received at least one week prior to program date.

Mail to: Professional Development Center, Administration Building, Westchester Community College, 75 Grasslands Rd., Valhalla NY 10595

For further registration information call Elaine Sall 914-285-6659

SESSION C

Workshop on How to Use Proper QA/QC Procedures, and the DQO Process, to Generate Scientifically Valid and Legally Defensible Data
—**Leon Lazarus**, USEPA Region II

9:00 am - 10:00 am	Quality Assurance Concepts
10:00 am - 11:00 am	Hazardous Waste Field Sampling Computer-Based Training Hands-On Demonstration
11:00 am - 11:30 am	Coffee Break
11:30 am - 12:30 pm	Data Quality Objectives
12:30 pm - 1:30 pm	Lunch
1:30 pm - 2:30 pm	Data Quality Objectives Computer-Based Training Hands-on Demonstration
2:30 pm - 3:00 pm	Questions and Answers

This workshop is designed for project managers who are responsible for sampling potentially hazardous waste and for environmental attorneys who need to understand the uncertainties in environmental data. The course consists of lectures, hands on computer training, and brief discussions on quality assurance project plan training materials which will be disseminated.

As buzz words, Quality Assurance, QA, and Quality Control, QC, seem to leave most individuals in the dark as to their meaning, their difference, and their significance. A brief introduction to both QA and QC will clarify the subject and give you insights into their importance at EPA. Also to be discussed is the Data Quality Objectives (DQO) process recommended by EPA. Most individuals recognize that the evolution of a project is a multistep process which entails several individuals that must function together. The DQO process is a systematic planning tool for ensuring that the type, quantity, and quality of data collected will correspond to the decision to be made and the importance of making the right decision. For example, a very low detection limit is needed if drinking water is sampled for volatile organic compounds, whereas, soils on a Superfund site would not need such low detection limits since contaminant regulatory action levels are much higher.

Appropriate QA/QC procedures are also delineated in the DQO process. Proper containers, preservatives, and holding times are essential if the data generated are assumed to be valid. For example, if sampling equipment or containers are not cleaned properly, samples may show the presence of contaminants that originated from the equipment or containers themselves. If monitoring wells are not properly constructed and evacuated, the resultant sample data may be too high or too low, even if the lab analyzed the sample perfectly. If proper chain of custody procedures are not followed, data will not be considered valid in court.

Conference on Quality Assurance in Environmental Monitoring and Workshop on Generating Scientifically Valid and Legally Defensible Data

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F. W. Olin Building, College of Business
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Alfred, NY 14802

WEDNESDAY MAY 18, 1994

The conference topics will be relevant to managers and staff from private industry, consulting firms, and regulatory agencies. For registration information, contact Roland Hale at (607) 587-8377. For program information, contact Leon Lazarus, USEPA Region II RCRA Quality Assurance Officer, at (908) 321-6778.

*Conference Chairmen: **Leon Lazarus** and **Phil Flax**, USEPA Region II*

Return reservation form by May 10, 1994

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SESSION A

Two concurrent sessions (A and B) will be held to present principles applicable to waste, soil, and water environmental monitoring. Media-specific monitoring topics will also be addressed.

8:50 am - 9:00 am	Opening Remarks
9:00 am - 10:00 am	Do Low Matrix Spike Recoveries Equal Bad Data: A Case Study of Hexavalent Chromium in Soil —**Rock Vitale**, Environmental Standards, Inc.
10:00 am - 10:30 am	Coffee
10:30 am - 11:30 am	Regaining Control of Your Environmental Investigation Through Auditing Your Environmental Laboratory —**Rock Vitale**, Environmental Standards, Inc.
11:30 am - 12:30 pm	How to Utilize Qualified Data in the SPDES Program --**Larry Bailey**, NYSDEC
12:30 pm - 1:30 pm	Lunch
1:30 pm - 2:30 pm	The Laboratory/Client Relationship: Two-way Communication for Selecting Appropriate Methodology & Deliverables —**Gale Sutton**, Galson Corporation
2:30 pm - 3:00 pm	Coffee
3:00 pm - 4:00 pm	Immunoassay Demonstration —**Bob Bednar**, Ensys Corporation

SESSION B

8:50 am - 9:00 am	Opening Remarks
9:00 am - 10:00 am	EPA'S Guidance for Sampling Demolition Debris Containing Lead Based Paint —**John Hansen**, USEPA Region II
10:00 am - 10:30 am	Coffee
10:30 am - 11:30 am	Improper Hazardous Waste Characterizations: Financial and Compliance Implications —**Richard Walka**, William F. Cosulich Associates
11:30 am - 12:30 pm	When is TCLP appropriate? When is TCLP *not* applicable? —**John Hansen**, USEPA Region II
12:30 pm - 1:30 pm	Lunch
1:30 pm - 2:30 pm	Immunoassay Demonstration —**Bob Bednar**, Ensys Corporation
2:30 pm - 3:00 pm	Coffee
3:00 pm - 4:00 pm	Hazardous Waste Minimization: Regulatory Requirement or Prescription for Survival? —**Richard Walka**, William F. Cosulich Associates

AN EVALUATION OF QC REQUIREMENTS IN THE CLP FOR FURNACE ATOMIC ABSORPTION ANALYSES

D.C. Hillman, *J.T. Rowan*, and *D.M. Boyer*, Lockheed Environmental Systems and Technologies Company, Las Vegas, NV 89119, and *L.C. Butler*, Environmental Protection Agency, Las Vegas, NV 89119

ABSTRACT

Under its mission of performing Superfund QA research for the Office of Research and Development (ORD), the Quality Assurance Branch of the EPA EMSL-LV has reviewed the method quality control (QC) for furnace atomic absorption analysis (AAS). The QC requirements for furnace AAS in the CLP program are quite stringent and contribute significantly to making furnace AAS the slow point in metals analysis. The QC could be modified to increase throughput and decrease reanalyses without significantly affecting the resulting data quality. Areas for modification include the duplicate-injection requirement, the criteria for the concentration of the analytical spike, and the corrective action dictated by a poor spike recovery.

Currently, the Superfund CLP Inorganic Statement of Work (SOW) requires that all furnace AAS analyses be performed using duplicate injections, which doubles the analysis time from 2-3 minutes/sample to 4-6 minutes/sample. Historically, this requirement was included in the analytical procedure because it was common for the single-measurement precision to be poor due to an atypical measurement or poor injection. Modern instrumentation, though, does not suffer from poor precision. Data from routine sample analyses over 6 months on multiple instruments was reviewed and the frequency of unacceptable results was less than 1% for As, Pb, Se, and Tl (>5000 injections). For the same data, precision and accuracy are equivalent for single and double measurements. The data also demonstrate that bad injections and atypical measurements are adequately detected using the post-digest spike recovery. Therefore, considerable time savings would be realized if only single measurements were required and data quality would not be affected.

The furnace AAS QC requirements specify that a post-digest analytical spike (PDS) must be analyzed for every sample. The PDS recoveries are used to determine if matrix interferences are affecting the quantification. If a significant effect is detected, the sample must be reanalyzed by the method of standard additions (MSA) or flagged as "W" or "E" (out-of-control). However, under the current procedures a significant fraction of PDS recoveries can be outside the acceptance criteria due to measurement variability rather than matrix effects. Additionally, the relative acceptance criteria can be more stringent than the analytical precision. Both issues lead to data flags or MSA analyses for reasons other than matrix interferences. By modifying the PDS concentration and the procedure for interpreting the recoveries, unnecessary MSA analyses and data flags can be minimized, with the benefit of reduced analytical costs and equivalent, or better, data quality. Proposed modifications are provided in this paper.

NOTICE: Although the research described in this article has been funded wholly by the U.S. Environmental Protection Agency through Contract 68-C0-0049 to Lockheed Environmental Systems & Technologies Company, it has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Quality control (QC) plays an important role in analytical procedures performed under the Superfund CLP program. QC data is used to evaluate the quality of associated sample data and to judge its usability. The amount of QC must be balanced with cost. Too much QC increases costs without providing any more information regarding data quality or usability, while too little decreases analytical costs but results in sample data of unknown quality. In support of the Office of Research and Development (ORD), EMSL-Las Vegas reviews the CLP analytical methodology and associated QC on a continuing basis to ensure that both are current with today's rapidly improving technology. This includes evaluating and balancing QC requirements. In this paper, the QC required for CLP furnace atomic absorption analysis (AAS) is evaluated. The QC requirements for furnace AAS in the CLP program are quite stringent and contribute significantly to making furnace AAS the slow point in metals analysis. However, technology advances over the years may permit modifying the current QC without impacting data quality or useability. Two specific aspects of furnace AAS QC are considered, the duplicate injection requirement and the post-digest analytical spike (PDS) procedure.

Under the Superfund CLP Inorganic Statement of Work (SOW) all furnace AAS analyses must be performed using duplicate injections, which doubles the analysis time from 2-3 minutes/sample to 4-6 minutes/sample. Historically, this requirement was included in the analytical procedure because it was common for the single-measurement precision to be poor due to an atypical measurement or poor injection. Modern instrumentation, though, does not suffer from poor precision or atypical measurements. Considerable time savings would be realized if only single measurements were required. In this paper, the precision and accuracy of single and double injection measurements are compared using data obtained from routine analyses over a period of several months. This paper discusses the data quality implications of removing the double-injection requirement and how the furnace AA QC decision tree could be changed to accommodate single measurements.

The furnace AAS QC requirements also specify that a PDS must be analyzed for every sample. The PDS recoveries are used to determine if matrix interferences are affecting the quantification. If a significant effect is detected, the sample must be reanalyzed by the method of standard additions (MSA) or flagged ("E" or "W"). However, with the current spiking levels, measurement variability can result in significant PDS recovery variability. As the variability of the recovery increases, an increasing number of recovery values will be outside the acceptance criteria due, not to a matrix effect, but to measurement variability. Consequently, samples are unnecessarily reanalyzed by MSA or the results flagged, which increases analysis costs and time, and can also taint the data useability. This paper discusses how the measurement variability affects the recovery values and how to minimize the effect. By modifying the concentration of the analytical spike and the procedure for interpreting analytical spike recoveries, unnecessary MSA analyses and data flags can be minimized, with the benefit of reduced analytical costs and equivalent, or better, data quality. Proposed modifications (with examples) will be provided in this paper.

EXPERIMENTAL

Lockheed has a commercial analytical laboratory equipped with 5 Perkin-Elmer and 1 Hitachi furnace AAS instruments. Each of these is busy 24 hours a day performing routine analyses for As, Pb, Se, and Tl in all types of environmental samples. Both CLP-type and non-CLP protocols are followed, depending upon the client. The non-CLP protocols utilize single-injection measurements and higher PDS concentrations.

To compare the precision and accuracy of single and double injection analyses, the QC data (ICVs, ICBs, CCVs, CRAs, CCBs) from single and double injection analytical runs were examined over the time period November 1993 - April 1994.

The PDS procedure was examined by first determining the theoretical effect of measurement variability upon the PDS recovery using progression of error calculations. The analytical spike data from the same analytical runs used above were then examined for PDS recovery distributions and the effect of measurement variability.

RESULTS & DISCUSSION

Double Injection vs. Single Injection Measurements

Modern instrumentation is very reliable. If the frequency of bad injections is very low, then having a QC step to detect the occurrence of a bad injection is not very useful or cost-effective. Routine data from double-injection analytical runs were examined to determine the frequency of bad injections. The data, summarized in Table 1, indicate that the overall frequency of bad injections is less than 1%. This low frequency for bad injection occurrences suggests that the double-injection requirement should be dropped. If the requirement is dropped, the question "What would be the effect on the data quality?" is raised. To answer this question, the precision and accuracy for both double- and single-injection analyses were compared using the results for ICB/CCB, ICV/CCV, and CRA QC samples. The results, summarized in Table 2, indicate equivalent precision and accuracy for double and single injection analytical runs.

Table 1. Bad Injection Summary

Analyte	No. Injections	% bad injections*
As	3984	0.8
Pb	3438	0.6
Se	1830	0.3
Tl	1628	0.2

* RSD > 20% and concentration > CRDL

Table 2. QC results for Single and Double Injection Analyses

Analyte	No. injections	ICB/CCB* (ppb)	ICV/CCV* (% recovery)	CRA* (% recovery)
As	Single	-0.03 ± 1.3 (140)	100.5 ± 5.5 (111)	103 ± 19 (23)
	Double	0.3 ± 1.1 (234)	103.3 ± 5.6 (186)	106 ± 14 (39)
Pb	Single	0.07 ± 0.86 (234)	98.8 ± 4.7 (242)	106 ± 27 (36)
	Double	0.01 ± 0.79 (225)	99.2 ± 3.7 (222)	114 ± 31 (46)
Se	Single	0.55 ± 0.89 (154)	101.8 ± 5.0 (153)	95 ± 26 (22)
	Double	0.36 ± 0.70 (115)	102.4 ± 4.8 (113)	101 ± 13 (18)

* The number of observations is indicated in ( )

The analytical spike data for samples analyzed in the same analytical runs can also be examined to determine if a difference exists between single and double injection measurements. Table 3 summarizes the distribution (by %) of analytical spike recoveries from double injection analyses and the results that would be obtained from the same analyses if only the first injection was utilized. The table shows that there is effectively no difference between double and single injection analyses.

Table 3. Distribution of analytical spike recoveries (by %)

Analyte (# samples)	# inj.	85 ≤ %R ≤ 115	%R < 40	40 ≤ %R < 85 or %R > 115
Arsenic n = 455	Double	54	2	44
	Single	55	3	42
Lead n = 420	Double	61	4	35
	Single	64	4	27
Selenium n = 246	Double	60	6	34
	Single	59	9	32
Thallium n = 312	Double	85	0	16
	Single	81	0	19

Another concern for single-injection analyses is "How is a bad injection detected during single-injection analyses?". During an analytical run there are essentially two types of samples, calibration QC samples (ICVs, CCVs, CCBs, CRAs) and "other" samples (field and related QC samples). A bad injection for a calibration QC sample will be apparent from the recovery of the true value. For the "other" samples, the PDS recovery, rather than injection precision, can serve as an indicator of a bad measurement. Bad measurements will affect PDS recovery values, which will trigger corrective action as specified by the furnace AAS QC flowscheme. The bad injection data from samples identified as having unacceptable duplicate precision in Table 1 were evaluated against the QC flowscheme. Examples are given in Table 4. In each case, the bad injection is detected and resolved by the required QC action.

Table 4. Examples of Bad Injection Data

Item	Analyte	Injection 1	Injection 2	RSD
Sample 1 (ppb)	As	***42.0****	16.5	61.0
Sample 1 + Spike (ppb)		39.4	37.4	3.7
% Recovery		-12.9	104.6	
Discussion: Bad injection (high bias) resulted in negative recovery, requiring reanalysis. Subsequent reanalysis of this sample resulted in acceptable recovery (104%) and verified the sample result for injection 2 (18.1 ppb).				
Sample 2 (ppb)	Pb	2U	-2.9	NA
Sample 2 + Spike (ppb)		22.2	***-3.5****	194
% Recovery		110.8	-17.5	
Discussion: Bad injection (low bias) resulted in negative recovery, requiring reanalysis. Subsequent reanalysis of this sample resulted in acceptable recovery (91%) and verified the sample result for injection 1 (2U ppb).				
Sample 3 (ppb)	Se	11.8	***20.6****	41.4
Sample 3 + Spike (ppb)		20.2	15.5	18.6
% Recovery		83.6	-50.8	
Discussion: Bad injection (high bias) resulted in low recovery, requiring reanalysis. Subsequent reanalysis of this sample resulted in acceptable recovery (98%) and verified the sample result for injection 1 (9.8 ppb).				
Sample 4 (ppb)	Tl	2.7	2.0	NA
Sample 4 + Spike (ppb)		22.8	***14.4****	26.1
% Recovery		100.4	61.8	
Discussion: Bad injection (low bias) resulted in low recovery, requiring reanalysis. Subsequent reanalysis of this sample resulted in acceptable recovery (92%) and verified the sample result for injection 1 (2 ppb).				

*Suspected bad injection

In summary, the data support dropping the double-injection requirement. Considerable time savings would be realized if only single measurements were required and data quality would not be affected. The precision and accuracy are equivalent to that for double injection measurements and bad injections (measurements) are still detected by other QC samples. An additional, minor requirement should be added for single-injection analyses in that the PDS sample must also be prepared and analyzed for the pre-digest matrix spike sample (in order to detect a bad injection).

Analytical Spike Procedure and Interpretation

A PDS must be prepared and analyzed for each element analyzed by furnace AAS in all samples (except the pre-digest matrix spike sample). For each PDS, a recovery is calculated using the following equation;

$$\% R = \frac{(SSR-SR)}{SA} \times 100$$

where

SSR	=	analytical spike sample result
SR	=	sample result
SA	=	spike added

The PDS recovery calculation endeavors to reflect the impact of the sample matrix on the reliability of an analytical determination. The recovery value is used to answer the question "Is the matrix significantly affecting the quantification of the analyte using the existing external calibration?". When a significant effect is detected, samples are either flagged or must be reanalyzed by MSA. A significant effect is defined using a fixed acceptance window. When PDS recoveries are within the window, the measurements are accepted as reliable, otherwise they are not. The acceptance windows should be wide enough to permit for reasonable precision and normal variability in the analytical measurements, but not so wide that significant matrix effects can go undetected. The spike should also be large enough that the method can reliably measure the difference between the spiked and unspiked samples. However, the current requirements for PDS samples and recovery interpretation do not address the issue of simple measurement variability.

To understand the impact of measurement variability, the error in *%R* must be considered. Through progression of error calculations, an estimate of the relative error in *%R* is calculated as follows;

$$\frac{s_{\%R}}{\%R} = \left(\frac{(s_{ssr}^2+s_{SR}^2)^{1/2}}{SSR-SR}\right)$$

where

$s_{\%R}$	=	estimated standard deviation for *%R*
s_{SSR}	=	estimated standard deviation for *SSR*, and
s_{SR}	=	estimated standard deviation for *SR*.

The terms s^2_{SSR} and s^2_{SR} tend to increase with increasing concentration. Spike levels (*SA*) are fixed for each analyte, and the term SSR-SR is equal to *SA* at 100% recovery. From this it is apparent that the variability of *%R* is very dependent upon both the sample concentration and the PDS concentration. As the variability increases, the chances of a recovery value being outside the acceptance criteria due to random error (i.e., measurement variability) also increase. Figure 1 is a plot of the frequency at which spike recoveries (assuming a mean of 100%) fall outside the

acceptance windows due to random errors as a function of the sample/PDS concentration ratio. The frequency was determined by calculating the standard deviation ($s_{\%R}$) of the PDS recovery (using the relative error equation above) and assuming a normal distribution around the mean. From this it is possible to determine the expected percentage of the values that lie outside of any given window around the mean. $s_{\%R}$ was calculated for several values of *SA* and *SR*. Since *%R* = 100, *SSR-SR* is defined by *SA*. The standard deviations of *SR* and *SSR* were assumed to follow a normal distribution around the mean and are based on a 1 ppb error for concentrations below 20 ppb and 4% error at concentrations above that. From Figure 1 it is apparent that the relative error becomes very significant as *SR/SA* increases. Consequently the frequency of recovery values outside of the acceptance windows due solely to random error increases as spike concentration decreases and as sample concentration increases.

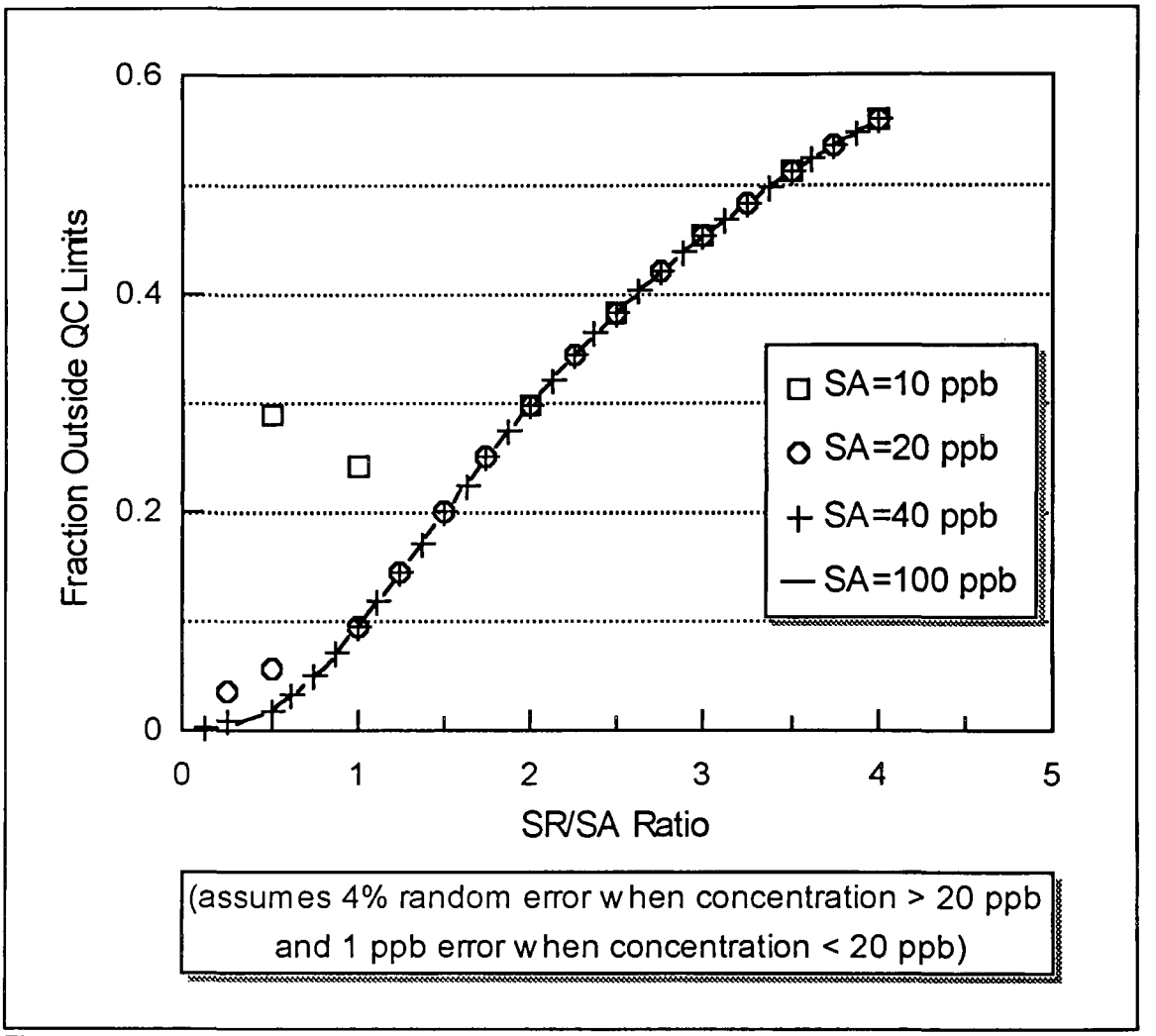

Figure 1. Expected Fraction of PDS Recoveries Outside of QC Limits vs. the *SR/SA* Ratio

When the ratio of *SR/SA* is large, a considerable portion of the unacceptable spike recoveries could be due to measurement variability rather than to matrix effects. Using lead as an example, Table 5 lists the theoretical frequency of false QC hits due to measurement variability for the current spiking level and for a higher spiking level.

Table 5. Frequency of false QC hits due to measurement variability

SR (ppb)	*SA* = 20		*SA* = 100	
	SR/SA	%>QC	*SR/SA*	%>QC
10	0.5	20.0	0.1	0.1
20	1.0	9.0	0.2	0.1
40	2.0	29.0	0.4	1.0
100	4.0	62.0	1.0	6.0

Direct evidence that current spiking levels and acceptance windows result in inappropriate QC hits can be obtained by examining the absolute recovery (rather than the relative recovery) for analytical spike samples. The absolute recovery is defined by the following equation:

$$D = |(SSR-SR) - SA|$$

If the value of *D* is not significant, then the recovery should be deemed acceptable (i.e., no significant matrix effects). "Not significant" is defined here as 2*IDL, which is based upon the 99% upper confidence interval for the IDL (2 ppb for each analyte in this work). The definition of an acceptable *D* at a given value of *SA* effectively defines the acceptance window for *%R*. For As, Pb, and Tl (IDL=2 ppb and *SA*=20 ppb) a 2*IDL (or 4 ppb) absolute window corresponds to an 80-120% acceptance window for *%R*. Similarly for Se (IDL=2ppb and *SA*=10 ppb), a 2*IDL absolute window translates to a 60-140% acceptance window for *%R*. Considering that the current windows are fixed at 85-115% regardless of analyte or spiking level, it is evident that the recovery values outside of these fixed windows will not always be due to a significant matrix effect.

Table 6 lists the distribution of PDS recovery data for two different PDS concentrations from a number of routine analyses. Included for each fraction outside the acceptance criteria is the percentage of the fraction for which the absolute recovery is acceptable. The data clearly show that, due to measurement variability, the value of *%R* is not always a reliable indicator of matrix interferences with the current spiking levels and *%R* acceptance criteria. Combined, the data in Figure 1 and Tables 5 and 6 indicate that there is a marked reduction in the number of unacceptable spike recoveries due to random errors as the concentration of *SA* is increased and if the absolute recovery is considered. Therefore, it is apparent that the way to minimize the effect of measurement variability and simplify interpretation of the *%R* values is to raise the value of the spike concentration. The concentration of the spike should be high enough such that the absolute recovery is not a factor and low enough so that spiked samples do not often require dilution for analysis. Increasing the value of *SA* will significantly reduce the number of data flags and MSA analyses that result from reasons other than matrix interferences, namely measurement variability.

In order to estimate suitable concentrations for *SA*, frequency distributions for As, Pb, Se, and Tl in both soil and water digests were obtained from the CLP Analysis Results Database (CARD), and are listed in Table 7. Suggested values for *SA* are included in the table. For Se, although the *SR/SA* ratio is less than 1 for most samples (~75%), the spiking level is close enough to the detection limit that the variability in the spike recovery is impacted significantly (from figure 1 it is estimated that greater than 20% of the recoveries could be outside the window due to chance alone). If the spiking level were raised to 40 ppb, more of the samples would have low *SR/SA*

Table 6. Distribution of *%R* Values

Anal.	spike (ppb)	n	Distribution of *%R* values*			
			<40	40 - 85	85 - 115	>115
As	20	457	3 (0)	14 (7)	53	30 (20)
	40	290	2 (0)	17 (0)	71	10 (0)
Pb	20	420	4 (0)	17 (11)	60	19 (18)
	40	474	6 (0)	9 (0)	80	5 (0)
Se	10	246	7 (0)	25 (25)	59	9 (9)
	40	365	4 (0)	10 (0)	71	15 (0)
Tl	20	312	0	13 (11)	85	2 (2)
	40	154	2 (0)	10 (0)	84	4 (0)

* Value in ( ) is the % for which the absolute recovery is OK

values (~95%) and the effect of variability near the detection limit would not adversely affect the recovery values. For As and Pb in water samples, spiking at 20 ppb results in acceptable *SR/SA* values for most samples (~75%). For soil samples, a 20 ppb spike will result in a large number of false QC hits. Increasing the spike level to 40 ppb for As and Pb would significantly reduce the chances of a false QC hit. For simplicity, a value of 40 ppb is also suggested for water samples. For Tl, spiking at 20 ppb results in acceptable *SR/SA* values for most samples (~95%). The linear ranges of most modern instrumentation should be able to accommodate spikes at these levels without requiring excessive dilutions.

Table 7. As, Pb, Se, and Tl in real samples

Analyte	Matrix	Distribution (ppb by percentile)				Suggested *SA*
		25th	50th	75th	95th	
ppb in digestate						
As	Water	3.1	6.4	16	86	40
	Soil	10	24	53	400	40
Pb	Water	2.4	4.7	15	123	40
	Soil	34	92	473	9700	40
Se	Water	2	3	10	31	40
	Soil	3	5	11	42	40
Tl	Water	1.2	2.1	5.2	20	20
	Soil	1.6	2.4	4	12	20

Although the linear range of furnace AA instruments is a limiting factor on the maximum PDS concentration, another factor is the matrix interference mechanism. If the interference causes equal suppression at all concentrations, then the PDS concentration is not a concern. However, if the mechanism is not linear with concentration, then it may be possible to overwhelm the effect by spiking so high that the effect, though significant at the level of the sample, is undetectable in the spiked sample. For example, a 10 ppb suppression on a 10 ppb spike will cause a 0% recovery

and corrective action will be necessary. That same suppression on a 100 ppb spike will yield a 90% recovery and the sample data will be reported down to the IDL. The data in this database does not suggest that such a mechanism commonly presents any difficulties (spike concentrations up to 60 ppb were evaluated), so the suggested spike concentrations should be acceptable.

In addition to increasing the PDS concentration, another simple change can be made to improve th furnace AAS procedure. Currently, when the PDS recovery is out of the acceptance criteria, the sample is diluted, reanalyzed, flagged ("E" or "W"), or reanalyzed by the method of standard additions (MSA). The institution of reanalyses and dilutions for samples that would otherwise have been flagged as "W" or analyzed by MSA will further reduce the time and number of injections involved in GFAA analyses by resolving analytical difficulties in ways that are less labor intensive and more appropriate. The GFAA database shows that a significant proportion of poor recoveries can be remedied simply by repeating the analysis (an indication that the original recovery was out of criteria due to measurement variability). Although poor recoveries that result from matrix effects can be handled by MSA, this is a time consuming procedure that is often unnecessary. An alternative to MSA for samples with analyte concentrations well above the IDL is simple dilution and reanalysis, which is much less labor intensive. Dilution is often effective because the matrix components causing the interference are diluted to insignificant levels while the analyte is maintained above the IDL.

Revised QC Procedure

Based upon the changes recommended above (single injections, increase spike concentrations, and alternate corrective action), the overall furnace AAS QC procedure should be revised. A suggested "Furnace AA Analysis Scheme" is pictured in Figure 2. Each step is discussed below. The functional changes to the tree consist mainly of eliminating the double injection requirement, allowing repeat analyses to compensate for suspected "bad" measurements and random error, and permitting the dilution of sufficiently concentrated samples as an alternative to MSA. These modifications reduce time, injections, and expense while maintaining the same level of quality assurance as is currently in place.

[1] Prepare a post-digest analytical spike for every sample except the calibration QC samples (ICV, ICB, CCV, CCB, CRA) and analyze along with the unspiked sample. The required spiking concentrations are listed below. The spiked sample can be prepared by the furnace AAS instrument directly in the furnace tube or manually by the operator. To prepare in an automated fashion using the instrument, consult the operator's manual. To prepare manually, add a known quantity of the analyte to an aliquot of the digested sample and the same quantity of acidified ASTM Type II water to another aliquot of the digested sample. The volume of spiking solution must not exceed 10% of the sample aliquot volume.

Post-digest analytical spike concentration (ppb)			
As	Pb	Se	Tl
40	40	40	20

[2] The concentration of analyte in the spiked and unspiked samples must fall within the calibrated range of the furnace AAS instrument. If not, the sample must be diluted, respiked, and reanalyzed (refer to Step 8).

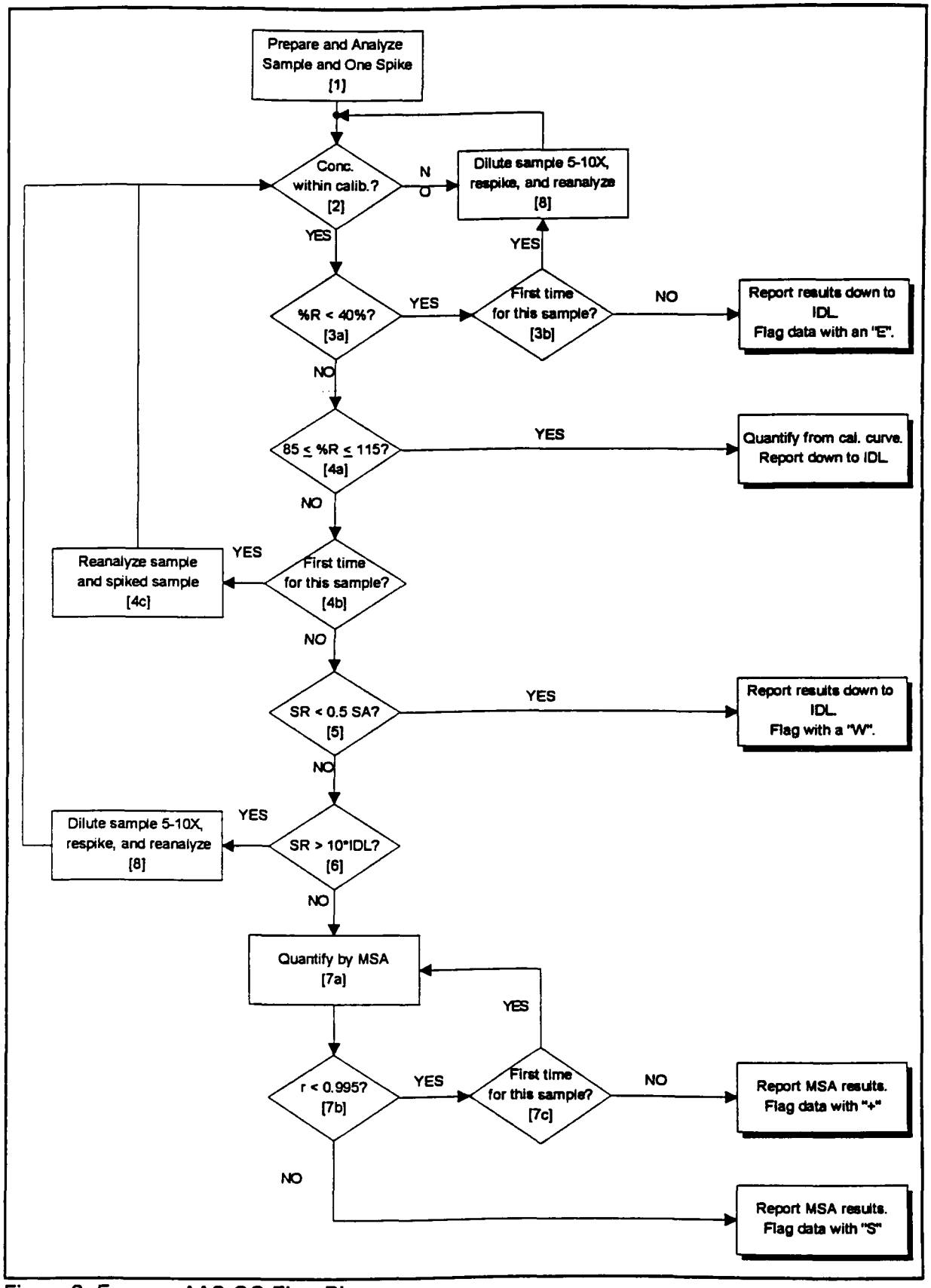

Figure 2. Furnace AAS QC Flow Diagram

[3a,b] If the analytical spike recovery is less than 40%, the sample must be diluted, respiked, and reanalyzed once. If after dilution and reanalysis, the analytical spike recovery is still less than 40%, the result is reported down to the IDL and flagged with an "E" to indicate matrix interference problems (refer to Step 8).

[4a-c] If the analytical spike recovery is within the windows of 85-115%, the results by direct quantification are "acceptable" and are reported down to the IDL. If the recovery is not within the acceptance limits, the analyst has the option of reanalyzing the sample and spike if this is the first analysis.

[5] If the analytical spike recovery is outside of the windows 85-115% and the sample concentration is less than half of the spike concentration, the results are reported down to the IDL and flagged with a "W". The "W" flag indicates that the analytical spike recovery is out-of-control for unspecified reasons (eg, slight matrix problems or poor spiking procedure). Because of the sample concentration, additional effort to resolve the problem is not expected to result in a better number.

[6] If the analytical spike recovery is outside of the windows 85-115% and the sample concentration is greater than half of the spike concentration and greater than 10 times the IDL, the sample is diluted, respiked, and reanalyzed (refer to Step 8).

[7a-c] If the analytical spike recovery is outside of the windows 85-115% and the sample concentration is greater than half of the spike concentration but less than 10 times the IDL, the sample is quantified by the method of standard additions (MSA). Samples for MSA analysis are prepared manually by the operator. Alternatively, the MSA aliquots can be prepared in an automated fashion by the furnace AAS instrument if it has the capability. In either case, the following steps must be incorporated into the MSA analysis.

a. Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

b. The MSA analysis is performed by consecutively analyzing the sample and three spikes.

c. The spikes must be prepared such that spike 1 is approximately 50% of the sample concentration, spike 2 is approximately 100% of the sample concentration, and spike 3 is approximately 150% of the sample concentration.

d. The data for each MSA analysis must be clearly identified in the raw data documentation using added concentration as the x-variable and absorbance (or found concentration) as the y-variable along with the slope, x-intercept, y-intercept, and correlation coefficient (r) for the least squares fit of the data. The results must be reported on Form 8.

e. If the correlation coefficient (r) for an MSA analysis is less than 0.995, the MSA analysis must be repeated once. If r is still less than 0.995, report the results of the run with the greater correlation coefficient "r" on Form 1 and flag the result with a "+", indicating that the results were obtained by MSA and that r was not acceptable. If r is greater than 0.995, report the results and flag the result with a "S", indicating that the results were obtained by MSA and that r was acceptable.

[8] If called for by steps 2, 3, or 6, samples are diluted, respiked, and reanalyzed. Generally, dilutions of 5-10 are acceptable. However, analyst judgement may be used to perform other dilutions. However, the sample must not be diluted so that the analyte is less than the IDL. If the sample is diluted below the IDL, it must be reanalyzed using a lower dilution factor, if possible.

CONCLUSIONS

A review of the GFAA data from this laboratory confirms that PDS recoveries are adequate indicators of data quality and that duplicate measurements are not necessary for the detection of bad injections. Modifications are warranted, however, to ensure that the PDS provides meaningful information. Current requirements are such that random measurement variability can cause a significant proportion of all GFAA analyses to be needlessly flagged or reanalyzed by MSA. Increasing the spike concentrations would alleviate the impact of random variability. Reanalysis and dilution are additional features of this proposal that would provide laboratories with sufficient latitude to deal with simple analytical problems so that data useability is not compromised and without having to resort to MSA when another approach would be more appropriate. Since the data quality would not be affected by these changes, the potential savings in time and cost as well as increases in productivity should provide ample driving force to get these changes incorporated into modern methodology.

The Quality Control Level: An Alternative to Detection Levels

David E. Kimbrough*, Public Health Chemist, and Janice Wakakuwa, Supervising Chemist, California Environmental Protection Agency, Department of Toxic Substances Control, Southern California Laboratory, 1449 W. Temple Street, Los Angeles California 90026-5698.

Abstract

Existing methods for the determination of reporting limits (e.g., MDL, LOD, etc) are based on a binary procedure that determines that lowest concentration of an analyte that is either detected or not detected within specified confidence limits. There is no assessment of the accuracy or precision of the results detected. An alternative procedure is presented, the Quality Control Level which determines the lowest concentration that meets the data quality objects of the data user in term of the minimum acceptable precision and accuracy.

To examine this hypothesis, a series of 15 soils and aqueous liquids were prepared with successively smaller concentrations of 16 toxic regulated elements. The range of the concentrations were over four orders of magnitude for both. Each of these liquids and soils were analyzed eight times and the accuracy and precsion of each analyte was measured against concentration. This paper will show that it is possible to use a quality control approach to reporting levels.

DETECTION LIMIT

Kelvin L. Wright, Waste Policy Institute, Gaithersburg, MD
Farideh Moghadami, Science Applications International Corp. (SAIC), Gaithersburg, MD
Raymond J. Bath, Ph.D., Waste Policy Institute, Gaithersburg, MD

ABSTRACT

Over the past thirty years, the definition of detection limits has been molded and designed by various groups to fit a specific need and purpose. The EPA, NRC, ANSI and instrument manufacturers have all developed or adopted generic definitions for detection limits, and each identifies a slightly different safety factor or component that should be included in the equations. Since the end users of environmental data are often not chemists, this has lead to increased confusion about detection limits. Generally, lawyers, engineers, hydrologists, and geologists are the frequent end users of environmental data and lack the background to interpret the intended meaning of "detection limit" This confusion and lack of understanding of detection limits can be costly. This paper will examine the various definitions of detection limits and attempt to qualify the differences between statistical approaches. It will also examine how selecting the proper method for estimating detection limit on environmental restoration projects will minimize the possibility of making incorrect decisions and possibly reduce sampling requirements.

SAMPLING/FIELD

EFFECT OF TRANSFORMER OIL, PETROLEUM HYDROCARBONS AND INORGANIC SALTS AS INTERFERENCES IN FIELD SCREENING FOR PCB CONTAMINATION IN SOIL

Alvia Gaskill, Jr., President, Environmental Reference Materials, Inc., PO Box 12527, Research Triangle Park, North Carolina 27709

ABSTRACT

A study was conducted to determine the effect of transformer oil and petroleum hydrocarbons on the accuracy of field test methods commonly used to determine PCBs in soil. Laboratory prepared soil samples spiked with Aroclor 1242 over the range 0-100 ppm were tested at both varying and constant levels of transformer oil (0-10%), diesel fuel oil (0-4%) and gasoline (1%). The effect of inorganic chloride on the accuracy of the field test methods was also determined. Samples were analyzed using draft SW-846 Method 4020, Soil Screening for Polychlorinated Biphenyls by Immunoassay, by a method based on the L2000™ PCB Chloride Analyzer, and by gas chromatography. Testing at action levels of 2 and 10 ppm Aroclor 1242, the L2000 and GC methods correctly classified all soil samples as to containing greater than or less than the action levels, even in the presence of 2-10% transformer oil, 0.25-4% diesel fuel and 1% gasoline. Method 4020 failed to correctly classify such soils due to a negative interference caused by the hydrocarbons. Because it isn't possible to visually determine if a soil contains more than 2% transformer oil or 0.5% diesel fuel (the levels at which Method 4020 began to fail to detect Aroclor 1242), Method 4020 cannot be used to rule out PCB contamination when other hydrocarbons are present as is frequently the case at waste dumps and spill sites. The full extent of the class of compounds capable of causing this interference is not known and should be the subject of future studies. Both the L2000 method and Method 4020 were able to correctly classify soil/salt mixtures containing 4 ppm Aroclor 1242 at the 2 ppm action level in the presence of up to 100% sodium and calcium chloride.

INTRODUCTION

Soil can become contaminated with PCBs through accidents involving the removal and maintenance of transformers and capacitors or through improper disposal of PCB containing substances. Accurate determination of the PCB content of soils suspected to be contaminated is necessary in order for the responsible parties to make the appropriate decisions regarding site clean-up and remediation.

Several proven laboratory analytical techniques have been used for nearly a decade to meet this need. Most of these have involved a gas chromatographic analysis of a cleaned-up extract of the soil. More recently, field test kits and portable laboratory systems using test kits have become a popular way to identify PCB "hot spots" on-site in suspected contaminated areas, thereby reducing the number of samples requiring the more expensive and time consuming laboratory tests and limiting the extent of soil excavation required in cleaning up the site. These have included test kits based on solvent extraction of the PCBs from the soil, followed by chemical dehalogenation of the PCBs and analysis by either colorimetric reaction or specific ion electrode determination of the resulting chloride (the L2000 PCB Chloride Analyzer of the Dexsil Corporation). A method based on the L2000 kit, "Screening Test Method for Polychlorinated Biphenyls in Soil" has been submitted to EPA for approval.

Recently kits based on enzyme-linked immunosorbent assays (ELISA) in which a competitive reaction between PCBs and a PCB conjugate is used to determine the PCBs in a sample, have been used. A kit method based on one manufacturer's ELISA kit (PCB RISc™ Soil Test System from Ensys, Inc.) has recently received a de facto endorsement by the EPA as draft Method 4020, Soil Screening for Polychlorinated Biphenyls by Immunoassay (1). Similar immunoassay-based (IA) kits have been developed and marketed by other companies who are also seeking EPA approval of their kits. However, there are at present no legal or regulatory requirements to use any particular test kit or kit-based method for the determination of PCBs in soil.

EPA's Office of Solid Waste Methods Hotline gives a recorded message that Method 4020 should not be used for regulatory purposes without the approval of a regulator. It is important that these test kit methods be properly validated so that regulatory agencies and industry will know which ones to recommend or require to meet their testing needs.

EXPERIMENTAL

Study Design

An examination of the published information on the ELISA-based kits did not indicate whether transformer oil above a given level would adversely affect the determination of PCBs in a soil sample. Ensys has reported (1, 2) that transformer oil, diesel fuel oil and gasoline do not result in false positive interferences with their

kits at levels greater than 1%, but the possible effect of such hydrocarbons as negative interferents has not been addressed. Baek (3) reported that a high concentration of substances such as oil, may hinder PCB extraction from soil by either saturating an extractant or blocking contact with an extractant. To test for possible negative interferences, laboratory generated soil samples contaminated with transformer oil, diesel fuel oil, gasoline and Aroclor were analyzed using this kit-based method. Comparison tests were performed using ASTM Method D3304 for PCBs in soils and by the method based on the Dexsil L2000 field test system for PCBs in soil and oil. Because the possible effect of inorganic chloride as an interferent was not investigated by the EPA in their validation of Method 4020 and is a possible positive interferent in the L2000 method, laboratory generated soil samples contaminated with inorganic chloride and Aroclor 1242 were also tested using the L2000 method and Method 4020.

The experiments were designed to simulate PCB contaminated oil spills covering a range of PCB and transformer oil concentrations as well as soils contaminated with diesel fuel oil and gasoline to simulate soils found in uncontrolled waste disposal sites or those associated with leaking underground storage tanks. Inorganic chloride interference experiments were designed to model several scenarios: that of soil contaminated with salt water, that of soil contaminated with road de-icing salt, and that of pure salt taken as a sample to model the worst possible case of inorganic chloride contamination in a sample.

All experiments involving IA testing were carried out using IA kits with detection levels of either 2 or 10 ppm Aroclor 1242. Aroclor 1242 was the only PCB used in this study as the IA kits used for this purpose must be ordered calibrated by the manufacturer specifically for each Aroclor. If a different Aroclor is tested than the one the kit is calibrated for, the results can vary by more than an order of magnitude.

Two types of hydrocarbon contaminated soils were prepared: those contaminated with Aroclor 1242 only and those contaminated with 1242 and transformer oil, diesel fuel oil or gasoline. Levels of 1242 in the soil containing only 1242 varied from 0 to 100 ppm. The co-contamination experiments involving transformer oil were conducted on soils contaminated with 1242 at constant levels while varying the concentration of the oil and at varying concentrations of 1242 while keeping the oil concentration constant.

To simulate a field testing scenario, two action levels were chosen: 2 and 10 ppm Aroclor 1242. All of the results for the IA method were interpreted based on these pre-set action levels. A total of 27 soil samples were analyzed by each of the methods and the results compared to the expected concentration of the Aroclor in the soil based on gravimetric preparation. The total numbers of both correct and incorrect classifications that resulted by using each of the methods were tabulated and used to evaluate each method. To avoid ambiguities due to possible sampling variations, the results from the analyses of soils contaminated at the action levels (i.e., 2 and 10 ppm) were used only as an indicator of the precision of the analytical methods. For concentrations other than the action level, the data were used to determine the percentage of correct determinations (i.e., whether or not the PCB concentration was identified corrrectly as greater or less than the action level).

The contamination levels used for the soil containing Aroclor 1242 and no transformer oil were 0, 10, 20, 50 and 100 ppm. The first series of co-contaminant experiments was conducted using soil to which 1242 had been added at two times the 10 ppm action level (20 ppm) and to which Shell Diala A transformer oil was added at 0.5, 1, 2, 4, and 10 percent. Based on the results of the first series, a second series of co-contaminant experiments was conducted using soil containing transformer oil at 4% and 1242 levels of 0, 10, 50, and 100 ppm. All of the above soils were analyzed using the L2000 PCB Analyzer Method, the ASTM GC Method and the PCB RISc kit method (4020) at an action level of 10 ppm.

A third set of experiments was conducted at an action level of 2 ppm 1242 using soils contaminated with 4% Diala A oil as the co-contaminant. The 1242 levels were 2, 5, 10 and 20 ppm.

The contamination levels for the soil containing Aroclor and diesel fuel or gasoline included levels of Aroclor 1242 of 4 ppm to which the diesel level was either 0.25 or 0.50%, levels of Aroclor 1242 of 10 ppm to which the diesel level was 1 or 4% and levels of Aroclor 1242 of 20, 40, and 50 ppm to which the diesel level was 4%. Gasoline was tested at a level of 1% with an Aroclor level of 10 ppm.

The contamination levels used to determine if inorganic chloride is an interference in these methods involved either samples of soil containing 10% or 100% sodium or calcium chloride and no Aroclor 1242 or 4 ppm Aroclor 1242.

Preparation of Spiked Soil Samples

To simulate typical soils, an 8 kg mixture of clay soils and sand, approximately 75:25 w/w was prepared. The soils and sand were obtained from residential areas and were determined to contain less than 0.1 ppm Aroclor 1242 and less than 1 ppm total organic chlorine. In addition, the base soils were analyzed for total petroleum hydrocarbons (TPH) using EPA Method 418.1 and found to contain less than 10 ppm TPH. The clay soil was broken up by hand and allowed to air dry for 24 hours. The clay and sand were sieved to pass a 0.850 um sieve, mixed together, and tumbled for 24 hours in a rotating pail. Most of the clay particles were observed to be considerably smaller than 0.850 um. The water content of the freely flowing mixture was 1%. The soil was transferred to aluminum cake pans prior to addition of contaminants. Subsampling to generate homogeneous splits for spiking was performed according to the procedure described by Schumacher (4) in which soil was transferred from one pan to another in random order five times. The soils were then spiked with Aroclor 1242, either in hexane or in Diala A (Shell) transformer oil to generate known levels of the Aroclor and the oil in the soil. The spikes were slurried with the soils and hexane was added to facilitate mixing. The soil mixtures were air dried to a constant weight, bottled in previously unused clean Qorpak™ 8 oz. glass bottles with Teflon™ lined caps and tumbled for 4 hours on a rotating tumbler. Samples containing diesel fuel were also prepared according to this procedure. Samples containing gasoline or salt were prepared individually by spiking samples of Aroclor containing soil. Diesel levels in the spiked samples were determined by Method 8015 to be >85% of the gravimetric value.

RESULTS AND DISCUSSION

The antibody test upon which the ELISA-based kits rely requires that the PCBs first be extracted from a 10 g soil sample into methanol. The methanol extract is diluted with more methanol, then an aqueous buffer, and is then added to the antibody coated reaction tube. A solution of enzyme conjugates is also added to the solution and the resulting mixture is allowed to equilibrate. After the solution phase is removed and the vessel washed, a color developing agent is added. The greater the color obtained, the lower the PCB content of the original sample. The test results are interpreted by comparing optical densities (OD) obtained for the sample with that of a standard. If the OD of the sample is less than that of the standard, the sample contains more than the level of Aroclor set for the kit by

the manufacturer. If the OD is greater than that of the standard, the sample contains less than the pre-set level of Aroclor. Other concentration ranges can be measured by serial dilution of the diluted sample or by use of kits set to respond at other thresholds.

The specific IA kits evaluated in this study were set to respond to Aroclor 1242 at 2 ppm and at 10 ppm. While the distributors of the kit recommend that the user perform a preliminary GC screen to identify the specific Aroclor present, Method 4020 provides no such guidance. There have also been at least five versions of the kit issued and two drafts of Method 4020 since EPA's SW-846 Organic Methods Working Group endorsed 4020 for PCBs in July 1992. Method 4020 is based on a 5 ppm threshold for PCBs and refers the user to the manufacturer (in this case Ensys) for specific instructions. The various generations of the kit have added, in succession, a QC step which may disqualify an entire set of analyses and a series of dilutions which complicate the implementation of the test. The latest version of the kit (Revision 5, 9/1/93) includes two QC criteria which are contradictory. One calls for rejection of test results if the optical densities obtained on duplicate standards run with the samples differ by greater than 0.20 absorbance units as read from the portable spectrophotometer supplied with the kit. The other calls for rejection if the results differ by more than 0.30 units. These changes make the evaluation of Method 4020 and the Ensys kit difficult and the comparison with previously published validation data of concern. The testing described in this study at the 10 ppm level for transformer oil was based on the Ensys kit involving the QC requirements and the double dilution of the sample extract as described in the December 1992 information supplied by the company (5) and the kits used were those set to expire in August 1993. Testing at the 2 ppm level for transformer oil, gasoline and diesel (1%) was based on the same kit system, but without one of the dilution steps, as per the instructions accompanying the kit. Thus, the evaluation at the 2 and 10 ppm levels involves the same kit, but with a different dilution of the sample extract prior to the IA reaction.

The testing described in this study for evaluating the effect of diesel fuel (all levels except 1%) and inorganic chloride at the 2 ppm level was based on the Ensys kit involving the contradictory QC requirements and the single dilution of the sample as described in Revision 5 of the kit. The kits used were those set to expire in April, 1995. The Dexsil Corp. L2000 Chloride Analyzer System was used according to the draft method and the instructions

supplied with the unit (6). As was the case with the IA method, a 10 g sample of soil is extracted with a solvent. As such, both kit methods experienced equivalent sample sizes and sample homogeneities. The extract is reacted in plastic tubes with a sodium metal dispersion which dehalogenates the chlorine from the PCBs and converts it to water soluble chloride. The chloride is then measured by a chloride specific ion electrode system included with the kit. The electrode response is reported by the unit in terms of either specific Aroclors or chloride. When the specific Aroclor(s) of interest are unknown, the instructions recommend that results be reported in terms of Aroclor 1242 to cover the worst case likely when transformer oil is present. The method is simple to use and the reaction and measurement steps are not as time dependent as for the IA method. While the IA method requires strict adherence to specific reaction time schedules set forth in the instructions, the L2000 method seems less sensitive to reaction times so long as the minimum times are met. The electrode system in the L2000 method requires frequent recalibration, which is prompted automatically by the unit. A system blank, which is to be run daily and subtracted from all results, is typically around 1-4 ppm expressed as Aroclor 1242.

ASTM Method D3304, which involves a Soxhlet extraction of the PCBs using iso-octane, followed by gas chromatographic analysis of the extract for specific Aroclors, was used as written. The method is essentially the same as EPA Method 3540A with iso-octane substituted as the extraction solvent, followed by analysis by Method 8080 and was developed specifically for determining PCBs in soil contaminated with insulating fluids. Approximately 30-40 g of each sample were extracted and analyzed in triplicate.

The effect of transformer oil as an interferent in the determination of Aroclor 1242 concentrations is presented in Table 1. Results of analyses of three replicate aliquots from each sample by each kit method and by Method D3304 (identified as "GC" in the table) are shown. Recoveries by the GC and L2000 methods were higher in the samples containing transformer oil than in those without transformer oil, probably because the PCBs tend to remain associated with the oil phase. When the oil is not present, the PCBs are more likely to become adsorbed to soil surfaces and thus more difficult to extract. While neither the GC nor L2000 methods result in 100% recoveries of the gravimetric levels of Aroclor 1242 added to the soil, in most cases the 95% confidence intervals for results by each include the gravimetric value, indicating that both methods produce acceptable quantitative

measurements of Aroclor 1242 in these samples. The mean values for the GC and L2000 results differ significantly at the 95% level of significance for about half the samples, indicating that the GC and L2000 results cannot always be considered identical.

When the results from the L2000 and IA methods are compared with the expected values based on gravimetric preparation, both methods correctly identified soil containing 20 ppm 1242 as being above the action level of 10 ppm when the transformer oil concentration was less than or equal to 1%. At transformer oil levels of 2% or greater and 20 ppm Aroclor 1242, the IA method failed to detect the Aroclor as >10 ppm. At 4% transformer oil the interference due to the oil (when testing using a kit set to respond at 10 ppm) disappears when the Aroclor content increases to >50 ppm. This interference is quite severe when it is considered that the real threshold for the IA kits is around 1 ppm (2). Thus, 95% of the response to PCBs must be blocked for a false negative to occur. There were no false negatives reported by the L2000 or GC methods. Because it isn't always possible to simply look at a soil and determine if it has >2% transformer oil, another means must be found to identify such samples prior to testing using this IA method in order to avoid excessive false negative classifications.

Subsequent testing of soil samples containing 2, 5, 10 and 20 ppm Aroclor 1242 and 4% transformer oil using the IA kit set to respond at 2 ppm, failed to show the presence of the Aroclor at actual Aroclor levels as high as ten times the action level of the kit. As the only difference between the 2 ppm and the 10 ppm kit is the dilution made, it can be concluded that the oil is once again responsible for the interference. The L2000 method properly classified all of these contaminated soils as did the GC method.

The effect of diesel fuel oil and gasoline as interferents in the determination of Aroclor 1242 is presented in Table 2. While the L2000 and GC methods correctly classified soils contaminated with 0.5-4% diesel fuel and gasoline at 1242 levels from 0-50 ppm, the IA method failed to correctly classify these soils at 1242 levels up to 20 times the action level of the kit. Levels of diesel oil as low as 0.25% interfered with the determination of 4 ppm Aroclor 1242. At higher levels of oil (4%) the interference persisted until the Aroclor concentration reached 50 ppm. Once again, as the real threshold for the kits is around 1 ppm PCBs, an interference at 40 ppm suggests that 98% of the response to PCBs must be blocked for a false negative to occur. Thus, the interference due

to diesel oil is even more severe than that observed for transformer oil. Similarly, because a visual observation of a soil sample will not identify diesel contamination at 0.5%, the IA kits cannot be used to correctly classify the Aroclor content of such samples.

Salt, either as sodium chloride (a model compound for salt water contamination of a soil) or calcium chloride (a model compound for road de-icing salt contamination of a soil) had no adverse effect on the correct classification of the Aroclor 1242 content of soils by either the L2000 or IA method. The results presented in Table 3 demonstrate that even with 100% salt, the kit methods were able to effectively detect Aroclor 1242 at levels as low as 4 ppm. This is especially important for the L2000 method as it is based on a total organic chlorine measurement and includes several steps to remove inorganic chloride from the soil sample prior to the determinative step. Some difficulty was experienced in filtering the 100% calcium chloride methanol extract in the IA test due to its viscosity. While it is unlikely that field samples containing 100% salt will be tested using these kits, the results from this study demonstrate that the incidental presence of inorganic chloride from seawater or estuarine water contamination of soils or from road de-icing salts, does not constitute a serious interference.

CONCLUSIONS

The results from the L2000 PCB Analyzer Method were not adversely affected by the presence of either transformer oil or fuels in the samples. This suggests that other hydrocarbons would also not present a problem in the analysis of contaminated soils. The co-contamination of the soil with transformer oil does appear to enhance the efficiency of the L2000 method's extraction of PCBs from soil. The GC results also show an extraction efficiency enhancement due to the presence of transformer oil as a co-contaminant. In neither of these two methods did the extraction efficiency enhancements affect the accuracy of the soil classifications. Inorganic chloride was also not found to be an interference, even when 100% salt was tested.

The IA method results, however, suggest that the ELISA-based kits of Method 4020 suffer from a severe negative interference due to transformer oil, diesel fuel and gasoline, although not inorganic chloride, at levels typically found in spill site and landfill samples. The full extent of the class of compounds capable of such a strong negative interference is not known and should be the

subject of future studies. It is widely known that immunoassays can be very specific in their positive response to the analyte of interest. These experiments have highlighted a less well advertised aspect of IA systems in that they involve complex, large molecules and may be susceptible to non-specific interferences, especially when used with non-aqueous solutions. Reduction of the interference by dilution alone may not be possible, as the kits as presently configured are responsive over a rather narrow range of parameters. Further dilutions on the order of those predicted necessary to eliminate the oil interference would likely render the kits insufficiently sensitive to determine PCBs at the levels of interest to government and industry. While the exact mechanism of the interference observed here and its correction are beyond the scope of this study, the EPA needs to fully investigate the potential of all such possible co-contaminants to produce false negative results. The EPA or the manufacturer of the IA kits has, as yet, made no published determination of the negative interference of any compounds and should do so immediately. Oils and fuels represent only a small fraction of the possible interferents likely to be present in environmental soil samples. This will undoubtedly require reanalysis of some field samples already determined non hazardous by using draft Method 4020.

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Table 1. Comparison of GC, L2000 and IA Kit Method Accuracy in Classifying Aroclor 1242 Levels in Soils Contaminated with Transformer Oil[a,b]

Aroclor 1242, Gravimetric Value, ppm	% oil	Method Results, ppm GC	L2000	IA	% correct GC & L2000	IA
		10 ppm action level				
0	0	0.1±0.04	1.4±0.6	<10	100	100
10	0	8.7±2.4	9.5±1.2	>10	NE	NE
20	0	15.1±1.7	13.4±2.3	>10	100	100
50	0	40.5±1.8	40.3±4.1	>10	100	100
100	0	77.3±2.0	78.9±2.3	>10	100	100
20	0.5	16.1±2.8	18.9±1.5	>10	100	100
20	1	17.3±0.9	19.5±1.7	>10	100	100
20	2	17.3±1.5	23.2±0.9	<10	100	0
20	4	18.0±1.0	21.5±0.7	<10	100	0
20	10	17.3±2.7	25.5±1.9	<10	100	0
0	4	0.1±0.04	0.0±0.0	<10	100	100
10	4	9.6±0.2	8.3±0.4	<10	NE	NE
50	4	46.1±4.6	49.8±0.2	>10	100	100
100	4	92.7±4.7	105.8±3.0	>10	100	100
		2 ppm action level				
2	4	1.8±0.1	2.8±0.6	< 2	NE	NE
5	4	4.3±0.2	5.2±0.7	< 2	100	0
10	4	8.3±0.1	9.4±0.2	< 2	100	0
20	4	18.0±1.0	21.5±0.7	< 2	100	0

[a] all results uncorrected for % water
[b] mean ± 1 standard deviation for triplicate GC and L2000 determinations; all three results from each IA method determination agreed in all cases
NE: not evaluated because expected value is the action level

Table 2. Comparison of GC, L2000 and IA Kit Method Accuracy at the 2 ppm Action Level in Classifying Aroclor 1242 Levels in Soil Contaminated with Diesel Fuel and Gasoline[a,b,c]

Aroclor 1242, Gravimetric Value, ppm	% Diesel	Method Results, ppm GC	L2000	IA	% Correct GC	L2000	IA
0	0	0	0.0±0.0	<2	100	100	100
4	0.25	2.9	3.7±0.8	>2,<2	100	100	50
4	0.5	3.0	3.9±0.9	<2	100	100	0
10	1	NA	9.0±0.1	<2	NA	100	0
10	4	9.1	11.0±1.6	<2	100	100	0
20	4	16.4	20.3±1.4	<2	100	100	0
40	4	NA	41.2±0.4	<2	NA	100	0
50	4	37.7	53.1±5.9	>2	100	100	100
10 (gasoline)	1	NA	9.2±1.4	<2	NA	100	0

[a]duplicate determinations
[b]all results uncorrected for % water
[c]mean ± 1 standard deviation for L2000 results; both results from each IA method determination agreed unless otherwise noted
NA: not analyzed

Table 3. Comparison of L2000 and IA Kit Method Accuracy at the 2 ppm Action Level in Classifying Aroclor 1242 Levels in Soils Contaminated with Inorganic Salts[a]

Aroclor 1242, Gravimetric Value, ppm	%Salt	Method Results, ppm L2000	IA	% Correct L2000	IA
0	10% NaCl	0[b]	<2	100	100
0	10% $CaCl_2$	0[b]	<2	100	100
0	100% NaCl	0[b]	<2	100	100
0	100% $CaCl_2$	1.0	<2[b]	100	100
4.1	10% NaCl	4.4	>2	100	100
4.2-4.6	100% NaCl	10.0	>2	100	100
4.1	10% $CaCl_2$	3.8	>2	100	100
4.3-7.0	100% $CaCl_2$	9.8[c]	>2[d]	100	100

[a]single determinations unless otherwise noted
[b]duplicate determinations
[c]expected value 7.0
[d]expected value 4.3

FIELD TESTING OF A PORTABLE TRICHLOROETHYLENE AND CHLOROFORM FIBER OPTIC CHEMICAL SENSOR

James C. Wells and David A. Gobeli
Purus, Inc.
2713 North First Street
San Jose, CA 95134-2010

Purus, Inc. has developed and field tested a portable fiber optic chemical sensor for the semi-specific determination of ppb levels of trichloroethylene and chloroform in water, soil and gaseous samples. This sensor configuration is an extension of our original laboratory fiber optic chemical sensor and allows the sensor to be used as a field screening device. The sensor is contained in a carrying case measuring 46 x 30 x 20 cm. and weighing less than 10 kg.

The sensor consists of an flow optrode, reagent delivery and recovery system, fiber optic transmitter-receiver, embedded micro controller, display, and communication port. The optrode is a miniature reaction chamber through which the chemical reagents are pumped. The reagents react with gaseous halogenated compounds that diffuse in through a gas permeable membrane to form a colored product, and the product is detected by its absorbance of light from a 560 nm diode. The reagents are based on the Fujiwara (K. Fujiwara, Chem. Abstr. 11:3201 (1917)) alkaline pyridine chemistry and optimized to measure trichloroethylene or chloroform. The minimum analysis time is 2.5 minutes at the detection limits of a few µg/L in water, and may be shortened at higher concentrations or by further refinements to the hardware.

Recent field trial results for chloroform in drinking water have demonstrated detection limits of 3 µg/L and repeatibility of ± 5% at the 40 µg/L level. The results of field monitoring trials for TCE contaminated groundwater will be presented that demonstrated a detection limit of 2 µg/L. Field trial results for TCE contaminated soil samples demonstrate a detection limit of 5 µg/kg. Quantitation results will be presented that demonstrate the viability of this fiber optic chemical sensor as low cost screening tool for site assessment, monitoring, and process control applications.

IMPROVEMENTS IN SAMPLE RECOVERY OF XAD-2 RESIN FROM METHOD 0010 TRAINS

Merrill D. Jackson and Larry D. Johnson, Atmospheric Research and Exposure Assessment Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, James F. McGaughey, Raymond G. Merrill, Jr., Joan T. Bursey, and Denny E. Wagoner, Radian Corporation, P.O. Box 13000, Research Triangle Park, North Carolina 27709

ABSTRACT

In a field evaluation study for semivolatile halogenated organic compounds listed in Title III of the Clean Air Act Amendments of 1990, dynamic spiking experiments using a liquid solution were performed in the field. Two of four quadruple sampling trains were spiked for eight sampling runs. Method 0010 train components were prepared and analyzed in three parts: filter/front half rinse, XAD-2® resin, and condensate/condensate rinse. In sixteen spiked trains, spiked analytes were detected with reasonable recoveries (>50%) in only four runs. In general, surrogate compounds spiked during preparation of the samples showed low recoveries from XAD-2®, and recoveries of spiked analytes which were observed ranged from 4 to 63 percent. Because these results were at variance with results obtained for analytes spiked in laboratory studies and a previous field study, the sample preparation process was investigated in detail. Sample preparation procedures had followed Method 0010, but use of some procedures which were not specifically prohibited by Method 0010 had depressed compound recoveries. Laboratory studies were performed to evaluate the effects of various sample preparation parameters on compound recoveries. To ensure that the sample preparation procedures for Method 0010 train components were clear and unambiguous, a new protocol to address preparation of Method 0010 train components for Method 8270 analysis was written. The new protocol has been used in a subsequent field study with excellent results.

INTRODUCTION

In order to evaluate the performance of SW-846 Method 0010 for sampling and Method 8270 for the analysis of semivolatile halogenated organic compounds listed in Title III of the Clean Air Act Amendments of 1990, a field study was performed using dynamic spiking techniques to establish the precision and bias of the overall methodology. Using the guidelines of EPA Method 301 (Protocol for the Field Validation of Emission Concentrations from Stationary Sources) for statistical design of the field testing experiments,

quadruple Method 0010 sampling trains with four collocated probes were used. Dynamic spiking equipment and procedures had been developed and evaluated to allow dynamic spiking of a methylene chloride solution of the compounds of interest for the duration of each Method 0010 sampling run. According to the guidelines of Method 301, two trains were spiked and two trains were unspiked.

EXPERIMENTAL

The field evaluation study was conducted at a chemical manufacturing facility where waste chemicals were incinerated in a coal-fired boiler. A "biosludge" consisting of 10 percent organic matter and 90 percent water was fed continually to the incinerator. A site presurvey, when preliminary samples were taken, showed that none of the proposed analytes was present in the background emissions from the boiler, and that the emissions were wet (approximately 10 percent moisture). Method 0010 sampling trains were recovered in the field, and components were shipped to the laboratory for preparation and analysis. Extracts (three per sampling train) were generated from methylene chloride extractions of the following train components:

- Filter/front half rinse;
- XAD-2® sampling module; and
- Condensate/condensate rinse.

The final extract volume for these sampling train components was 5 mL, rather than the 1 mL final volume specified by Method 8270.

Results for the GC/MS analysis are summarized in Table I. To perform a thorough statistical analysis according to Method 301 procedures, results from six paired spiked runs are required. Eight sampling runs using quadruple trains had been performed in the field; acceptable results were obtained for only four runs (1,2,3,6). For those four runs, for most compounds results appear generally comparable to laboratory and field results obtained previously (Table II). However, results from other sampling runs showed very low recoveries for the surrogate compounds and many of the spiked compounds were not detected.

RESULTS AND DISCUSSION

Careful examination of the data for all of the sampling runs showed that, in general:

- Recoveries of the surrogate compounds spiked in the laboratory were low for the XAD-2®, where most of the organic compounds were expected to be retained;

- Isotopically-labeled compounds spiked in the laboratory to track recovery were frequently not observed at all; and

- The majority of the analytes spiked in the field were not observed. Recoveries for field-spiked analytes that were observed ranged from 4 percent to 63 percent.

Since the surrogate compounds and isotopically-labeled compounds are spiked in the laboratory after return of the sampling train components, problems were obviously encountered in the laboratory preparation rather than in the field spiking.

The critical parameter is recovery of spiked compounds from XAD-2®. Recovery results for these field samples were sufficiently at variance with previous recovery results from a laboratory study[1] and a field study[2] that an explanation for the low recoveries was pursued. Quality Control results from Method Blanks were examined. Method Blanks consist of sampling train media (filters, water, solvents, XAD-2®) that are spiked with surrogate compounds in the laboratory, extracted, and analyzed. Recoveries from Method Blanks were acceptable to high, indicating that general laboratory sample preparation and analysis procedures were done properly.

Method Spike recovery data were also examined. Method Spikes consist of train components spiked with analytes and surrogate compounds in the laboratory. The Method Spikes are extracted and analyzed with the field samples. The results obtained for the XAD-2® Method Spikes are typical (Table III): acceptable to high recoveries indicated that surrogate and sample spiking, preparation, and analysis procedures were in control.

From an examination of the Quality Control samples, we concluded that a systematic error in sample spiking, sample preparation, or analytical procedures did not appear to be the cause of the low recoveries: Method Blanks and Method Spikes were prepared and analyzed with the field samples, using the same spiking solutions and the same procedures. The original extracts, which had been archived after mass spectral analysis, were next examined visually to determine if the appearance of these extracts was qualitatively or quantitatively different from the appearance of the Quality Control samples. Several key differences were observed:

- Method Blanks and Method Spikes were light yellow in color and had the appearance of several mL of clear organic solvent. The color of field sample extracts ranged from clear to nearly brown.

- Some of the field extracts were clearly completely aqueous, with only small pools of organic liquid floating on top;

- Two phases were clearly visible in some of the field extracts; and

- Many of the field samples were not methylene chloride extracts, since only a slight odor of methylene chloride was detected when vials were opened.

Laboratory sample preparation procedures and observations were carefully reviewed with laboratory staff. The observation was reported that many of the field samples required far longer (3-4 hours) than the usual amount of time (20-30 minutes) to achieve concentration to 5 mL using Kuderna-Danish concentration procedures.

The obvious difference between the Quality Control samples and the field samples was that the laboratory-generated sampling train media were dry, while the field XAD-2® samples were wet because of the moisture content of the source. Dry XAD-2® can simply be poured from the sampling module to the Soxhlet extraction apparatus. Wet XAD-2® does not pour: the wet resin sticks to the glass walls of the sampling module and is not readily moved from the sampling module with methylene chloride rinses. Typical procedures used for the removal of wet XAD-2® from the sampling module include repeated rinses with methylene chloride, which frequently leaves significant amounts of the wet XAD-2® in the sampling module, or tapping the sampling module against the laboratory bench top, which often results in breakage of the sampling module. Laboratory staff had tapped the XAD-2® from the modules to remove as much as possible, rinsed the walls of the module with methylene chloride to remove as much of the remaining wet XAD-2® as possible, and performed a final rinse of the sampling module with methanol to remove all of the remaining XAD-2®. If a sufficiently large amount of methanol is present when sample concentration is performed, methylene chloride will be driven off rather than methanol, and the final extract will consist of a methanol solution with significant losses of surrogate compounds and analytes.

The rinses used in the field recovery of Method 0010 train components consist of 50:50 methylene chloride: methanol, which form a homogeneous solution. The methanol can be separated from the methylene chloride only if sufficient water is added to create two distinct phases. However, 100 mL of

methylene chloride can hold up to 15 mL of water without separating into two distinct phases. According to the method, sample extracts are dried by filtering through a bed of dry sodium sulfate. If sufficient water is present, the sodium sulfate will cake and will not dry the extract efficiently. Thus, after drying, if the sodium sulfate cakes, an extract may consist of methylene chloride, water, and methanol, all in one phase. If a solution of this composition is concentrated, methylene chloride will be lost before the water and methanol are lost, resulting in a water/methanol solution if sufficient quantities of water and methanol are present in the original extract. However, if sufficient water (50-100 mL) to effect separation of phases is added prior to extraction, the methanol will be driven into the aqueous phase and excellent recoveries of spiked surrogate compounds and analytes can be obtained.

Laboratory experiments were conducted to reproduce the conditions under which the field samples had been extracted. Replicate samples of dry XAD-2® were spiked with surrogate compounds and analytes to provide a baseline for recovery. Excellent recoveries and good reproducibility were obtained. Next, wet XAD-2® was prepared and spiked with surrogate compounds and analytes. The 40 g quantity of XAD-2® which is contained in the sampling module of the Method 0010 train retains approximately 50 mL of water when water is poured through the resin bed. This 50 mL of retained water does not produce a distinct water layer when the spiked wet XAD-2® is extracted and analyzed. When the extracts from the wet XAD-2® were concentrated and analyzed, recoveries were slightly lower than the recoveries obtained with dry XAD-2® and reproducibility was slightly poorer, but both recovery and reproducibility were acceptable. The wet XAD-2® was prepared and spiked in the Soxhlet extractor, so no transfer of wet XAD-2® was required. Wet XAD-2® alone does not depress recoveries significantly.

The major problem appeared to occur in the transfer of the wet XAD-2®. A procedure was therefore developed to transfer the wet XAD-2® without the use of methanol. The apparatus shown in Figure 1 is used to transfer the XAD-2® if the resin is too wet to pour. The glass wool is removed from the end of the sampling module and placed in the Soxhlet extractor to ensure extraction. A small piece of pre-cleaned glass wool is placed in the arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm. The XAD-2® sampling module is inverted (glass frit up) over the Soxhlet extractor, approximately 5-10 mL of methylene chloride is added above the glass frit, and air pressure created by squeezing the rubber bulb shown in Figure 1 is used to gently but firmly push the methylene chloride through the frit, forcing the XAD-2® out of the sampling module. This process is repeated 3 to 5 times, and a Teflon® wash bottle containing methylene chloride is used to rinse the walls of the sampling module to transfer XAD-2® which adheres to the walls of the sampling module.

After 3-5 methylene chloride rinses, no more than a monolayer of XAD-2® usually remains in the sampling module. This XAD-2® transfer procedure has been used successfully to transfer XAD-2® from sampling modules used in sampling a source with 55 percent moisture: excellent recoveries of both surrogate compounds and spiked analytes were obtained. In addition, this procedure is far more efficient than the procedure of tapping the resin out of the sampling module: three transfers using the rubber bulb can be performed in one or two minutes.

The investigation with subsequent laboratory study illustrates the value of sufficient Quality Control data in determining the cause of a problem with data quality. A new procedure for the preparation of Method 0010 train components for analysis by SW-846 Method 8270 has been written. A flowchart for the overall method is shown in Figure 2. In this procedure, the use of methanol in the laboratory is directly and specifically prohibited to ensure that the final extracts consist of methylene chloride, not a mixture of methylene chloride and methanol. Also, addition of sufficient water to ensure that two distinct phases are produced when both water and methanol are components of the solution (for example, in the sampling train rinses of the front half and the condensate) is a required part of the procedure. This procedure is being subjected to EPA review.

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DISCLAIMER

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Table I

Summary of Results for All Eight Runs and All Sampling Trains, Using Surrogate-Corrected Data

	Train A Spiked			Train B Spiked			Train C Unspiked			Train D Unspiked		
Run	X	C	F	X	C	F	X	C	F	X	C	F
1	y	y	y	y	y	y	y	y	y	y	y	y
2	y	y	y	y	y	y	y	y	y	n	y	y
3	y	y	y	y	y	y	y	y	y	y	y	y
4	n	y	n	n	y	n	y	y	n	y	y	y
5	Z	y	y	Z	y	n	y	y	y	y	y	y
6	y	y	n	y	n	n	Z	y	y	Z	y	y
7	n	n	n	y	y	y	Z	y	Z	y	y	Z
8	n	y	Z	y	y	y	Z	y	y	y	y	Z

Note: Recoveries for C and D Trains refer to recoveries of surrogate compounds and isotopically-labeled analogs.

X = XAD-2® module.
C = Condensate fraction.
F = Filter fraction.
Z = Partial success; some but not all analytes detected.
y = All analytes detected.
n = No analytes detected.

Table II

Comparison of Percent Recoveries of Semivolatile Halogenated Organic Target Compounds in Laboratory and Field Studies (Uncorrected for Surrogate Recoveries)

Compound	Mean Results		
	Laboratory[1]	Field 1[2]	Field 2[3]
Bis(chloromethyl)ether	18.3	0.0	0.0
Epichlorohydrin	75.2	6.0	13.4
cis-1,3-Dichloropropene	21.9	49.1	50.3
trans-1,3-Dichloropropene	20.4	52.0	79.8
1,1,2-Trichloroethane	53.1	56.4	60.3
1,2-Dibromoethane	66.3	58.9	62.5
Tetrachloroethene	49.7	53.2	49.4
Chlorobenzene	76.0	62.3	65.1
Bromoform	99.3	59.8	69.3
1,1,2,2-Tetrachloroethane	81.1	64.0	73.9
Dichloroethyl ether	75.8	60.9	77.0
1,4-Dichlorobenzene	68.2	56.2	73.5
Benzyl chloride	78.7	67.4	73.9
Hexachloroethane	85.4	74.0	70.9
1,2-Dibromo-3-chloropropane	66.2	44.8	73.8
1,2,4-Trichlorobenzene	58.2	59.5	76.1
Hexachlorobutadiene	58.3	65.4	77.1
Benzotrichloride	67.0	60.1	72.4
2-Chloroacetophenone	79.7	56.0	79.5
Hexachlorocyclopentadiene	513.0	42.3	59.6
2,4,6-Trichlorophenol	45.6	49.8	75.4
2,4,5-Trichlorophenol	52.7	62.7	76.6
Hexachlorobenzene	32.9	44.6	56.5
Pentachlorophenol	8.9	42.4	60.3
Pentachloronitrobenzene	38.2	43.4	58.5
Chlorobenzilate	43.6	40.7	61.8
3,3'-Dichlorobenzidine	86.4	4.4	0.6

[1]Mean of 16 replicates.
[2]Mean of 12 replicates.
[3]Mean of 4 replicates.

Table III

Spiked Compounds and Surrogates Recovered from Dry Method 0010 XAD-2® Traps

Compound	Theoretical Amount	% Recovery			
Surrogate	(μg)	MS-A	MS-B	MS-C	MS-D
2-Fluorophenol	991	107	99	108	102
Phenol-d_5	1010	112	106	113	108
Nitrobenzene-d_5	509	112	95	104	98
2-Fluorobiphenyl	490	119	115	122	111
2,4,6-Tribromophenol	997	67	74	73	66
Terphenyl-d_{14}	501	135	112	115	108
Epichlorohydrin-d_5	250	99	68	76	71
Chlorobenzene-d_5	350	94	91	106	93
1,1,2,2-Tetrachlorotthane-d_2	254	114	93	99	91
Bis(chloroethyl)ether-d_8	333	104	91	95	87
Benzyl chloride-d_7	244	103	122	130	117
2,4,5-Trichlorophenol-d_2	129	ND	ND	106	ND
Targets	**(μg)**	**% Recovery**			
Epichlorohydrin	199	991	68	72	74
cis-1,3-Dichloropropene	159	87	67	71	76
trans-1,3-Dichloropropene	34	365	77	80	86
1,1,2-Trichloroethane	195	98	77	84	86
1,2-Dibromoethane	196	95	84	94	95
Tetrachloroethene	195	86	82	92	92
Chlorobenzene	200	99	92	96	100
Bromoform	202	101	104	120	127
1,1,2,2-Tetrachloroethane	200	101	84	91	92
Bis(chloromethyl)ether	252	80	70	72	74
1,4-Dichlorobenzene	226	96	119	125	131
Benzyl chloride	202	102	95	105	104
Hexachloroethane	185	107	103	112	114
1,2-Dibromo-3-chloropropane	272	103	109	118	121
1,2,4-Trichlorobenzene	198	104	120	132	135
Hexachlorobutadiene	200	107	126	139	148
Benzotrichloride	199	106	126	141	142
2-Chloroacetophenone	229	112	108	116	120
Hexachlorocyclopentadiene	204	135	133	133	133
2,4,6-Trichlorophenol	237	109	121	129	129
2,4,5-Trichlorophenol	194	101	127	130	139
Hexachlorobenzene	222	102	110	124	121
Pentachlorophenol	202	83	100	87	54
Pentachloronitrobenzene	216	101	106	113	114
Chlorobenzilate	200	116	110	123	130
3,3'-Dichlorobenzidine	190	142	140	171	158

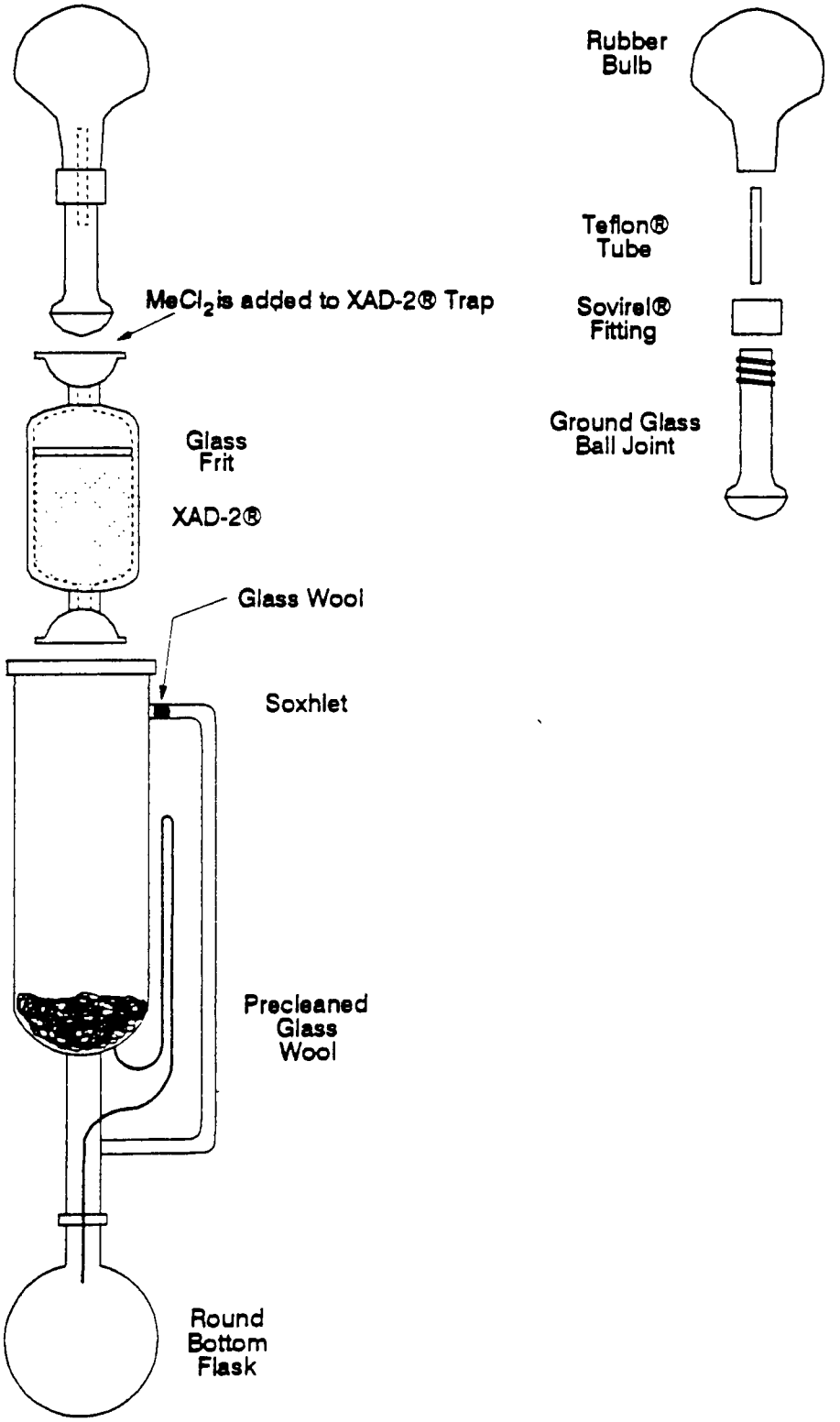

Figure 1. Transfer of Wet XAD-2®

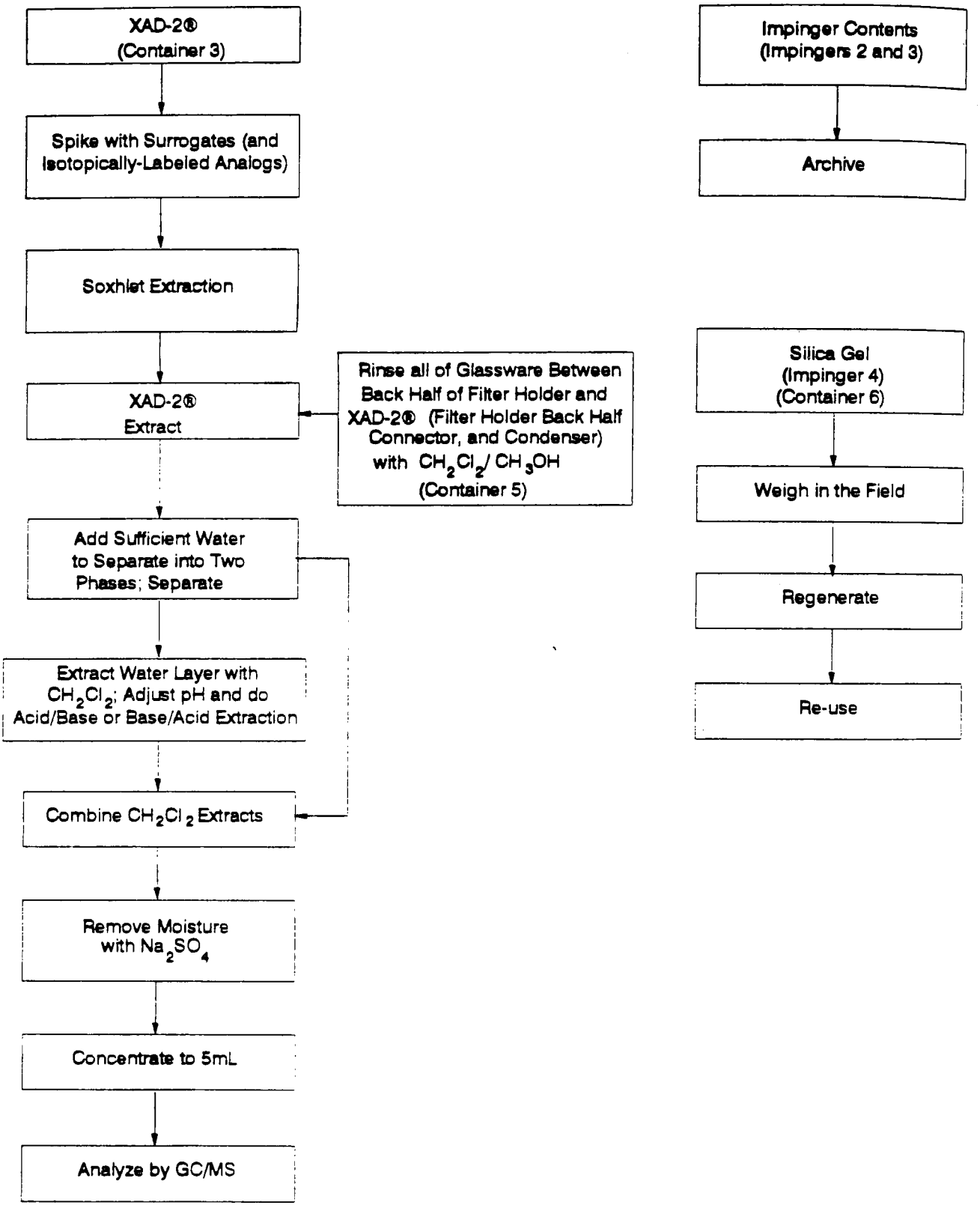

Figure 2. Sample Preparation Scheme for Method 0010 Train Components

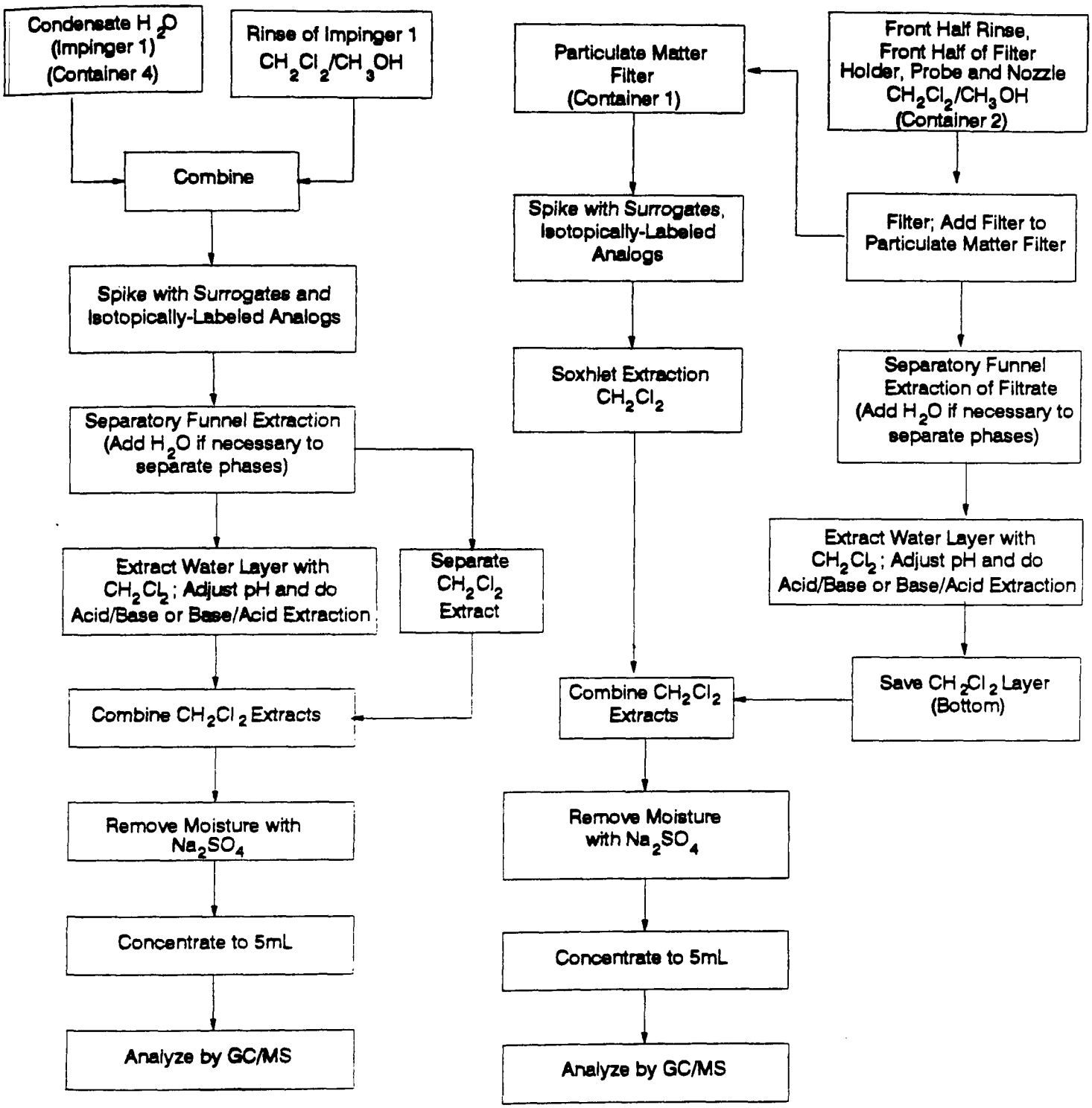

Figure 2. (Continued)

EVALUATION OF A NEW NON-IMMUNOASSAY FIELD TEST KIT FOR TOTAL PETROLEUM HYDROCARBONS IN SOIL

T.B. Lynn, S. Finch, L. Sacramone, Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517 and K.A. Wright, 2094 Hideaway Ranch Road, Placerville CA 95667

Abstract

A new TPH field test has been evaluated. Soils spiked with known amounts of both diesel and number 6 fuels were used to determine the relative response factors for the two different analytes as well as the method precision and bias. The results indicate that the response factor for number 6 fuel is 90% of the diesel fuel calibrator. Very little bias was found and the precision is better than +/- 10% for both analytes.

Introduction

A novel new analytical procedure has been developed to determine the hydrocarbon content of soil samples using environmentally safe reagents which will be simpler and less expensive than alternative methods. The data presented here illustrates the effectiveness of the new Petro-Flag™ technology on two analytes; diesel fuel and number 6 fuel oil.

The Petro-Flag technology has been in use in the field in a non-commercial form for over two years. A commercial version will be available soon for use in the field by environmental professionals. The colorimetric test is easy to use and contains no hazardous chemicals. A specially designed hand-held colorimeter will be available to provide a digital readout in ppm of the analyte. Using the prepackaged reagents 10 to 20 samples can be run in one batch in under 30 minutes. The anticipated cost per test is $10 to $15 and the colorimeter will cost under $300.

The patent pending kit chemistry relies on a unique system of extraction solvents and color-forming reagents. Because of its broad linear response range the Petro-Flag test kit can be used on a wide variety of hydrocarbon analytes including fuels, lubricants, hydraulic fluids and greases. It does not only test for specific compounds or aromatics but all petroleum hydrocarbons which makes the kit useful as a low cost general screening tool as well as for quantitative determination of TPH concentrations is easily

performed at contaminated sites requiring lateral and vertical definition, as well as for soil remediation projects to monitor the status of the remediation and for determining when samples should be taken for expensive laboratory analysis for final closure. The field test is especially useful during underground storage tank removals to screen the excavated area during the excavation and prior to collecting confirmatory samples. The test uses field calibration standards to achieve a high degree of accuracy in a large variety of soil types.

The PETRO-FLAG technology is currently in the beta-testing stage. Evaluations on different soil types with different analytes indicates that the extraction efficiencies are very high for most petroleum hydrocarbon contaminants.

Preparation of Spiked Soil Samples

To simulate typical soils, an 8 kg mixture of clay soils and sand, approximately 75:25 w/w was prepared. The soils and sand were obtained from residential areas and were analyzed for total petroleum hydrocarbons (TPH) using EPA Method 418.1 and found to contain less than 10 ppm TPH. The clay soil was broken up by hand and allowed to air dry for 24 hours. The clay and sand were sieved to pass a 0.850 um sieve, mixed together, and tumbled for 24 hours in a rotating pail. Most of the clay particles were observed to be considerably smaller than 0.850 um. The water content of the freely flowing mixture was 1%. The soil was transferred to aluminum cake pans prior to addition of contaminants. Sub-sampling to generate homogeneous splits for spiking was performed according to the procedure described by Schumacher (4) in which soil was transferred from one pan to another in random order five times. The soils were then spiked with either diesel fuel or number 6 fuel oil. The fuels were dissolved in an excess of hexane to facilitate uniform mixing through out the soil. The soil mixtures were air dried to a constant weight, bottled in previously unused clean 8 oz. glass bottle with PTFE lined caps and tumbled for 4 hours on a rotating tumbler.

Analysis

Each of the spiked soils were analyzed in triplicate using the Petro-Flag test kit. Using the Petro-Flag procedure, 5 grams of soil were weighed into the extraction tube, 10 grams of extraction solvent were added and the sample was extracted for 5 minutes with intermittent shaking. The extract was then filtered using a 0.2 um filter fitted with a glass wool pre-filter. The filtered extract was added directly to the analysis vial

containing the premeasured color reagent. The vial was then capped and shaken vigorously to ensure mixing. The color was allowed to develop for a minimum of 10 minutes, shaking intermittently. After the color development step, the vial was placed in the colorimeter. The absorbance reading was then used to quantify the TPH content of the sample using the standard calibration curve.

The calibration solutions were made up using diesel fuel in the extraction solvent at 50 ppm and 250 ppm. For the 5 gram sample size used for this study this is equivalent to 100 ppm and 500 ppm in the soil. In the field the Petro-Flag kit will use a soil spike at two levels to determine the response factors and background corrections for site specific soil samples. For this study, using solvent standards allowed for an estimation of the extraction efficiencies for the new method.

Results and Discussion

The diesel fuel results are presented in table 1. As indicated by the relative standard deviation between replicates the method is very reproducible. The comparison with the gravimetric value indicates that the extraction efficiency is greater than 95%. There is also very little bias.

Table 1 Petro-Flag Diesel Results

Conc. (ppm)	Trial A (ppm)	Trial B (ppm)	Trial C (ppm)	Mean (ppm)	Std. Dev. (ppm)
54	69	69	71	70	1.09
106	107	114	114	112	3.82
255	239	254	245	246	7.58
516	504	507	516	509	6.43

The number 6 fuel oil results shown in table 2 indicate that the response factor is approximately 90% at 500 ppm. The repeatability as indicated by the standard deviation is again at least +/- 10%.

Table 2 Petro- Flag Number 6 Fuel Results

Conc. (ppm)	Trial A (ppm)	Trial B (ppm)	Trial C (ppm)	Mean (ppm)	Std. Dev. (ppm)
50	75	71	75	73	2.18
100	105	117	117	112	6.55
251	222	234	234	230	6.55
500	438	449	449	446	6.55

Summary

The data for the two analytes investigated show that the method is very reproducible. The 95% confidence intervals for the replicates indicate the method should be expected to have repeatability of better than 10%. Although the two analytes differ in composition they give a response that is within 10% at the 500 ppm level.

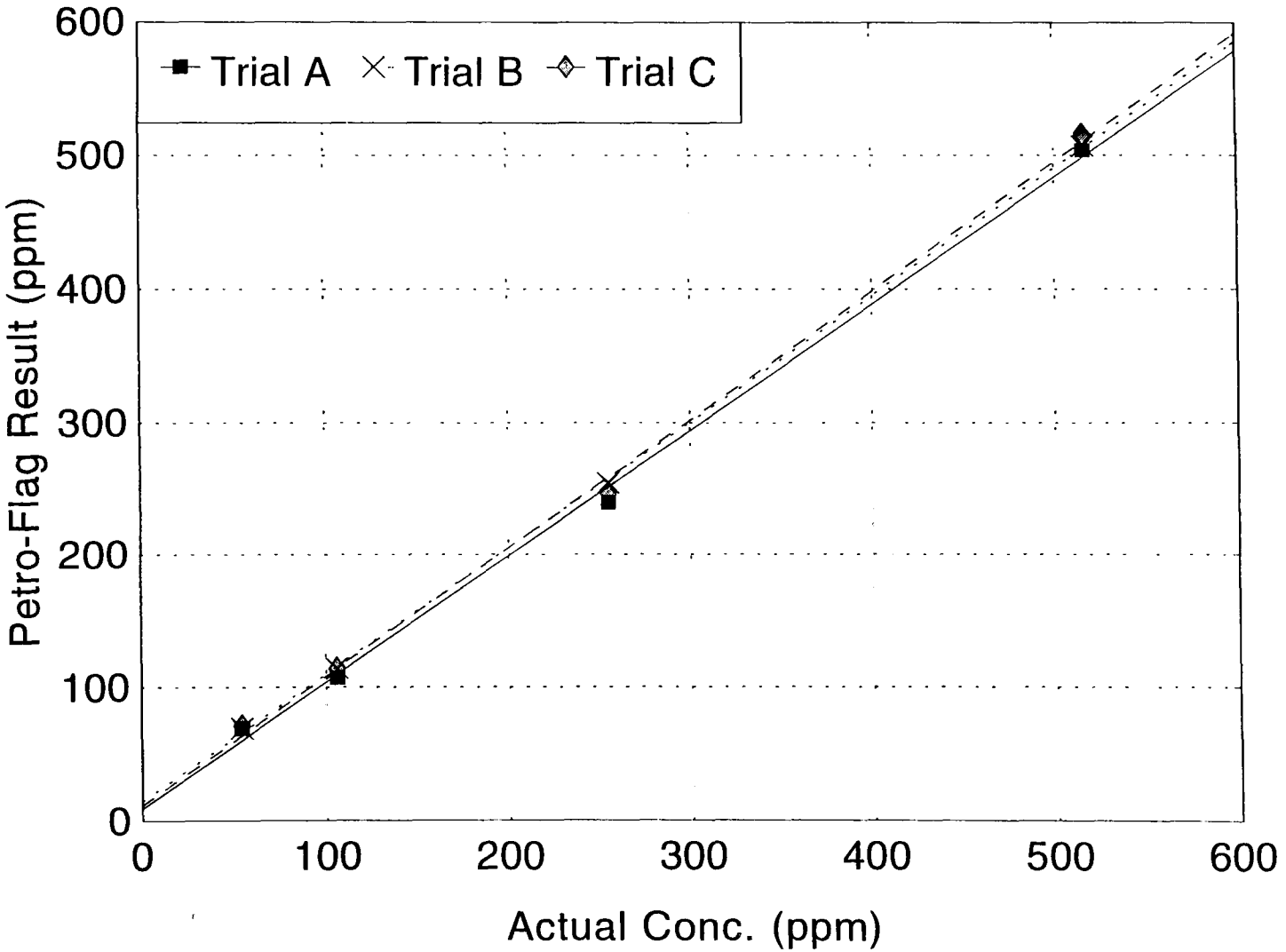

Figure 1: Petro-Flag Diesel Results

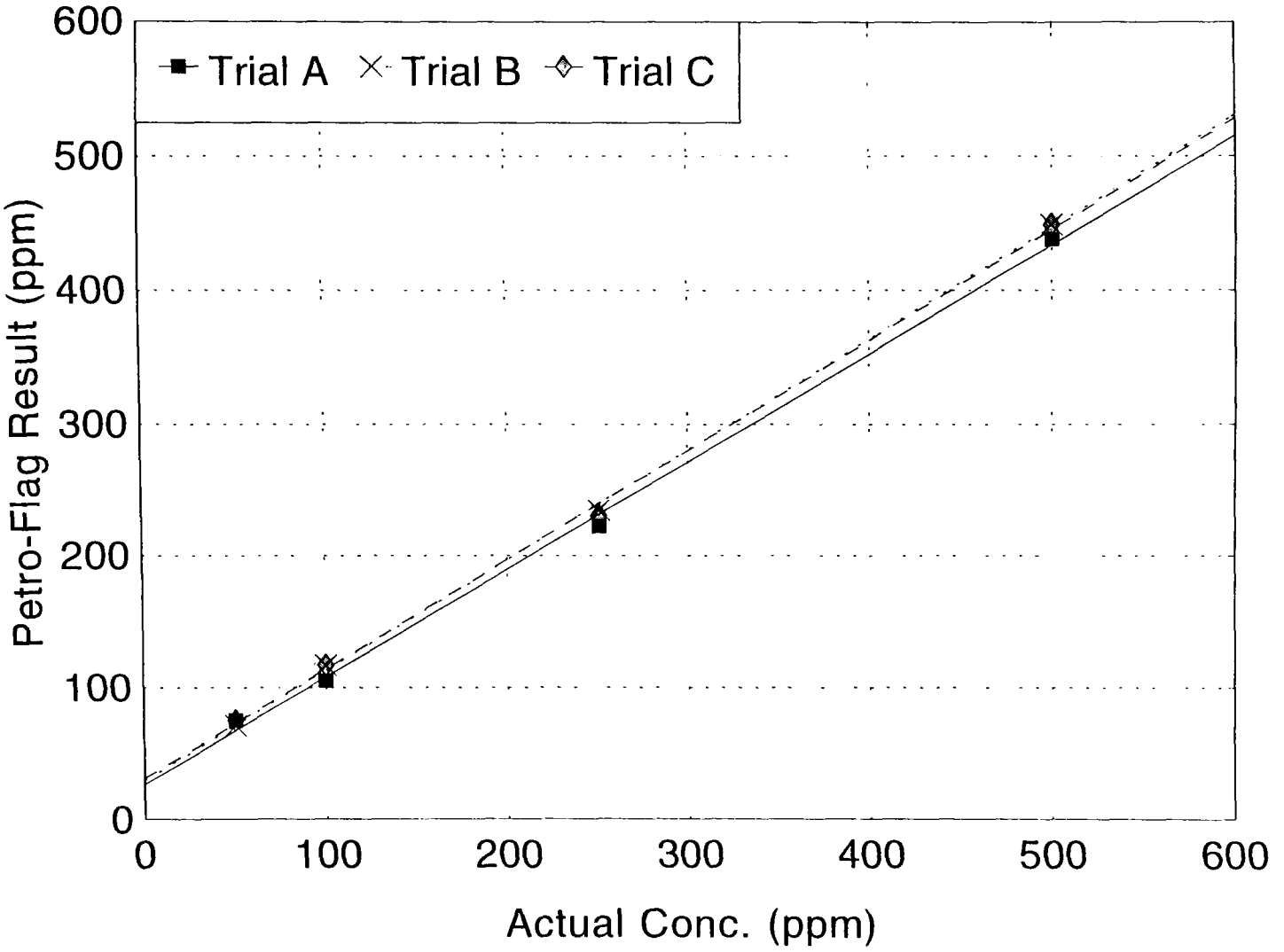

Figure 2: Petro-Flag Diesel Results

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Multi-Element Multi-Media Analysis of Air-Borne Emissions at Secondary Lead Foundries

David Eugene Kimbrough, Public Health Chemist II, California Environmental Protection Agency, Department of Toxic Substances Control, Hazardous Materials Laboratory-Southern California 1449 W. Temple Street, Los Angeles, California 90026-5698

Dr. Irwin "Mel" Suffet, Professor of Environmental Health, UCLA School of Public Health, Department of Environmental Health Sciences, 10833 Le Cante Ave. Los Angeles, CA 90024-1772

Abstract

The principal focus of public health concern regarding air borne emissions from secondary lead smelters has been lead. Antimony, arsenic, cadmium, and copper also are present in the metallic part of these batteries, as are selenium and silver in some cases. Additionally, air samplers can also pick up wind blown dusts and soils which can contain the above mentioned elements as well as barium, cobalt, chromium, nickel, vanadium, and zinc.

In order to fully distinguish the sources of air borne lead (smelters, automobiles, the soil) and to fully characterize the potential health effects from all toxic elements that may be emitted by a source it is essential to analyze for all toxic elements. In this paper, a method for the solublization of sixteen regulated toxic elements from glass fiber filters and analysis by ICP-AES is presented. The method is an application of USEPA SW-846 method 3055, an agua regia method. The results from high volume field samplers from two secondary lead smelters located on and off site are shown similar patterns of concentration and type of elements as found in the parent material and in the surrounding soil.

NEIC FORMS II: AUTOMATING FIELD RECORDS MANAGEMENT

Kaye I. Mathews, Quality Assurance Manager, EPA National Enforcement Investigations Center, Denver Federal Center, Denver, Colorado 80225; Jeffrey C. Worthington, CQA, Director of Quality Assurance; David T. Lark, Senior Programmer/Analyst; Chia-Ying Teng, Senior Programmer/Analyst; Tracy A. Phillips, Audit Program Manager; Brian K. Patlen, Project Manager; TechLaw, Inc., 12600 W. Colfax Avenue, Suite C-310, Lakewood, Colorado, 80215.

ABSTRACT

Application of technology to field sample collection has come of age with development of a specialized software system that automates routine field sampling tasks. Originally conceived as part of EPA Analytical Operation Branch's (AOB) Quick Turnaround Method (QTM), EPA's National Enforcement Investigations Center (NEIC) has broadened the scope of the project to include the Contract Laboratory Program (CLP) and make it flexible enough to handle most sampling scenarios.

The Field Operations Records Management System II (FORMS II) was developed by NEIC with support provided by the Contract Evidence Audit Team (CEAT). The initial prototype was developed by EPA Region 4.

FORMS II automates evidence-related field sampling documentation including bottle labels, sample tag labels, traffic reports, chain-of-custody records, and custody seals. FORMS II enables field personnel to download information to the laboratory, RSCC, and regional users. FORMS II improves field time management, standardizes information management, and captures collection information in an electronic format early in the field sampling process.

The authors provide a summary of FORMS II development activities and review features of the system. Directions for obtaining FORMS II are provided in the summary of this paper.

INTRODUCTION

FORMS II was developed to:

- ❑ Facilitate capture of field information during sampling events, and
- ❑ Automate production of bottle labels, sample tags, bottle-specific custody seals, chain-of-custody seals, chain-of-custody records, cooler seals, PRP sample receipt records, and field reports.

The background and history of FORMS II development is presented here, followed by a discussion of EPA Life Cycle Documentation Guidance. Design criteria are provided. A brief description of the development process is presented. Three field tests of FORMS II are discussed, followed by a summary description of system operations and features.

BACKGROUND AND HISTORY

The EPA NEIC conducts environmental enforcement investigations and develops and implements EPA enforcement strategies for EPA and other federal and state agencies. NEIC functions include forensic laboratory services, field investigations, litigation support, information services, and training.

In the early 1980s, NEIC established the Evidence Audit Program for the Superfund Contract Laboratory Program (CLP). This program established documentation and sample-handling requirements for laboratories generating environmental data for the Agency based on NEIC evidentiary policies and procedures.

NEIC experience with evidence issues provided a basis for a request to assist in an effort to streamline the resource intensive field documentation functions that occur during sampling activities. The EPA AOB requested that NEIC develop a state-of-the-art software system especially for the model CLP QTM analytical service. NEIC directed their Contract Evidence Audit Team to provide system development in support of this project.

NEIC participated in QTM workgroup meetings which focused on considerations to streamline each analytical service phase from sampling effort through data delivery using uniquely tailored software. Although automation had not been widely used to support EPA sampling activities, a prototype system for automating the documentation task had been developed in EPA Region 4. The Region 4 system was ultimately used as the basis for development of the NEIC FORMS II system.

EPA SYSTEM LIFE CYCLE MANAGEMENT

FORMS II was developed using life cycle documentation guidance prescribed by EPA. OSWER's Life Cycle Management Guidance provides a structured approach for the solution of information management problems, particularly those that require consideration of automated solutions.

The benefits of system life cycle management include:

- ❑ Full consideration of a system's operating environment, and associated systems and data requirements.
- ❑ Early identification of technical and management issues.
- ❑ Early assessment of resource needs.
- ❑ Realistic expectations of user community.
- ❑ Balanced consideration of all aspects of proposed system modifications.
- ❑ Periodic evaluations of system effectiveness.

The stages of a system life cycle include initiation, concept, definition, design, development, implementation, production, evaluation, and archival.

The following life cycle documents were developed for this pilot project:

- ❑ System Concept Paper
- ❑ Detailed Data Requirements
- ❑ Detailed Functional Requirements

- ❑ Data Management Plan
- ❑ Project Management Plan
- ❑ System Test Plan
- ❑ Data Dictionary
- ❑ Users Manual/Operation and Maintenance Manual

DESIGN CRITERIA

During requirements analysis in initiation and concept stages of FORMS II, a variety of design criteria were identified and incorporated into the FORMS II design. Following is a discussion of design criteria.

C/C++ language

FORMS II was programmed in C/C++ language. C/C++ language is a third generation universal programming language which is widely used in the programming industry.

Object-oriented techniques

Object-oriented programming techniques were employed in FORMS II design. This approach allows programmers to design and program "objects." Objects perform individual functions and they may be re-used at any time or in other programs and systems. Objects are saved in a library of objects and often include data elements that objects act on.

When a new object is needed, coders may use an old object to make a new object which "inherits" designated characteristics from previous objects. The technique results in programs which may be easily modified. New programs may be designed and programmed faster using previously created objects.

Hardware portability/compatibility/versatility

Because field samplers cannot guarantee access to an AC power source or a stable computer working environment, FORMS II is compatible with existing portable hardware including portable computers, portable printers, and portable bar code

scanning devices. While FORMS II is mouse-compatible, unknown field conditions prohibit FORMS II reliance on a mouse.

Field conditions can pose considerable obstacles for many hardware components. Specific hardware units were selected for field testing to minimize likelihood of failure or downtime.

Bar code application

Use of bar code technology was established as a priority because bar coding can accelerate the sample packing process for sample shipment to laboratories. Also, laboratory personnel may use sample bottle bar codes to facilitate receipt and associated records management activities.

Flexibility for multiple samplers/samples

Field samplers and field sampling organizations often use unique numbering and identification schemes when collecting samples. They also vary in their approach to many other activities. For that reason, FORMS II design includes choices for:

- ❑ Identification scheme
- ❑ Activity names
- ❑ Choices for label information
- ❑ Choices for number and types of labels/tags/seals

Sample Definitions

FORMS II design criteria is based on the following definitions of a sample and related sample types:

- ❑ Sample "environmental sample," a single, discrete portion or piece of the environment collected from a specified physical location at a specific time. The single sample may be placed in multiple vessels. Parts of the same sample in different vessels are not referred to as separate samples.

- ❑ Fraction a part of an environmental sample which may be designated for a specific type of analysis or analyses. Multiple fractions may be placed in a single vessel. One fraction may be in several vessels.

- Duplicate - represents additional amounts of an environmental sample which are placed into additional vessels identical to the vessels used for the sample. This additional sample is not a different sample. The same identification number is used and the duplicate may be designated by a "D" suffix. FORMS II creates a separate sample record for a duplicate.

- Blind duplicate a duplicate where the identification number used is not identical to the identification number of the original environmental sample. FORMS II creates a separate sample record for a blind duplicate.

- Split "PRP" split, a duplicate which is numbered with the identification number of the original environmental sample and also marked with a PRP designation. FORMS II creates a separate sample record for a split.

DEVELOPMENT PROCESS

During FORMS II development, existing software was reviewed to determine compatibility with proposed EPA uses. No commercially available software met EPA needs at that time. Research was conducted to identify and itemize data and functional requirements for FORMS II.

Data entities and their relationships were drafted and flow charts were presented to field samplers for review. Borland® C++ Turbovision™ was selected for the programming language based on the object-oriented approach inherent in the language and ease of use for developing applications. Code Base was selected as the data base manager. A bar code library was purchased to print bar codes on labels. Universal Code 39 was selected as the bar code format.

Internal, unit, and integration testing were performed as described in the FORMS II Test Plan. System screens were presented to field samplers for review. Example system screens are provided in the attachment to this paper. Draft copies of FORMS II on disc were also presented for review.

FIELD TESTS

The final phase of software testing is system testing. An important part of system testing for FORMS II included field tests in three EPA Regions. A discussion of the field tests in each region is provided below.

Region 2 Field Test

FORMS II was used at a former landfill site in Region 2. Sampling efforts consisted of collection of stream and other surface water sources. Sampling was performed by an EPA contractor. EPA personnel from Region 2 and Headquarters observed the field test. FORMS II was tested concurrently with the field sampler's manual documentation efforts to compare system efficiency and error rates.

Region 3 Field Test

Region 3 contractors and EPA personnel reviewed FORMS II operations and outputs during a sample collection event at a former transportation, storage, and disposal (TSD) facility. Samples were collected from large storage tanks. FORMS II was used in parallel to actual sample collection efforts in a staging trailer adjacent to field collection operations. Use of portable equipment was not necessary because there was a power source in the trailer and a stable computer environment.

Region 8 Field Test

FORMS II was tested at a former mine site in the Rocky Mountains. Region 8 contractors were collecting soil samples in an ongoing sampling effort. FORMS II hardware was tested during cold weather conditions which resulted in alternate label selection.

SYSTEM OPERATION

FORMS II operates in a modular fashion. Prior to entering the first module, field samplers may customize the system for their own use by doing the following:

- Choosing the number of labels to be printed for bottle labels, sample tag labels, and bottle-specific custody seals.

- ❑ Designing analysis fractions and customizing sample parameters such as bottle size, preservative, and number of bottles.

- ❑ Entering names of all possible field samplers.

- ❑ Entering names of laboratory destinations.

- ❑ Designing analysis requests (a series of fractions tied together).

After customizing the system to individual preferences, samplers can enter data working down through the system from the largest entity to the smallest. Site information can be entered first. If site information is not available to enter into every field provided, a sampler can simply name the site (with any name) which is the minimum data requirement for this module.

The activity level is the module below the site module and is simply a management tool for the sampler to organize sample collection events. Some sample collection efforts are time-dependent (activities = spring, summer, etc.), some are matrix-dependent (activities = soils, waters, etc.), some are physical location-dependent (activities = west side, east side, hill area, tank area, etc.), and some are regulatory-dependent (activities = remedial investigation, field study, etc.). Individuals reading this will no doubt have their own additions to this list.

Samplers are not required to name an activity. If this section is by-passed, FORMS II will assign a number as the name of the activity.

The plan level is the module below the activity module and is also a management tool to further organize a specific collection event, whether the event is one day or more. Samplers can name the plan. Plans are much like activities. If samplers want to use this as an organization tool to distinguish between different sampling activities, they can do so.

The default module is actually a part of the plan module. If specific information about samples will be very similar (e.g., matrix, fractions designated for analysis, sample date, level), defaulting these items in FORMS II will help accelerate entry of information. In a straightforward sampling event, it is possible that the sampler may need to enter only the sample ID and time if all other information was entered in the default mode.

The collection mode is within the plan mode and is the place where a sampler can enter all information about an individual sample if the information has not already been defaulted. Defaulted information can be changed on a sample-specific basis.

After entering sample collection information, the sampler can elect to print labels. Alternatively, if the field sampler wants to print labels in advance in a staging area or the hotel room and they have advance knowledge of all samples to be collected, they can print labels which contain all required information except date and time. The date and time can be handwritten on the labels and later entered into FORMS II. Label formats are provided in the attachment to this paper.

After sample bottles are labeled, the field sampler is essentially in the same situation as any person who has an inventory to prepare for shipment. At this point, a peripheral bar code scanning device can increase the efficiency of packing sample shipments. Bottle bar codes can be scanned as the bottles are loaded into coolers. The information is attached to the Traffic Report/Chain-of-custody file and will automatically print on the shipment forms. Traffic Report/Chain-of-custody formats are provided in the attachment to this paper.

Estimated training for new FORMS II users is less than two hours. If new users do not need to enter customized information, training time may be reduced.

SUMMARY

NEIC, with system development support by the CEAT, developed FORMS II to:

- ❑ Support quick turnaround sample collection,
- ❑ Automate sample collection documentation,
- ❑ Improve time management in the field,
- ❑ Standardize management of field information, and
- ❑ Capture collection information in an electronic environment early in the process.

FORMS II is currently managed by David Eng, AOB National Automated Data Processing Manager of Superfund Analytical Information. If you are interested in using FORMS II, please contact David at (703) 603-8827.

Site Activity Plan Default Collection shIpment Reports Utilities

View/Edit Container Information

Container No	COOLER 1	Project Code	84644
Traffic No	834576	Account Code	84566
COC Seal No	8735	Regional Info	
		Non-Superfund Program	RCRA

Shipper	Lark
Destination	IT Analytical Services-Export
Carrier	Federal Express
Airbill No	98456-5468576
Date Shipped	04/11/1994
Time Shipped	16:00

Available Bottles	Bottles Packed
AW345 04/BNA	MAW345 01/TOT METALS
AW345 05/BNA	MAW345 02/CN
AW345 06/VOA	MAW345 03/DIS METALS
AW345 07/VOA	MAW346 01/TOT METALS
AW345 08/VOA	MAW346 02/CN

OK Cancel List Traffic/COC Custody Seal

Alt-X Exit F1 Help | Enter Container Number (required) 16:36:24 105664

Site Activity Plan Default Collection shIpment Reports Utilities

View/Edit Sample Information

Site:	M.G.D Landfill Site
Activity:	Spring Sampling
Plan:	Monday Sampling
System ID:	259487743-0001
Related QC System ID:	N/A
Regional ID:	DTL-01-001
Field ID:	SW-041194-01
QC Designator:	--
Matrix:	Sur. Water (Aq)
Default:	Surface Water
Anal. Request:	Std. Surface Water
Station ID	SW01
Sample Type	Grab
Sampler	Lark
Con. Level	Low
Date Began	04/11/1994
Ended	/ /
Time Began	:
Ended	:
Status:	Uncollected
Number of Bottles:	8

Protocol IDs Mark Collected Bottles List

Ok Cancel List Notes Print Labels

Alt-X Exit F1 Help | Press F3 for a list 16:33:25 111296

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:VOA Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: AW346 08

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:VOA Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: AW346 07

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:VOA Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: AW346 06

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:BNA Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: AW346 05

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:BNA Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: AW346 04

Sample ID:259487743-0002 Date:_____ Time:_____
Frac.:DIS METALS Matrix:Sur. Water (Aq)
Regional ID:DTL-01-002
RAS Bottle ID: MAW346 03

Traffic Report and Chain-of-Custody Record
RAS Inorganic

Project Information

Region: 1 Case No.: 84566 [ ] Case Complete

Lead: Superfund Early Action: RI Long Term Action: FS

Project Code: 84644 Account Code: 84566

Regional Information:
Non-Superfund Program: RCRA

Site: M.G.D Landfill Site
Boston, PA Site Spill ID: MA86

Shipping Information

Date Shipped: 04/11/1994 Airbill No.: 98456-5468576

Carrier: Federal Express

To: David Dunlap
IT Analytical Services-Export
5103 Old William Penn Highway
Export, PA 15632-

Sample ID	Matrix/ Sample Type	Preserved/ Conc Level	Analysis	Tag Numbers	Bottle Number	Collection Station ID	Date/ Time	Sampler/ QC Designator
MAW345	Sur. Water (Aq) Grab	HNO3 Low	DIS METALS	3-84568778	3	SW01	04/11/94 08:45	Lark --
MAW345	Sur. Water (Aq) Grab	HNO3 Low	TOT METALS	3-84568776	1	SW01	04/11/94 08:45	Lark --
MAW345	Sur. Water (Aq) Grab	NaOH Low	CN	3-84568777	2	SW01	04/11/94 08:45	Lark --
MAW346	Sur. Water (Aq) Grab	HNO3 Low	DIS METALS	3-84568786	3	SW02	04/11/94 09:30	Lark --
MAW346	Sur. Water (Aq) Grab	HNO3 Low	TOT METALS	3-84568784	1	SW02	04/11/94 09:30	Lark --
MAW346	Sur. Water (Aq) Grab	NaOH Low	CN	3-84568785	2	SW02	04/11/94 09:30	Lark --
MAW347	Sur. Water (Aq) Grab	HNO3 Low	DIS METALS	3-84568794	3	SW03	04/11/94 10:45	Lark --
MAW347	Sur. Water (Aq) Grab	HNO3 Low	TOT METALS	3-84568792	1	SW03	04/11/94 10:45	Lark --
MAW347	Sur. Water (Aq) Grab	NaOH Low	CN	3-84568793	2	SW03	04/11/94 10:45	Lark --

Sampling Company: Sample-It,Inc.

Sampler Name _____ Additional Signature _____

Sampler Signature _____ Additional Signature _____

CHAIN-OF-CUSTODY RECORD

Relinquished by: (Sign)	Date	Time	Received by: (Sign)	Relinquished by: (Sign)	Date	Time	Received by: (Sig

Relinquished by: (Sign)	Date	Time	Received by: (Sign)	Relinquished by: (Sign)	Date	Time	Received by: (Sig

Relinquished by: (Sign)	Date	Time	Lab Received by: (Sign)	Date	Time	Remarks: Is custody seal Intact? (Y / N / none

Custody Seal Number: 8735

Traffic/COC Report Number: 834576

REGION/SMO

FIELD VERIFICATION OF METALS CONTAMINATION IN SEDIMENTS BY STRIPPING ANALYSIS

Khris Olsen, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352 and Professor Joseph Wang, Rossi Setiadji, and Jianmin Lu, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

ABSTRACT

Stripping analysis is targeted for the determination of chromium, lead, cadmium, copper, and zinc concentrations in sediment samples in the field during characterization and remedial activities at hazardous waste sites. Sediment samples are dried and digested using microwave digestion procedures tailored to meet the needs of field activities and electrochemical measurements. Adsorptive stripping voltammetry was used to determine chromium concentrations. Conventional anodic stripping voltammetry and potentiometric stripping analysis were used for cadmium, zinc, copper, and lead determinations in sediment leachate samples. Stripping analysis was demonstrated in the field during site characterization activities at the Unlined Chromic Acid Pit (UCAP) and 1960's Pits located at Sandia Laboratory's Chemical Waste Landfill. Stripping analysis results of sediment leachate solutions were compared to conventional atomic or mass spectroscopy methods approved by the U. S. Environmental Protection Agency (EPA). Stripping analysis for chromium contamination in sediments was conducted at UCAP. Maximum chromium concentrations observed at UCAP were approximately 10,000 ppm. Stripping analysis for chromium, cadmium, zinc, copper, and lead contamination was conducted at the 1960s Pits. Only chromium and copper contamination were identified at the 1960s Pits. Maximum concentrations observed were 5313 ppm and 1749 ppm, respectively.

Stripping analysis has been successfully employed for field verification of metals contamination in soils and sediments at a hazardous waste site. The results demonstrate that stripping analysis is capable of onsite identification of contaminate layers in soils and sediments. Concentration values measured by stripping analysis correlated well with those obtained by EPA approved methods. The remarkable sensitivity, portability, low power need, and low cost makes stripping analysis an attractive choice for onsite analysis of selected metals during site characterization and remediation activities.

This work was funded by Department of Energy's Office of Technology Development through the Mixed-Waste Landfill Integrated Demonstration Project at Sandia National Laboratory through a contract with Pacific Northwest Laboratory. Pacific Northwest Laboratory is operated for the Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

COMPARISON OF THE RESPONSE OF PCB FIELD TEST METHODS TO DIFFERENT PCB AROCLORS

Stephen Finch, Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517

ABSTRACT

Polychlorinated biphenyls (PCB) are one of several environmental analytes that are not composed of single compounds but rather groups of related compounds. Because the analyst is looking for a number of different compounds, he or she must be aware of exactly what a particular analytical technique is detecting. To evaluate how well several popular field methods (2 immunoassays and one chemical method) can test over the range of possible Aroclors, a study was performed where each of the three methods was used to test a broad range of available Aroclors. Results show that on the lower chlorinated Aroclors (e.g.1221) and the more highly chlorinated Aroclors (e.g.1268) the chemical method may be off by a factor of three and the immunoassay methods by a factor of 100. Analysts using these techniques, therefore, should know ahead of time exactly what Aroclors they are dealing with or should implement proper correction factors to eliminate the chance of false negative results.

INTRODUCTION

Several methods currently exist to test for PCBs in soil samples. The most established and most quantitative is gas chromatography (GC), usually capitalizing on the high sensitivity of the electron capture detector (SW-846 method 8080). GC is an excellent technique for quantifying PCBs because it separates out different congeners and quantifies them individually, alerting the analyst to any Aroclor mixtures or weathering that may have occurred while the PCBs have been exposed to the environment.

Field screening methods usually do not quantify individual compounds when testing for PCBs but make an estimate based on one or more characteristics of the target analyte. Therefore, field testing methods may give results that differ from other test methods even though they are operating exactly as designed. Three such field methods were compared on soils contaminated with a variety of Aroclors to see how they would respond in relation to each other. Two of the methods tested are immunoassay (IA) based tests (Millipore EnviroGard™, Ensys PCB RISc™) and one is a chemical based testing device (Dexsil L2000 PCB Analyzer™).

BACKGROUND

Immunoassay based test kits (ELISA) that are currently available for PCB analysis are specific devices that are designed to test exclusively for PCBs. When an animal is

immunized to produce antibodies for PCBs, it is injected with a derivitive of a single or several PCB congeners, but not all 209. Therefore, the antibodies that it produces will be sensitive to specific congeners, but not to all PCBs. For instance, if antibodies are produced to respond to 3,4,3′,4′ tetrachlorobiphenyl, the test kit that utilizes this antibody will be highly sensitive to 3,4,3′,4′ tetrachlorobiphenyl but less sensitive to PCBs that contain different numbers of chlorine atoms or have chlorine atoms at different locations on the biphenyl molecule. As a result of this variation in sensitivity to different PCB congeners, the analyst using an IA test kit may obtain vastly different responses to different Aroclors.

The L2000 PCB Analyzer is not based on an immunoassay, but instead, chemically detects the presence of PCBs by analyzing the sample for total organic chlorine and translates the amount of chlorine detected into ppm PCBs. All PCBs contain some chlorine and therefore, if the percent chlorine in the PCB being analyzed is known, the amount of PCB present can be easily quantified. The percent chlorine contained in a specific Aroclor is usually given by the last two numbers in the four digit Aroclor designation, e.g., Aroclor 1260 is composed of 60% chlorine. Aroclors vary in chlorine content from 21 to 68 percent. This means that for a given concentration of PCB, the amount of chlorine will vary by about a factor of three.

Because both the IA methods and L2000 method may vary in response among Aroclors, a study was designed to determine what that variation might be. If the analyst is testing at a specific level for a certain Aroclor, then what levels of the other Aroclors would need to be present to avoid a false negative? or to avoid a false positive?

PREPARATION

Each field method was purchased or calibrated to test for Aroclor 1242 at a level of 2 ppm. The following Aroclors were included in the study:

1221 1232 1016 1242 1248 1254 1260 1268

Neat standards from General Electric (1254, 1260), Ultra Scientific (1268), Analabs (1248, 1242, 1016), Monsanto (1232) , and Chem Services (1221) were used to make standards in hexane at a level of 1000 μg/g.

A standard soil was made by mixing 6 kg dried clay with 2 kg dried sand after passing each through a 850 μm sieve. The mixture was then tumbled overnight to assure uniformity. The mixture was analyzed by method 8080 to assure that it was PCB free. Soil standards were prepared by placing 200 g of soil on an aluminum pan and spiking with the appropriate amount of PCB in hexane standard. Enough additional hexane was added to form a slurry. Samples were mixed and allowed to dry over night in a fume hood. Samples were then placed in glass jars and tumbled for four hours to assure uniformity.

Soil samples were prepared at the following concentrations:

Aroclor	Concentrations ($\mu g/g$)
1221	40, 200
1232	20
1016	5
1242	2, 5
1248	1, 2
1254	5
1260	10
1268	10, 100

PROCEDURE

Each field test was run according to the instructions supplied by each manufacturer. All the Aroclors were run on each test and the PCB concentration in each soil was adjusted and reanalyzed until a result was obtained that gave a response equal to or just greater than the response obtained from 2 ppm of Aroclor 1242. Soil samples were initially tested at concentrations determined from the "detection limit" information provided by each manufacturer. The levels at which the L2000 was tested were simple to calculate because the percent chlorine of each Aroclor is well known. The levels for the IA kits were more difficult to choose because predicting the response of the kits to various Aroclors is not straightforward. This involved an iterative process of lowering or raising the PCB concentrations until a response equal to or greater than that of 2 ppm 1242 was obtained. PCB concentrations below those in the originally prepared soil samples were made by cutting the soil samples with the appropriate amount of blank soil to arrive at the final concentration. For example, a 6 ppm 1232 sample was prepared by mixing 3 g of 20 ppm 1232 standard with 7 g of blank soil.

RESULTS

For each of the eight Aroclors tested, Table 1 lists the PCB concentration that was required to yield a response equal to that of 2 ppm Aroclor 1242. For both of the IA kits, a level of 40 ppm 1221 was required to yield a positive test result. The L2000 provided a positive result at 4 ppm of the same Aroclor. The most sensitve Aroclors for the Millipore test were 1248 and 1254 which yielded positive results at 0.9 ppm. The most sensitive Aroclor for the Ensys test was 1260 which resulted in a positive test at a level of only 0.4 ppm. The L2000 exhibited the greatest sensitivity to the most highly chlorinated Aroclor, 1268, and gave a positive response at a level of 1.2 ppm.

Table 1

Aroclor	Millipore	Ensys	L2000
1221	40	40	4
1232	7	3	2.6
1016	3	3	2
1242	2	2	2
1248	0.9	1.1	1.8
1254	0.9	0.7	1.6
1260	1.5	0.4	1.4
1268	25	3	1.2

The sensitivity ratios for each method, defined as the ratio of the concentrations required to yield a positive test between the most sensitive and least sensitive of the Aroclors, was determined to be the following:

For the Millipore test, 1221:1248 = 40:0.9 = 45
For the Ensys test, 1221:1260 = 40:0.4 = 100
For the L2000 test, 1221:1268 = 4:1.2 = 3.3

This means, that depending on the method, a specific test may require that one type of PCB be at a concentration 100 times greater (Ensys) than another type in order to yield the same response. This ratio should remain a constant for each method and will not vary with a change in calibrating Aroclor or concentration.

CONCLUSION

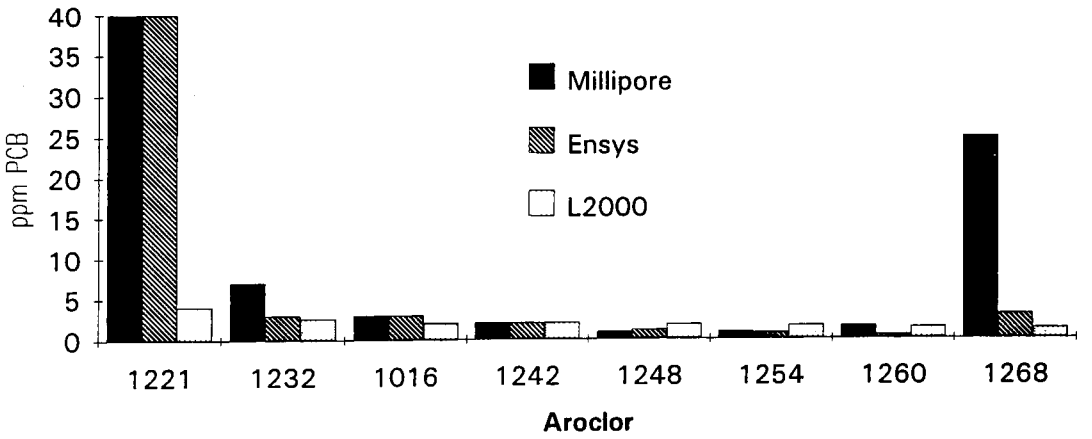
What are the consequences of these results? Suppose an analyst is field testing for PCBs at a site known to contain a variety of Aroclors, some of them partially weathered. The regulator has stated that the site must be cleaned up to a level of PCBs no greater than 2 ppm. Now the analyst has a decision to make. If he or she uses an immunoassay test should the test be calibrated using the most sensitive Aroclor, least sensitive Aroclor, or something in between? By calibrating on the Aroclor with the highest sensitivity, (1248 or 1254 for Millipore and 1260 for Ensys) if Aroclor 1221 is present, the test will not yield a positive result until the level reaches 90 ppm for the Millipore test or 200 ppm for the Ensys test meaning that there is a very high probability of obtaining a false negative result. If the analyst chooses to calibrate on the least sensitive Aroclor (1221) in an effort to avoid false negatives, then false positives would result for anything above a level of 0.045 ppm 1254 for the Millipore test and for anything above 0.02 ppm 1260 for the Ensys test. The odds of obtaining a false positive result are huge! If an Aroclor with average sensitivity is choosen, then the false positive/false negative debate is split down the middle and the potential for either one is still quite high.

As an alternative to either one of these methods, the L2000 could be used and calibrated to yield a positive test at 2 ppm 1221. Because the sensitivity ratio for the L2000 is so low (3.3), even the most sensitive Aroclor for this method, 1268, would have to be at a level at least as high as 0.6 ppm before a false positive result is obtained and there would be no chance of a false negative for any of the Aroclors.

The most important point to remember is that just because a particular method delivers acceptable results for the Aroclor on which it is calibrated, it does not mean that these results will be the same across the entire range of Aroclors. Unless it is known that a particular site contains one and only one Aroclor the analyst must take care to be sure that 1) less sensitive Aroclors are not missed and 2) more sensitive Aroclors do not cause excessive amounts of soil to be removed or remediated.

Chart 1

The concentration of each of eight Aroclors required to yield a positive result when test methods are calibrated to give a positive result at 2 ppm Aroclor 1242



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GUIDING FIELD ACTIVITIES BY USING RAPID, COST-EFFECTIVE ANALYSES PERFORMED IN A FIXED LABORATORY

Gomez, Richard T., Project Manager, Inchcape Testing Services, Aquatec Laboratories, 55 South Park Drive, Colchester, Vermont, 05446.
Loring, Deborah A., President, Loring Environmental Associates, 10 Graham Ter, West Roxbury, Massachusetts 02132-1822.

I. INTRODUCTION

Much has been documented in previous years regarding the availability, reliability, and cost-effectiveness of analytical results derived from field screening techniques. The application of screening methodology using both portable equipment and test kits can minimize both cost and turnaround time involved in preliminary site assessments and field and sampling efforts performed in support of RCRA and CERCLA investigations.

However, very little focus has been placed on the ability and willingness of a fixed laboratory to provide high quality, low cost, quick turnaround analyses to support field efforts. In fact, laboratories have been somewhat restricted in their ability to use their technical expertise to develop new or modified methodology and reporting formats based on project specific data quality objectives. When performing analyses in support of both RCRA and CERCLA programs, laboratories have historically been required to use traditional SW-846 and/or CLP methodology, and in many cases have been obliged to supply extensive data packages. Given the complexity of the methodologies and data reporting requirements, the cost and turnaround times have been commensurate with the level of effort required in performing the method and assembling the data packages.

This paper will document, through a real example, how a client was able to use the expertise of a fixed laboratory to provide cost-effective, quick turnaround results by allowing the lab to use modified EPA methodologies with specified objectives in terms of sensitivity, precision, and accuracy; and a shortened reporting format.

Based on the client's objectives in terms of the required target analyte list, accuracy and precision, detection limit, cost, level of documentation and turnaround time, the laboratory was able to critically review the options available in terms of sample preparation, traditional and modified analytical methodology, and reporting formats, and then to design an analytical method and reporting format that met the client's objectives.

The target analytes included volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and 22 metals. The required detection limits were those found in the current Contract Laboratory Protocol (CLP) methodology, with the exception of those for lead, arsenic, selenium, and thallium. Reports were generated automatically, using a combination of internal software developed at the laboratory and reports generated directly from the Hewlett Packard (HP) ChemServe software. The reports included target compound results, internal standard area and retention time summaries, Laboratory Control Sample (LCS) results, surrogate recovery summaries, and chromatograms. The laboratory transmitted VOC and metals reports to the field office in 24 hours and SVOC reports in 48 hours. The cost for each analysis was 30-50% of the cost of providing the traditional methodology and data package. The screen results were subsequently used to direct field activities and focus the sampling efforts at the site, while providing technically sound, defensible data upon which decisions were made.

This paper will also examine further options available to the client that can minimize overall project costs and will point out the advantages of using a fixed laboratory for certain types of analytical activities.

II. CLIENT OBJECTIVES

The purpose of the field program was to determine the extent of contamination and delineate the migration of volatile organics, semivolatile organics and a number of metals known to be present at the site. Due to the size of the site and the tight field sampling schedule imposed, the client initially considered directing the daily activities of several drill rigs on-site using data supplied from a mobile laboratory.

The duration of the field program was estimated to be 6 weeks with sampling taking place daily. Approximately 6-20 samples were to be collected 5 days a week and analyzed for VOCs, SVOCs, and metals. Given the expense of maintaining a mobile laboratory equipped to perform the sophisticated analyses requested, the client opted to have the analyses performed in the fixed laboratory, assuming the laboratory could meet the following goals:

- The rapid data delivery schedule of the project could be met.
- The fixed laboratory could provide documented data of a higher quality than achievable in a mobile laboratory.
- The first two goals could be achieved at a cost equal to or less than the mobile laboratory's rate over the same time period.

ITS-Aquatec achieved all of the goals established for this study by:

- Designing the appropriate analytical methods in order to achieve the tight data delivery schedule established without compromising the integrity and quality of the data.
- Assigning a fixed amount of time to each task beginning with sample login to ensure that turnaround times were met, and strictly adhering to this timetable.
- Establishing a rapid response team within the laboratory to execute the program.
- Committing to the success of the program.

Different stages of planning were required in order to fulfill the project goals. Certainly, designing the "Rapid Analysis" (RA) program was a prerequisite to the overall success of the study.

III. LABORATORY APPROACH BASED ON THOSE METHODS

Based on the compound list, the detection limits, and the required level of precision, accuracy, and documentation, the laboratory was able to modify the EPA CLP methods and integrate these with their own computer data systems, so that in most cases, reports were automatically generated overnight. Minor modifications were made to the methodologies to allow the laboratory to turn the work around faster, while sacrificing little in the way of precision, accuracy, or sensitivity. The approaches that the laboratory took are outlined below:

Metals

The Metals Target Analyte List (TAL) and required detection limits are listed in Table 1. One of the critical aspects that allowed the laboratory to provide such a quick turnaround was the flexibility in the metals detection limits. Often, EPA CLP Contract Required Detection Limits (CRDLs) are requested for site activities by default, whether or not these detection limits are necessary. In general, meeting the CRDLs requires that two separate digestions be performed, one for Inductively Couple Plasma (ICP) analysis and one for Graphite Furnace Atomic Absorption (GFAA) analysis, and five separate analytical runs (one ICP run and four GFAA runs) be performed. The extra digestate and 4 extra analyses are necessary because analysis for arsenic, selenium, lead, and thallium by ICP does not meet the CLP CRDLs[1].

Table 1 Metals Target Analyte List and Detection Limits (in ug/L)

Element	Laboratory ICP Detection Limits	CLP Required Detection Limits
Aluminum	29	200
Antimony	26	60
Arsenic	**41**	**10**
Barium	22	200
Beryllium	0.6	5
Cadmium	3	5
Calcium	440	5000
Chromium	1	10
Cobalt	4	50
Copper	3	25
Iron	14	100
Lead	**23**	**3**
Magnesium	548	5000
Manganese	1	15
Nickel	6	40
Potassium	1068	5000
Selenium	**39**	**5**
Silver	3	10
Sodium	532	5000
Thallium	**36**	**10**
Vanadium	4	50
Zinc	2	20

Because this site assessment did not require the low arsenic, selenium, thallium, and lead detection limits, the laboratory was able to cut the turnaround time considerably by using a single digestion and single analysis to generate all of the metals data.

The methodology used was based on the EPA CLP Methodology. Some modifications were made to the methodology that did not significantly affect the accuracy of the data, but did enhance the laboratory's ability to meet the 24 hour turnaround time by limiting the number of reanalyses required.

The modifications made by the laboratory are outlined in Table 2:

Table 2 EPA CLP Method ILM01.0 Modifications

Method Element		Modified	EPA CLP ILM01.0
Digestion		1 for ICP	1 for ICP 1 for GFAA
Instrument Detection Limits (IDLs)	Lead	23 ug/L	3 ug/L
	Selenium	39 ug/L	5 ug/L
	Thallium	36 ug/L	10 ug/L
	Arsenic	41 ug/L	10 ug/L
Initial Calibration		ILM01.0	ILM01.0
Interference Check (ICSA/AB)		ILM01.0	ILM01.0
Detection Limit Standard (CRI)		ILM01.0	ILM01.0
Initial Calibration Verification (ICV)		ILM01.0	ILM01.0
Initial Calibration Blank (ICB)		ILM01.0	ILM01.0
Continuing Calibration Blank (CCB)		ILM01.0	ILM01.0
Continuing Calibration Verification (CCV)		90% to 110%, allowed up to 85%-115% if that element is not detected in bracketed samples.	90%-110%
Final Values		Wet Weight	Dry Weight
QC Samples (LCS/MS/MD)		ILM01.0	ILM01.0

Organics

The Contract Required Quantitation Limits (CRQLs) were not the determining factor in the ability of the laboratory to perform volatile and semivolatile organics at a faster rate. The main factor influencing the laboratory turnaround time was the modification of the quality control criteria in the methodology.

In the CLP methodology, matrix effects are required to be "proven" (i.e., the chemist must rerun any sample that does not meet internal and surrogate standard QC limits to prove that it is the sample matrix, and not laboratory error, that is responsible for the QC outages observed). However, a trained chemist can often conclude that an instance of exceeding the QC criteria is caused by a matrix effect without rerunning the sample to prove the theory. This can often be done by examination of total ion chromatograms, mass chromatograms, mass spectra of interfering peaks, extraction notes, etc.

Examination of the total ion chromatogram and the specific mass chromatograms and mass spectra can often times provide sufficient evidence that a particular internal or surrogate standard's response is suppressed or increased due to an unresolved mixture. A GC/MS chemist trained in mass spectral interpretation can often times reach this conclusion without reanalyzing the sample. Requiring that this be proven by reanalysis can often be unnecessary, as long as the decision is documented and is technically supportable.

Additionally, surrogate recovery ranges are very narrow in the VOC methods, particularly in comparison with the related requirements for response factors in the standards. For example, the response factor for Bromofluorobenzene (BFB), one of the VOC surrogates, is allowed a variance of up to 25.0% in the continuing calibration standard. If the intial calibration is assumed

valid, then the "acceptable" variance in the actual quantitation of BFB is at least 25.0%, without taking into account cumulative error from other steps in the analytical process. The QC criteria for the percent recovery of BFB in the sample is 86% - 115%, which is restrictive in comparison with the level of error allowed in the response factor. Given the fact that the sample analysis adds variance due to the sample matrix, the approximate variance of ± 15% in the surrogate may not always be necessary to meet project objectives.

Other modifications were made to the method that did not significantly affect the accuracy of the results reported, but which allowed the laboratory to achieve quicker turnaround times. Dilutions were only made if the mass spectrometer was saturated. Tentatively Identified Compounds (TICs) were not reported, and all final results were reported directly from the HP ChemServe Data Station in wet weight. Percent solids resulted were reported separately. Gel Permeation Chromatography (GPC) cleanup was not performed on the semivolatiles fraction prior to analysis. Modifications that allowed the laboratory to achieve the turnaround time of 24 hours for volatiles and 48 hours for semivolatiles are outlined in Table 3. The Organics Target Compound List (TCL) and required detection limits are listed in Table 4.

Table 3 Organics EPA CLP OLM01.0 Method Modifications

Method Element	Modified	EPA CLP OLM01.0
Volatiles		
Tune	OLM01.0	OLM01.0
Initial Calibration	OLM01.0	OLM01.0
Continuing Calibration	OLM01.0	OLM01.0
Method Blank	OLM01.0	OLM01.0
Internal Standard (ISTD) Area	Rerun if necessary, based on professional judgment. Flag data if outside limits.	Rerun if any ISTD varies by more than a factor of 2.
Internal Standard Retention Time	OLM01.0	OLM01.0
Surrogate Standard Area	Rerun if necessary, based on professional judgment. Flag data if outside limits.	Rerun if outside QC limits.
Dilutions	Dilute if detector is saturated.	Dilute if above calibration range.
TICs	Not reported Not reported	Report 10 - VOC Report 20 - SVOC
Final Value	Wet Weight	Dry Weight
QC Samples (MS/MSD)	OLM01.0	OLM01.0
Semivolatiles		
Same as above except:		
GPC	Not performed	Required

Table 4 Organics Target Compound List and Quantitation Limits

Compound	Quantitation Limit-ug/L
Chloromethane	10
Bromomethane	10
Vinyl Chloride	10
Chloroethane	10
Methylene chloride	10
Acetone	10
Carbon Disulfide	10
trans-1,2-dichloroethene	10
1,1-dichloroethene	10
1,1-dichloroethane	10
1,2-dichloroethene (t)	10
Chloroform	10
1,2-dichloroethane	10
2-butanone	10
cis-1,2-dichloroethene	10
1,1,1-trichloroethane	10
Carbon tetrachloride	10
Bromodichloromethane	10
1,2-dichloropropane	10
cis-1,3-dichloropropene	10
Trichloroethene	10
Dibromochloromethane	10
1,1,2-trichloroethane	10
Benzene	10
t-1,3-dichloropropene	10
Bromoform	10
4-methyl-2-pentanone	10
2-hexanone	10
Tetrachloroethene	10
1,1,2,2-tetrachloroethane	10
Toluene	10
Chlorobenzene	10
Ethylbenzene	10
Styrene	10
Xylene (m,p)	10
Xylene (o)	10
Xylene (total)	10
Phenol	10
bis(2-chloroethyl)ether	10
2-chlorophenol	10
1,3-dichlorobenzene	10
1,4-dichlorobenzene	10
1,2-dichlorobenzene	10
2-methylphenol	10
2,2'-oxybis (1-chloropropane)	10
4-methylphenol	10
N-nitroso-di-n-propylamine	10
Hexachloroethane	10
Nitrobenzene	10
Isophorone	10
2-nitrophenol	10

Compound	Quantitation Limit-ug/L
2,4-dimethylphenol	10
bis(2-chloroethoxy)methane	10
2,4-dichlorophenol	10
1,2,4-trichlorobenzene	10
Naphthalene	10
4-chloroaniline	10
Hexachlorobutadiene	10
4-chloro-3-methylphenol	10
2-methylnaphthalene	10
Hexachlorocyclopentadiene	10
2,4,6-trichlorophenol	10
2,4,5-trichlorophenol	25
2-chloronaphthalene	10
2-nitroaniline	25
Dimethylphthalate	10
Acenaphthylene	10
2,6-dinitrotoluene	10
3-nitroaniline	25
Acenaphthene	10
2,4-dinitrophenol	25
4-nitrophenol	25
Dibenzofuran	10
2,4-dinitrotoluene	10
Diethylphthalate	10
4-chlorophenyl-phenylether	10
Fluorene	10
4-nitroaniline	25
4,6-dinitro-2-methylphenol	25
N-nitrosodiphenylamine	10
4-bromophenyl-phenylether	10
Hexachlorobenzene	10
Pentachlorophenol	25
Phenanthrene	10
Anthracene	10
Carbazole	10
Di-n-butylphthalate	10
Fluoranthene	10
Pyrene	10
Butylbenzylphthalate	10
3,3'-dichlorobenzidine	10
Benzo(a)anthracene	10
Chrysene	10
bis(2-ethylhexyl)phthalate	10
Di-n-octylphthalate	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Indeno(1,2,3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(g,h,i)perylene	10

IV. REPORT FORMAT

A key element that allowed ITS-Aquatec to meet the turnaround time for this project was the ability to rely heavily on the computer to produce reports overnight upon completion of the autosampler runs. For organics, which were run entirely on HP GC/MS systems, the HP ChemServe software reports were used without change. By allowing minor variations from the CLP Forms, the reports can be automatically produced from the instrument, thus saving a considerable amount of time and effort in uploading to another computer system.

The metals data were uploaded directly from the ICP to the laboratory's VAX system, and inorganics reports were produced from it. To accomplish this, the laboratory's Information Services group was able to write software that automatically uploaded the data, and after an overnight autosampler run, the reports were waiting for review in the morning when the analysts arrived.

By allowing the lab a small amount of flexibility in the reporting format, the reports could be produced automatically without manipulation through another computer system, and then reviewed, approved, and faxed directly to the field office. The analytical report generated for this study provided far more quality control information than that attained with field screening instrumentation. In addition, the data were initially reviewed by in-house data review groups for validity prior to release to the field office on site. Most laboratories archive all sample data, standards data, and related QC logs (i.e., instrument logs, standards records, etc.) for a specified number of years, and will guarantee their ability to provide a data package at a later date if required.

The laboratory's reports contained the following information:

1. Cover letter
2. Chain of Custody

<u>Volatiles and Semivolatiles</u>

3. Form I's - HP ChemServe Software
4. Surrogate Recovery Report - HP ChemServe Software
5. Matrix Spike Recovery Report - HP ChemServe Software
6. Internal Standard Area and Retention Time Summary - HP ChemServe Software
7. Chromatograms

<u>Metals</u>

8. Analytical Results Sheet - VAX generated, direct upload from ICP

V. REASONS FOR AN ALTERNATIVE APPROACH

By allowing the laboratory to make minor deviations in "standard" methodology and reporting formats, laboratories are able to overcome most of the obstacles which cause long turnaround times and avoid the escalating costs of producing data in support of various types of site activities. However, this flexible approach is rarely, if ever taken.

One reason may be the lack of awareness that these options exist. In order to stay competitive in an increasingly cost-conscious market, laboratories must adapt their approaches to site specific investigations, and do neither more nor less work than is required to achieve site specific goals.

Some of the burden for this approach must lie with the various regulatory agencies and commercial Quality Assurance firms, who through audits, data validation criteria, and specific project management approaches, have made the laboratories painfully aware of what can happen if they deviate from a standard approach. Often, laboratories have had data rejected, or have been forced to use inferior methodology and technology as a result of data validation or walk through audits by both government and commercial personnel. Audit criteria are generally derived by using a specific set of regulatory guidelines, often developed under the CLP program, whether or not these criteria are relevant to a specific project with specific goals in terms of compound lists, detection limits, and precision and accuracy requirements.

Project specific goals must drive analytical data gathering activities, instead of the present situation, in which the application of CLP or SW-846 methods drive data gathering, and use one level of precision, accuracy, and sensitivity for all data generation regardless of the data quality objectives for that particular site activity.

This approach is particularly off-course in the application and validation of data generated under RCRA, in which SW-846 should be used as a ***guidance*** document only (with the four exceptions as outlined in the regulations, in which the methods must be followed). Unfortunately, there are many state agencies as well as private companies who require that the methods as contained in SW-846 be followed line by line, without deviation. And to further the misuse of the available documents, data generated using the SW-846 methodology as a "guide" is often validated using CLP validation criteria.

VI. PROJECT SUMMARY

The case study presented here took place over a 5 week period. During this time, approximately 175 soils and 75 groundwaters were analyzed for organic and inorganic constituents. Metal and volatile organic compounds were determined and reported within 24 hours of sample receipt and semivolatile organics were reported in 24-48 hours. The success of the analytical approach was measurable in 3 principal ways:

1. Data of known quality were generated and reported in near real time allowing field activities to advance based on sound analytical information.

2. The turnaround times established in the beginning for this program were met in nearly all cases and did not delay the project's rapid field sampling schedule.

3. The results of the RA program complimented the results of the QC sample analyses performed by the CLP protocols.

The success of this laboratory program could be attributed to several other factors as well. Participation in the planning stage of the field program provided valuable insight into the goals of the client. Laboratory methodologies could be modified to enhance the analysis and reporting speed and yet still maintain the key elements of the methods that would allow for cross correlation with QC sample results. A project specific, rapid response team was formed to focus on the logistics of the project to ensure that the turnaround times were met. Above all, the willingness of the laboratory to operate outside of the normal day to day production mode in order to serve the client's needs was an important factor that cannot be overlooked.

VII. ADVANTAGES OF A FIXED LABORATORY

There are a number of advantages in using a fixed laboratory, and allowing flexibility in application of standard methods to guide field activities. Certainly, the **quality of data** achievable in a fixed laboratory is most often not routinely achievable in the field. Some issues affecting the quality of the data include:

- First, in a fixed laboratory, analyses are performed in a controlled environment, free from potential air contamination. Many analyses require the use of sophisticated instrumentation, in which stable power sources and controlled environments (in terms of air contamination, temperature, and humidity) are required. ITS-Aquatec's laboratory processes incoming air to the building through charcoal filtration and all of the laboratories are positive or negative pressure rooms as appropriate. This is crucial, particularly when performing volatile organics analysis.

- A fixed laboratory generally possesses redundant instrumentation. This may not be an option when generating data on-site. As such, rapid laboratory analyses can be performed on schedule despite any unforeseen problems that may cause an instrument such as a GC/MS system to go down. ITS-Aquatec committed 5 GC/MS systems to this study to ensure the client's goals and data delivery schedule were met. In addition, an in-house service technician was on call in the unlikely event that an instrument required service. It is important to assess the ability of the laboratory or field crew to respond to instrument failure during the planning stage of the field program.

- To ensure the quality of the data generated, a team approach was developed for this study. A technical project director was assigned to oversee the project and the delivery schedule. Since the methods employed were modified CLP protocols, final data review was performed by PhD's specializing in inorganic chemistry and mass spectrometry.

Rapid analyses can often times be performed more **cost effectively** in a fixed laboratory because the unit costs are determined in advance and are fixed. The client does not have to pay an on-site analytical testing crew if there happens to be down time in the field. For the purposes of this study, a unit cost was determined for each analysis to be performed.

In addition and most importantly, the overall cost of the analytical program can be reduced by allowing the laboratory the flexibility to modify existing methods where appropriate. By slightly modifying the "official" methods slated for an investigation and allowing the laboratory to judge the validity of the experiment performed, one can more closely correlate the "screen" data to that generated by "official" methods. In other words, one may only have to analyze 10 or 20% of the samples collected by these official methods and still be able to correlate the results to those of the screen, thereby reducing the overall cost of the project.

VIII. CONCLUSION

As was stressed in the introduction, laboratories have been burdened with unnecessarily strict QC protocols, excessive reporting requirements, and very little flexibility to adapt methodologies to meet project specific goals. In some cases, the laboratories themselves have perpetuated this problem by standardizing the lab to such a production line approach that flexibility no longer exists. In the last ten years, environmental chemists working in a commercial laboratory have had fewer and fewer options in their technical approach to solving specific problems. A point

that should be emphasized is that environmental chemistry is not so straightforward and routine that it can be run through a production lab. Chemists must be allowed to use their scientific training, to develop methodology, to use new products and innovations, and to customize their approach to help laboratory clients meet their goals.

Strong QA functions exist at the government, private, and laboratory levels. Data validation and systems and data auditing should be used to ensure that data generated in support of specific field activities is scientifically sound and legally defensible, while allowing the chemist the flexibility and creativity that they need to approach and solve environmental problems.

There are a myriad of screening techniques that a laboratory can utilize to expedite data generation and reporting. As an example, GC/MS Single/Multiple Ion Monitoring can be used to identify specific organic compounds in very complex mixtures at ppb and ppt levels. This is an especially quick, effective tool, in both the field and the laboratory. In the example as outlined, ICP was used quite effectively with minor increases in some detection limits, and resulted in the laboratory generating data with approximately 25% of the effort that would be required in the traditional approach.

Finally, the case presented here is only one example of an approach to direct field activities. Many fine field screening instruments and immunoassay techniques can be used to provide valuable, real time answers in the field. The most appropriate approach is generally chosen on a project specific basis. However, by allowing a fixed laboratory more flexibility, considerable time and money can be saved in generating analytical data of known quality to support field activities.

IX. FOOTNOTES

[1]Detection limits achievable with specific ICPs vary depending on the instrument and laboratory. The new trace ICPs reach the CLP CRDLs for these elements, but these have just recently been put into operation in a limited number of laboratories, and thus are not yet a common option.

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Reducing Laboratory Costs with a Field Portable Ion Chromatography System

W. Mozer, Analytical Magnetics, Inc. The Mill,. 73 Princeton Street, North Chelmsford, MA 01863

ABSTRACT

Field portable Ion Chromatography (IC) has become a reality with the advent of improved instrument design and microprocessor technology. It is now possible to determine anion and cation levels in surface and waste waters at field sites without compromising analytical performance. This paper will demonstrate that in-field and laboratory results for various water matrices are analytically equivalent. The benefits of on-site work are obvious: the need to collect large numbers of samples to be brought to a central laboratory for analysis, and the costs associated with this procedure, is no longer required. Samples can now be analyzed as collected and only a few "check" samples need be returned to the laboratory for verification. Should the need to review the in-field work arise, the instrument has all the chromatographs stored in the microprocessor and the results may be reworked at any point using a personal computer. Thus, with the need to obtain more rapid, site specific information, reduce manpower and the costs involved with sample collection a field portable IC proves to be a rapid, low cost means to accomplish these goals.

ENFORCEMENT

EPA COMPLIANCE PROGRAM IN WASTE TESTING

Francisca E. Liem, Chief, Laboratory Data Integrity Branch, Office of Compliance, U.S. Environmental Protection Agency, Washington, DC 20460, Frederic L. Siegelman, Chemist, Office of Compliance, U.S. Environmental Protection Agency, Washington, DC 20460.

ABSTRACT

The U.S. Environmental Protection Agency (EPA) uses data that are submitted or self-reported. In the Resource Conservation and Recovery Act (RCRA), the regulated communities are required to identify themselves, obtain permits and periodically sample, analyze and self-report. Concerns exist about the quality and integrity of self-reported data. Congress asked the General Accounting Office (GAO) to assess the RCRA program at EPA.

EPA has undertaken a reorganization of the various enforcement and compliance monitoring functions into a single office, the Office of Enforcement and Compliance Assurance (OECA). OECA will be the national program manager for all inspection activities. OECA will use a broad range of tools to achieve compliance with environmental statutes. The Office of Compliance (OC) within OECA will have the responsibility for developing targeting, training and national guidance for inspections and will have the lead within OECA for compliance assurance and assistance. The Laboratory Data Integrity Branch (LDIB) of OC will be responsible for compliance monitoring and quality assurance of laboratory data submitted or self-reported by the regulated community. Compliance assurance of laboratory data for the RCRA program will be an LDIB responsibility. LDIB can be anticipated to increase the scrutiny of the laboratories providing health and environmental data for the various programs.

The RCRA program does not require inspections of laboratories or the determination of the laboratory's capability to perform analysis. The RCRA program needs to institute controls over the laboratories, including inspections and performance evaluations. A laboratory accreditation program may be the answer. Mechanisms are also needed for overseeing quality assurance within the regulatory agencies themselves.

Because of the GAO audit and organizational changes at EPA the RCRA program is at a crossroad. This paper only discusses data integrity issues of laboratories that are analyzing groundwater samples.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) uses data for several programs that are submitted or self-reported by regulated communities. In some programs, such as the Resource Conservation and Recovery Act (RCRA) and the National Pollutant Discharge Elimination System (NPDES) programs, members of the regulated communities are required to identify themselves, obtain permits and periodically sample, analyze and self-report according to regulations and specific permits. Similarly under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), members of the regulated community must carry out required studies and submit the results. Concerns exist about the quality and integrity of submitted or self-reported data. EPA has undertaken a reorganization of the various enforcement and compliance monitoring functions into a single office, the Office of Enforcement and Compliance Assurance (OECA). As part of this reorganization, the Laboratory Data Integrity Branch (LDIB) of the Office of Compliance (OC) within OECA will be responsible for compliance monitoring and quality assurance of laboratory data submitted or self-reported by the regulated community.

EPA and forty-seven authorized states and U.S. territories that carry out the environmental program under RCRA rely on information that approximately 300 permitted land disposal facilities themselves submit to determine their compliance with environmental laws. However, some facilities may not voluntarily invest the time and resources to obtain accurate data and report environmental violations. It is EPA's responsibility to determine that self-reported data are accurate and valid, and to determine that facilities are complying with environmental regulations.

RCRA facilities are required to monitor the groundwater underlying their facilities in order to detect any contamination. These results must be reported to EPA or an authorized state once a year. However, if the analyses show contamination, facilities must immediately notify authorities and begin more extensive monitoring.

Congress was concerned about the potential avoidance of regulation or submission of inaccurate or fraudulent data to EPA, and so, in 1992 has asked the General Accounting Office (GAO) to assess the RCRA program at EPA. GAO reviewed EPA and authorized states procedures to ensure that (1) subjected facilities identify themselves, (2) sampling results are representatives of its compliance, and (3) oversight of facilities collecting and laboratories analyzing samples is adequate to prevent error and fraud.

Because of the GAO audit and organizational changes at EPA the RCRA program is at a crossroad: What is EPA Headquarters role in the program? This paper only discusses data integrity issues of laboratories that are analyzing groundwater samples.

DISCUSSION

The OECA reorganization

OECA includes the various compliance assurance and enforcement capabilities of EPA. The proposed organization is made up of the Office of Criminal Enforcement, the National Enforcement Investigations Center, Office of Regulatory Enforcement, Office of Compliance (OC), Office of Site Remediation Enforcement, Office of Federal Activities as well as Administration and Resource Management Staff, Enforcement Capacity and Outreach Office and Federal Facilities Enforcement Program. OECA's incorporation of the capabilities of compliance and enforcement into a single organization recognizes that the primary goal is to protect human health and environment by obtaining compliance and that enforcement is a part of compliance. OECA will use a broad range of tools to achieve compliance with environmental statutes. OECA will measure success based on compliance and environmental results. Traditional enforcement should be seen as a tool for achieving the broader goal of compliance and not as an end unto itself. Risk-based strategies are necessary.

OECA will be the national program manager for all inspection activities including compliance assistance. OC will have the responsibility for developing targeting, training and national guidance for inspections and will have the lead within OECA for compliance assurance and assistance. The laboratory data integrity function will be established as a branch, Laboratory Data Integrity Branch (LDIB), in the Agriculture and Ecosystems Division in OC and will be responsible for compliance assurance of laboratory data including inspections, audits, targeting and evaluation.

Education and assistance should be recognized as an important tool for achieving compliance. Resources should be directed toward the greatest risks to human health and the environment. EPA needs to encourage and promote voluntary compliance. The need for effective enforcement, and the ability to deal with serious offenders will persist. If serious offenders are not punished for their violations, the credibility of a compliance program is seriously endangered. Successful enforcement "catches" the worst offenders and helps achieve compliance by the population as a whole.

OC will be organized on a sector approach. Compliance assistance activities will complement traditional enforcement and program efforts. National enforcement strategies will increasingly be oriented around sectors of the economy. The sector perspective should allow change and the development of innovative compliance and enforcement strategies. OC will be responsible for setting national priorities and collecting and integrating quality compliance data. In addition, OC will develop effective compliance assurance programs to support inspections and self reporting and

will build capacity for more effective compliance assistance to the regulated community. Finally, OC will work in partnership with Regions, States, municipalities, citizens and industry.

Compliance assistance is information or technical advice provided to help the regulated community and interested parties understand and meet statutory and regulatory requirements. Compliance assistance includes outreach (publications, training seminars etc.) and technical assistance. Inspectors can play an important role in providing on-site assistance. Compliance assistance should help prevent as well as correct violations.

The historical major activity of the LDIB staff was the inspection and monitoring of the Good Laboratory Practice (GLP) standards regulations under FIFRA and the Toxic Substances Control Act (TSCA). The GLPs are management standards for operating laboratories active in environmental matters and are a major factor in efforts to assure high quality data primarily in support of pesticide and toxic chemical registrations. Compliance assurance issues related to laboratory data integrity in other areas also will be LDIB's responsibility. All of the compliance assurance activities that used to be in the program offices will be combined within OECA. At EPA Headquarters, compliance assurance of laboratory data for the RCRA program will be an LDIB responsibility.

LDIB responsibility will be to ensure data quality and integrity by assuring compliance through a variety of activities including inspections, compliance oversight of delegated (e.g., state and regional) efforts, outreach, and compliance assistance. Inspectors will take part in compliance assistance efforts when they are part of a predetermined strategy.

EPA's Current Hazardous Waste Enforcement Program

EPA at Headquarters in Washington, DC provides guidance for management of the compliance assurance and enforcement of the RCRA program. The RCRA compliance and enforcement program at Headquarters was situated in the Office of Solid Waste and Emergency Response, Office of Waste Programs Enforcement, RCRA Enforcement Division. Inspection and audit manuals to be used by EPA regional and authorized state inspectors have been established. EPA regions write the permits and carry out the inspections in unauthorized states and are also responsible for overseeing that authorized states meet federal requirements. The RCRA program is responsible for developing quality assurance techniques, guidance, and technical support to EPA regions and authorized states to use and specific sampling and analysis procedures for incorporation into a facility's permit. The program officials are also responsible for developing oversight procedures that EPA regions

and authorized states can implement to ensure that facilities carry out sampling and analysis properly.

EPA's quality assurance guidance requires that EPA and state regulatory agencies inspect facilities periodically to ensure that facilities are collecting samples properly. The EPA quality assurance guidance also calls for inspections of laboratories that analyze samples and testing their performance by requiring them to analyze blind samples. EPA's RCRA program, however, does not require inspections of laboratories or the determination of the laboratory's capability to perform analysis.

The RCRA program has two types of inspections that are designed to verify sampling procedures and techniques at the facility. According to EPA policy, all RCRA land disposal facilities are required to receive one of these inspections at least once every three years. The operation and maintenance inspection is to determine whether the groundwater monitoring system is adequate to produce accurate data. The comprehensive groundwater monitoring inspection is to evaluate and review the groundwater monitoring system in more detail and often includes sampling. Most authorized states routinely review sampling procedures during their inspections.

Considerations for EPA's RCRA program in the Office of Compliance

EPA recognizes that errors can occur at any point during sampling and analysis. Potential errors in sampling and analysis are in the design of a sampling strategy, collecting, handling, preparing and analyzing samples. Errors could even be made during the interpretation of data.

EPA has sent guidance to the regions, that outlines the most recent Data Quality Objective/Quality Assurance Project Plan for groundwater monitoring and corrective action. In addition, EPA is developing a Compliance Monitoring Evaluation interactive training video that will emphasize the importance of complete and effective reviews of groundwater sampling procedures.

To ensure that facilities are collecting and analyzing samples according to the sampling design and procedures, EPA or the authorized state periodically inspects facilities where samples are taken and should inspect laboratories where samples are analyzed.

In addition to facility level controls and oversight, certain mechanisms are needed for overseeing quality assurance within the regulatory agencies themselves, i.e. EPA Headquarters oversight of the regions and authorized states.

Although EPA regions and most states were reviewing sampling procedures during their inspections, EPA regional officials who observed state inspections found problems with their quality, e.g., the state inspector used improper sampling equipment, did not have sufficient knowledge of the facility's sampling and analysis plan, and did not adequately review the facility's hydrogeology or site characterization information. Because of improper collection and preservation of samples for the duration from the field to the laboratory, there were difficulties in analyzing samples properly. These deficiencies could effect the ability of state inspectors to detect errors in the procedures used and the data reported by the facilities. Because of these problems, the RCRA program decided to emphasize oversight inspections and to increase regional oversight of state inspections to ten percent.

At laboratories, regulatory agencies can perform several types of oversight. The first is an inspection to determine the availability of analytical instruments and controls at the laboratory. The objective of the inspection is to determine the laboratory's capability to perform analysis and generate reliable and valid data. This type of inspection would review calibration and maintenance records of analytical instruments, general cleanliness of the laboratory, condition of equipment and facility, documentation of procedures and other related components.

A second oversight mechanism is a performance evaluation to determine whether the laboratory can perform analysis and produce reliable and valid data. To conduct a performance evaluation, samples of known content and quantity are prepared and sent to the facility for analysis. The facility sends the samples to the laboratory that it usually uses for analysis. After the laboratory analyzes the samples, the state or EPA compares the results with the known values to determine the laboratory's performance in analyzing the samples.

The RCRA program has never required inspections or performance evaluations of laboratories used by RCRA land disposal facilities. The rationale for not implementing laboratory inspections or not developing performance evaluations is the same, the potential for error is greater during sampling at the facility than during analysis of the samples at the laboratory and the EPA has therefore focused its attention on the sampling program. In addition, conducting performance evaluations in the RCRA program would require the program to develop a complex set of samples for use in performance evaluations, which is beyond its current resources. However, some EPA officials believe that the RCRA program needs to institute controls over the laboratories, including inspections and performance evaluations. A laboratory accreditation program may be the answer.

Participation in the proposed National Environmental Laboratory Accreditation Program is being considered. The Agency is pursuing a national environmental laboratory accreditation program. A committee was established to solicit information from outside the Agency on the need for and operation of a national laboratory accreditation program. The committee with representatives from states, federal agencies, the laboratory and the regulated community, recommended establishment of a voluntary national accreditation program for environmental laboratories.

In late Fiscal Year 1994 or early Fiscal Year 1995, EPA plans to sponsor a national meeting with federal and state officials and private sector representatives to develop consensus standards for a national environmental laboratory accreditation program. The result will be published in the Federal Register. It is anticipated that EPA will adopt these standards without going through a separate regulatory process, and that states will voluntarily modify their own accreditation program to be consistent with these consensus standards.

In 1988, EPA's RCRA Groundwater Task Force found that laboratories analyzing groundwater data did not have quality assurance/quality control procedures and did not always use correct analytical methods. Consequently, the task force recommended that the agency develop the resources and expertise to conduct inspections at these laboratories for use by both EPA and authorized states.

The RCRA program agreed to implement this recommendation and developed a guidance for a new inspection called the laboratory audit inspection. This type of inspection is to detect the use of improper procedures, identify violations and provide a mechanism to investigate anomalies in the facility's groundwater data or other concerns over the quality of data by individual laboratories, and, determine whether laboratories were capable of generating high-quality analytical data.

A third oversight mechanism could be an audit of laboratory raw data and records to determine if they validate the reported results and if the results were obtained as planned and reported. The Agency is developing a module on laboratory fraud in the RCRA Inspector Institute and Advanced RCRA Institute. The module will train inspectors on laboratory fraud and data quality problems to enable inspectors inspect laboratories and determine any data quality problems.

LDIB can be anticipated to increase the scrutiny of the laboratories providing health and environmental data for the various programs. This will be accomplished by direct inspections by LDIB staff, oversight of state and regional inspections, review of EPA regions and states management of their quality assurance programs, and inspector training and guidance efforts.

CONCLUSION

Based on GAO recommendations and EPA's reorganization, changes to the RCRA compliance assurance program on laboratory data integrity issues have been considered: (1) Inspections of facilities include complete and effective review of groundwater sampling procedures. (2) Regional oversight of state inspectors is emphasized. (3) EPA Headquarters oversight of regions and authorized states. (4) Inspectors will be trained in quality assurance, sample collection techniques, data quality problems and laboratory fraud. (5) Laboratory inspections will be carried out. (6) The Agency is pursuing a national laboratory accreditation program for environmental laboratories.

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NOTICE

This paper contains the views and opinions of the authors. It does not necessarily reflect the current position or policy of the USEPA.

HOW TO PREPARE FOR AND MANAGE A LABORATORY INSPECTION

Robert L. Cypher, Director of Quality Assurance, EA Engineering, Science, and Technology, Inc., 11019 McCormick Road, Hunt Valley, Maryland 21031; Mary M. Uhlfelder, Manager of Quality Services, EA Laboratories, 19 Loveton Circle, Sparks, Maryland 21152; Michael M. Robison, Quality Assurance Officer, Maryland Spectral Services, Inc., 1500 Caton Center Drive, Baltimore, Maryland 21227.

ABSTRACT

The majority of environmental analytical laboratories will experience several laboratory inspections over the course of a year. The nature of these inspections are to initially qualify, certify, or validate the laboratory or provide annual renewal by outside groups. The majority of the inspecting groups will be from a federal or state agency and the minority will be commercial or private clients. Most inspections will last a day, or two, with usually one, sometimes two or more inspectors.

The objective of this presentation is to give you some insights into how to prepare for and manage a laboratory inspection. In this presentation, we will ask a number of questions such as: What should you be doing before, during and after each inspection? Does your laboratory have a company policy and procedure for handling inspections? Do you have a statement of intent? Have you designated an individual to function as an official escort or representative? Do you conduct training sessions and pass out handouts regarding inspections? Has the receptionist been briefed on what to do when an inspector arrives? Who in the laboratory is to be notified? Do you have an inspector's survival kit? What are the "Dos" and "Don'ts" of an inspection? Do you have a debriefing at the completion of every inspection? We will provide answers to these questions and provoke other questions that should stimulate your thinking as to how you handle your future inspections.

INTRODUCTION

To perform analytical work in the environmental arena today, your laboratory will be required to be certified or validated by a federal or state agency. All of your federal and most of your state certification/validation procedures will include an on-site inspection of your laboratory. The first impression that you as a laboratory make on the inspecting team must be a good one, because that impression sets the tone for the rest of the inspection.

From our viewpoint, any inspection is an opportunity for your laboratory to show off your facility and qualifications. Inspections are to be taken seriously, but at the same time use them as a learning experience, a chance to correct any deficiencies and to have another pair of eyes examine your systems and procedures. For most state certifications you have to pay for your inspection, so you might as well make the most of it. The best way to be prepared

for any inspection is to practice. Over the next couple of sections I'll be discussing some of our experiences and how we handle some of the situations. We can't say it is the best way, but it is the way that works for us.

"WHEELS OF MOTION"

The phrase "Wheels of Motion" is used to get you to start thinking about inspections before they happen, to develop an action plan, and to test the system. This is where I discuss the "before, during, and after" the inspection; you're constantly in an evolving circle. Inspections are a way of life in most laboratories because of regulations, regulators, and demands of your clients. Also, because of the recent incidence of laboratory fraud you may find an increased frequency of inspections.

BEFORE THE INSPECTION

A laboratory can do a lot in preparing for any inspection by building its inspection procedures into its daily laboratory activities. First, develop a policy and procedure on inspections that will serve as a road map for everyone to follow in your laboratory.
A brief example of a company policy and procedure for inspections is presented in Table 1. Second, maintain a "high state of readiness"; this means that if an inspector walked in unannounced you would be prepared. Many times, a laboratory will receive prior notification of an inspection, so they usually devote the day before cleaning up, checking the books, conducting a quick lab inspection, and looking for clean lab coats. Although rare, there are unannounced inspections that count just the same. Third, conduct "mock" inspections to test the system and get the general laboratory population exposed to what possibly could be the "real thing." Fourth, select a room where you will house the inspectors during the course of the inspection? Things to consider when selecting a room:

- Size, table, and chairs
- Blackboard (requests, schedules)
- Projection screen
- Telephone
- Proximity to rest rooms
- Availability of refreshments
- Isolated from the work flow

DURING THE INSPECTION

The arrival of the inspectors at the laboratory is the first critical step in the inspection process. From an inspector's viewpoint there are three critical periods:

- During the reception
- In the laboratory
- At the completion of the inspection

During each of these critical periods an "impression" is formed about the laboratory, the personnel, systems, and procedures. As an example, if your laboratory is dirty and cluttered, the natural tendency is to think bad data. The inspector may decide to look for problems or make issues of minor items. This is not to say that a clean looking laboratory wouldn't have problems either.

Once the inspectors have been received and taken to the designated room, their credentials should be checked. If they are not presented you should ask to see them. You should satisfy yourself that the inspector is an authorized employee of the inspecting agency.

Next, the company representative (escort) should request an explanation from the inspector as to the purpose of the inspection. With a Food Drug Administration (FDA) or an Environmental Protection Agency (EPA) inspector they will usually present a "Notice of Inspection." Discussing the reasons for the visit is beneficial to each of the parties, because this can increase the efficiency of the inspection. Note that, if the inspection is directed towards a particular client, the laboratory needs to get authorization from the client before the inspector can review their data.

After the purpose of the inspection has been discussed, the company representative should describe the company's Statement of Intent (Table 2), the so-called ground rules for the inspection. At this point, the inspectors usually will take an orientation tour of the facility or just start the inspection.

Prior to the reception of the inspectors, the company escort (or alternate) should have made a quick tour of the laboratory noting any problem areas, talking to each supervisor about work schedules and status of personnel.

The key to managing any inspection is having a qualified escort (Table 3). This individual can make or break any inspection. Another key component of an inspection is what I call an "Inspector's Survival Kit" (Table 4). It is a cardboard box with all of the information that I carry from inspection to inspection.

During any inspection, there are certain guidelines that you should follow. I call them the "dos and don'ts" (Table 5) of an inspection.

During the inspection, the escort should be taking notes of the areas inspected, personnel interviewed, records reviewed, any problems noted, etc. As you're progressing through the inspection you should be developing a "gut feeling" for how the inspection is going and the direction the inspector is taking. Anytime that the escort perceives that there may be a problem, the escort should ask the inspector for more details to determine whether it is or isn't a problem. At this point, you should be passing the word to the other areas that will be inspected as to what to expect and the approach being taken. If the inspection lasts for more than a day, at the end of the day the escort should get a quick debriefing from the inspector and confirm the schedule for the next day. If it's only a one-day inspection, during the lunch break, you may be able to get a quick debriefing. Why should you be concerned about getting a debriefing while the inspection is on-going? Because, if there is any way of

correcting a situation while the inspector is still in the facility and has not given a final debriefing, you may be able to have the problem removed from the list.

During the course of the inspection, if copies of data are requested by the inspector, a duplicate copy (for your record) should be made, the data stamped as "Company Confidential" and a receipt prepared. Many laboratories may not know that any information a federal agency acquires during an inspection becomes part of the agency record, which may be disclosable to the public (Freedom of Information Act) or used as evidence by the agency to support application of civil penalties, seizure, injunction, or criminal penalties.

At the completion of the inspection, a debriefing should be held. The laboratory should determine the list of attendees, designate a spokesperson and a recorder. The laboratory should discuss each finding point-by-point. The inspector may document your response and could delete a finding if evidence can be produced. The inspector will usually indicate that a report will follow in so many weeks and that you will have a specified number of days to respond.

AFTER THE INSPECTION

After the inspector has left the facility, you should have the debriefing notes typed and hold a meeting with key personnel to go over the findings and outline corrective actions, if any, that need to be taken. Set up an inspection file. Upon receipt of the inspector's letter, you should make copies and distribute them to key personnel, set up a meeting, and develop an action plan. Usually the quality assurance group will oversee this function and perform a follow-up inspection to verify that the corrective actions have been implemented.

The best way for a laboratory to learn from each inspection is to conduct training sessions with your laboratory staff. Go over the findings from past inspections and have the escort discuss what its like to be with an inspector and what they look for. The best way to handle any inspection is to have your laboratory personnel educated.

SUMMARY

We realize that this may seem like a lot to ask of any laboratory, but if you want to prepare for and manage your laboratory inspections some type of system needs to be in place. Most of your laboratory inspections are the responsibility of the quality assurance group, but we want to remind you that the real responsibility falls upon everyone that works in the laboratory. If you don't pass an inspection it may have repercussions that could affect the future of the laboratory.

TABLE 1

COMPANY POLICY AND PROCEDURE FOR INSPECTIONS

Every company should have a policy and procedure on inspections by outside organizations.

POLICY

- Specify the nature of Company X's activities that are subject to federal, state, and local regulations.
- Be cooperative, courteous, and candid.
- Obtain authorization from client.
- Identify circumstances under which legal counsel is to be notified.
- Check all questions of legal rights with legal counsel.
- Identify disclosable and nondisclosable documents.
- Make company personnel familiar with Policy and Procedure.
- Maintain copy of each document supplied to inspector.
- Assign responsibility for coordination of inspections:
  - Reception
  - Designation of company escorts and alternates
  - Notification of key personnel
  - Conduct of inspection
  - Approval for release of requested data
  - Debriefing
  - Post-inspection report
  - Corrective action plan
  - Follow-up of plan
- Prepare a set of "ground rules" for inspector.
  - Statement of Intent

TABLE 2

STATEMENT OF INTENT

1. Company X recognizes the proprietary nature of its programs for clients and will not release information without authorization of the client.

2. Company X recognizes the authority of regulatory agencies to inspect—at reasonable times and in a reasonable manner (state normal operating hours).

3. A representative of a regulatory agency wanting to inspect will provide the following information:

   - Personal Identification
   - Identification of the Agency
   - Purpose of the Inspection
   - Approximate Duration of Inspection

4. A representative (escort) of the company will accompany the inspector(s) at all times. The inspector(s) requests for information, documentation, or interviews will be handled through the escort.

5. Company X forbids photographs, videotapes, or tape recordings to be taken.

6. The inspector will sign a receipt for data or samples taken. Data may be stamped as "Company Confidential Information." At the discretion of management a reasonable fee may be charged for collection of data or samples.

7. The inspector(s) will not be given access to personnel files, financial information, or internal audit reports.

8. The inspector(s) will follow all company safety rules and regulations at all times when on company property.

9. Affidavits may not be signed upon ADVICE of legal counsel.

10. At the conclusion of the inspection a debriefing will be held.

TABLE 3

QUALIFICATIONS OF A DESIGNATED ESCORT

- Excellent Reputation - Both Inside and Outside Company
- Knowledgeable about:
  - Federal, State and Local Regulations
  - Company Policies and Procedures
  - Standard Operating Procedures, Methods
  - Personnel
  - Laboratory Functions/Areas
- 6th Sense—ability to anticipate an inspector's interest, reactions, and conclusions
- Pleasant, but Business-like
- Persuasive, but not Argumentative
- Alert and Observant
- Clear in Speech and Writing
- Experienced in Laboratory and Technical Area
- Diplomatic and Flexible

TABLE 4

CONTENTS OF AN INSPECTOR'S SURVIVAL KIT

- History of the company
- Organization charts
- Floor plans
- Last inspection findings with corrective action
- Index of standard operating procedures/methods/procedures, etc.
- CVs of key personnel
- List of key personnel with phone numbers
- Company policy and procedure on inspections—ground rules
- Authorization as designated escort
- Inspection checklist
- Work flow patterns/charts
- Security/safety procedures
- Validation records (data, LIMS, environmental, etc.)
- Employee training records
- Pencils, pens, paper, and clipboard

TABLE 5

"DOS" AND "DON'TS"

- Take a lawyer's approach to questions: "yes", "no" or "I don't know"
- Give positive constructive answers—but don't stretch the truth
- Do not lie or ask others to do so
- Do not hide or make changes in requested documents
- Be helpful—but don't volunteer unnecessary information
- Respond promptly—but don't guess or pretend to know answers
- Ask for feedback—but don't concede violations
- Explain company ground rules in advance—but don't be quarrelsome or obstructive
- Make suggestions—but don't dominate or push
- Prepare other personnel for questions—but don't "huddle secretively"
- Show that you are knowledgeable about the law and regulations—but don't be rude
- Recognize the inspector's position—but don't be servile
- Do not offer gifts

IMPROPER HAZARDOUS WASTE CHARACTERIZATIONS - FINANCIAL AND COMPLIANCE IMPLICATIONS

Richard M. Walka, Senior Associate, William F. Cosulich Associates, 330 Crossways Park Drive, Woodbury, New York, 11797-2015;
Frank A. Langone, International Business Machines Corporation, Thomas J. Watson Research Center, Mail Code 31061, PO Box 218, Yorktown Heights, New York, 10598;
Richard P. Russell, Project Engineer, William F. Cosulich Associates, 330 Crossways Park Drive, Woodbury, New York, 11797-2015.

ABSTRACT

Generators of waste often assume that "when in doubt" concerning whether a waste material is hazardous or nonhazardous, transporting and disposing of the material as a hazardous waste, with an accompanying manifest, affords them some "protection" that ordinarily would not otherwise exist. The purpose of this paper is to present an array of potential environmental regulatory and financial liability implications regarding generators who subscribe to this "protective filer" approach in lieu of proper waste characterizations. As the paper presents, those generators who do not render accurate and well-founded waste characterizations pursuant to appropriate federal and/or state requirements, can actually increase their liability. This is particularly important when the waste is not a hazardous waste but is managed as if it were by electing to use a hazardous waste manifest accompanying its management.

Based on a review of various federal regulatory and certain state regulatory and financial requirements, the paper reviews the responsibilities attendant to the use of a manifest and the costs associated with these responsibilities. Basically, generators of hazardous waste must comply, at some cost, with the hazardous waste management regulations of the federal government, or an authorized state as prescribed by RCRA. These requirements include, but are not necessarily limited to, the following:

- Increased accumulation and storage costs.
- Compliance with hazardous waste generator requirements, including:
  - EPA ID Number
  - Accumulation requirements
  - Storage requirements
  - Inspections
  - Manifest
  - Record Keeping

- Increased transportation costs.
- Increased disposal costs.
- Waste minimization certification and associated waste minimization implications.
- Increased financial liability associated with taxes and regulatory fees.
- Cost associated with non-compliance.

Overall, the paper supports the approach that proper and judicious hazardous waste characterizations can go a long way toward reducing regulatory compliance and financial liabilities for generators of waste. Toward that end, the design and implementation of a properly crafted and implemented Quality Assurance/Quality Control Plan with clear Data Quality Objectives is likely to be the cost-effective approach in reducing overall long-term waste management costs.

INTRODUCTION

This paper is *not* a "how to" on when or under what circumstances one is required to make a hazardous waste determination, or a primer reviewing a step by step approach to rendering a proper characterization. Rather, the purpose of this paper is to illustrate why generators of waste should render accurate and well-founded determinations as to whether the material is a hazardous waste pursuant to appropriate federal and/or state requirements. The paper will also review the potential financial and compliance implications of managing nonhazardous waste as hazardous waste in New York State. When waste is classified as hazardous, its management requires the use of a manifest for off-site transportation. Utilizing a manifest results in a number of explicit and implicit protections and liabilities. The implications of using the hazardous waste manifest will be a major portion of the discussion.

The recognition of the uniform hazardous waste manifest among waste generators across the nation is probably second only to the IRS 1040 Form. Since its creation by the Environmental Protection Agency in the late 1970's, the hazardous waste manifest and the vast information network it supports, remains the cornerstone of RCRA's national "cradle to grave" hazardous waste tracking system. We will explain why the manifest possibly has more *responsibilities* than protections associated with its use.

It has been our experience that some clients firmly believe that "when in doubt" waste should be classified as hazardous. These clients assume that transporting the material as a hazardous waste, with an accompanying manifest, is always "safer," affording them some protection that ordinarily would not otherwise exist. This "protective filer" mentality has a number of enforceable regulatory liabilities, as well as financial

implications, associated with it which can be burdensome when the facility actually does *not* generate any hazardous waste. These considerations are in addition to the high cost of hazardous waste disposal.

Obviously, this paper supports utilizing the hazardous waste manifest when appropriate, and fosters the concept of proper and judicious hazardous waste characterizations. However, we are opposed to using hazardous waste manifests when solely generating/transporting, nonhazardous industrial waste.

Before we discuss the financial and compliance liabilities associated with transporting manifested nonhazardous waste, we will briefly describe the hazardous waste program.

WHEN IS A WASTE A HAZARDOUS WASTE?

Section 1004(5) of RCRA defines hazardous waste as a "...solid waste, or combination of solid wastes, which because of its quantity, concentration or physical, chemical or infectious characteristics may:

(A) cause or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness;
or

(B) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported or disposed of, or otherwise managed."

While this statutory definition is subjective, it clearly states that in order for a material to be a hazardous waste, it must first be a "solid waste," as defined by RCRA. In order for a solid waste to be defined as a hazardous waste, it must meet the following conditions:

- Is not excluded from regulation as a hazardous waste, and;
- Exhibit any of the **characteristics** of a hazardous waste, and/or;
- Be named a hazardous waste and **listed** by regulation as such, or;
- Is a **mixture** containing a characteristic waste/listed hazardous waste and a nonhazardous solid waste, unless the mixture is specifically excluded or no longer exhibits any of the characteristics of hazardous waste. A mixture containing a nonhazardous waste and a listed hazardous waste will remain a listed hazardous waste.

In the preceding section, we provided a general definition of hazardous waste. However, there are two principle mechanisms to determine whether a waste is a hazardous waste. First, one must determine if it is a "listed waste," so named because it is specifically listed as such by the EPA or a State as part of its hazardous waste regulations. Secondly, based on knowledge or laboratory analysis, one must determine if it exhibits any *characteristics* of a hazardous waste: ignitability, corrosivity, reactivity and toxicity.

CHARACTERISTIC WASTE

Ignitability

A solid waste that exhibits any of the following properties is considered a hazardous waste due to its ignitability:

- A liquid, except aqueous solutions containing less then 24 percent alcohol, that has a flash point less than 60°C(140°F);
- A nonliquid capable under normal conditions of spontaneous and sustained combustion;
- An ignitable compressed gas in accordance with Department of Transportation (DOT) regulation;
- An oxidizer per DOT regulation.

EPA's reason for initially including ignitability as a characteristic was to identify waste that could cause fires during transport, storage or disposal.

Corrosivity

A solid waste that exhibits any of the following properties is considered a hazardous waste due to its corrosivity:

- An aqueous material with pH less than or equal to 2.0 or greater than or equal to 12.5;
- A liquid that corrodes steel at a rate greater than 0.25 inch per year at a temperature of 55°C (130°F).

EPA chose pH as an indicator of corrosivity because waste with high or low pH can react dangerously with other waste or cause toxic contaminants to migrate from certain waste. Steel corrosion was chosen because waste capable of corroding steel can escape from its container.

Reactivity

A solid waste that exhibits any of the following properties is considered a hazardous waste due to its reactivity:

- Normally unstable and reacts violently without detonating;
- Reacts violently with water;
- Forms an explosive mixture with water;
- Generates toxic gases, vapors or fumes when mixed with water;
- Contains cyanide or sulfide and generates toxic gases, vapors or fumes at a pH of between 2 and 12.5;
- Capable of detonation if heated under confinement or subjected to strong initiating source;
- Capable of detonation under standard, temperature and pressure;
- Listed by DOT as Class A or B explosive.

Reactivity was chosen as a characteristic to identify unstable waste that can pose a problem at any stage of that waste management cycle.

Toxicity

The toxicity characteristic test is designed to identify waste likely to leach particular toxic constituents into the groundwater as a result of improper management.

To ascertain if a solid waste is hazardous because of the toxicity characteristic, constituents are extracted from the waste in a manner designed to simulate the leaching action which occurs in landfills. The extract is then analyzed to determine if it possesses any hazardous constituents listed in Table 1. If the concentrations of the toxic constituents are equal to or exceed the regulatory levels listed, the waste is classified as hazardous.

Characteristic hazardous wastes are defined by certain physical/chemical criteria which may require a representative waste sample analysis by the generator. The Toxicity subcategory is more likely than the other characteristics to require chemical analysis. Consequently, a waste generator must be very careful in selecting/paying for the correct protocols to characterize his waste for Toxicity.

Table 1

TOXICITY CHARACTERISTIC CONTAMINANTS AND REGULATORY LEVELS

EPA Hazardous Waste Number	Contaminants	Chronic Toxicity Reference Level (mg/l)	Basis*	Regulatory Level (mg/l)+
D004	Arsenic	0.05	MCL	5.0
D005	Barium	1.0	MCL	100.0
D018	Benzene	0.005	MCL	0.5
D006	Cadmium	0.01	MCL	1.0
D019	Carbon tetrachloride	0.005	MCL	0.5
D020	Chlordane	0.0003	RSD	0.03
D021	Chlorobenzene	1	RfD	100.0
D022	Chloroform	0.06	RSD	6.0
D007	Chromium	0.05	MCL	5.0
D023	o-Cresol	2	RfD	200.0[a]
D024	m-Cresol	2	RfD	200.0[a]
D025	p-Cresol	2	RfD	200.0[a]
D026	Cresol	2	RfD	200.0[a]
D016	2,4-D	0.1	MCL	10.0
D027	1,4-Dichlorobenzene	0.075	MCL	7.5
D028	1,2-Dichloroethane	0.005	MCL	0.5
D029	1,1-Dichloroethylene	0.007	MCL	0.7
D030	2,4-Dinitrotoluene	0.0005	RSD	0.13[b]
D012	Endrin	0.0002	MCL	0.02
D031	Heptachlor (and its hydroxide)	0.00008	RSD	0.008
D032	Hexachlorobenzene	0.0002	RSD	0.13[b]
D033	Hexachloro-1,3-butadiene	0.005	RSD	0.5
D034	Hexachloroethane	0.03	RSD	3.0
D008	Lead	0.05	MCL	5.0
D013	Lindane	0.004	MCL	0.4
D009	Mercury	0.002	MCL	0.2
D014	Methoxyclor	0.1	MCL	10.0
D035	Methyl ethyl ketone	2	RfD	200.0
D036	Nitrobenzene	0.02	RfD	2.0
D037	Pentachlorophenol	1	RfD	100.0
D038	Pyridine	0.04	RfD	5.0[b]
D010	Selenium	0.01	MCL	1.0
D011	Silver	0.05	MCL	5.0
D039	Tetrachloroethylene	0.007	RSD	0.7
D015	Toxaphene	0.005	MCL	0.5
D040	Trichloroethylene	0.005	MCL	0.5
D041	2,4,5-Trichlorophenol	4	RfD	400.0
D042	2,4,6-Trichlorophenol	0.02	RSD	2.0
D017	2,4,5-TP (Silvex)	0.01	MCL	1.0
D043	Vinyl chloride	0.002	MCL	0.2

* MCL = Maximum Contaminant Level or National Interim Primary Drinking Water Standard
RSD = Risk-Specific Dose
RfD = Reference Dose

\+ The regulatory level equals the chronic toxicity reference level times a dilution/attenuation factor (DAF) of 100, unless otherwise noted.

[a] If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. Note that D026 was added to the final rule for this purpose, but is not a new constituent.

[b] The quantitation limit (i.e., five times the detection limit) is greater than the calculated regulatory level; thus, the quantitation limit becomes the regulatory level.

Source: 55 FR 11804 and 11815-11816.
1-24-94

There are financial implications tied to Toxicity wastes in two areas. First, the prescribed leaching protocol (Toxicity Characteristic Leaching Procedure - TCLP) is an expensive protocol to run. However, it may not be required if the waste is a 100% solid matrix or a solid/water matrix, for which a total constituent analysis has been performed. The extraction is also not required if the waste is a liquid with no solid phase. Thus, an understanding of when the TCLP is needed has a significant influence on the cost of waste characterization.

Secondly, it is important to compare the appropriate Toxicity analytical result with the regulatory level to avoid incorrect hazardous waste determinations (false positives) which will result in the compliance/financial implications that will be discussed below. For example, the total constituent analysis of a 100% solid waste sample would be reduced by a factor of 20, before comparing it to the regulatory level (the 1 to 20 factor is derived from the 1 to 20 dilution factor that is part of the TCLP protocol).

A good source of information on the entire Toxicity category and, in particular, on correctly using the TCLP procedure/interpreting analytical results is: "Technical Assistance Document for Complying with the TC Rule and Implementing the Toxicity Characteristic Leaching Procedure (TCLP)," May 1993, U.S. EPA-Region II.

LISTED WASTE (SPECIFIC/NONSPECIFIC)

As we mentioned above, solid waste is considered hazardous waste if it is "listed" as one of the following:

- Nonspecific source waste - These are generic wastes, commonly produced by manufacturing and industrial processes. Examples from this list include spent halogenated solvents used in degreasing and wastewater treatment sludge from electroplating processes.

- Specific source waste - This list consists of wastes from specifically identified industries such as wood preserving, petroleum refining and organic chemical manufacturing. These wastes typically include sludges, still bottoms, wastewaters, spent catalysts and residues; e.g., wastewater treatment sludge from the production of pigments.

- Commercial chemical products - The third list consists of specific unused commercial chemical products or manufacturing chemical intermediates. The key criterion for this category is that the waste is unused, e.g., off-spec or spilled materials. This list includes chemicals such as chloroform and creosote, acids such as sulfuric acid and hydrochloric acid, and pesticides, such as DDT and kepone.

These lists were developed by examining different types of waste and chemical products to ascertain if they:

- Exhibit one of the four characteristics of a hazardous waste(listed above);
- Meet the statutory definition of hazardous waste;
- Are acutely toxic or acutely hazardous;
- Are otherwise toxic.

It should be noted that individual States may designate additional materials as listed hazardous wastes. For example, New York State regulates PCB wastes as listed hazardous wastes (B-codes).

REGULATORY REQUIREMENTS

If a facility produces hazardous waste based on the regulatory criteria discussed above, it may be classified as a hazardous waste generator. Hazardous waste generators are the first link in the "cradle to grave" hazardous waste management system established pursuant to the Resource Conservation and Recovery Act (RCRA). Generators of 100 kilograms of hazardous waste or 1 kilogram of acute hazardous waste per month must comply with certain enforceable generator standards.

The pretransport regulatory requirements for hazardous waste generators include:

- Obtaining an EPA ID number. One way that EPA monitors and tracks generators is assigning each generator a unique identification number. Without this number, the generator is barred from treating, storing, disposing, transporting or offering for transport any hazardous waste to any transporter or treatment, storage or disposal facility;
- Adhering to procedures for handling hazardous waste before transport;
- Manifesting hazardous waste for off-site transportation;
- Maintaining a 24-hour Emergency Contact for each shipment;
- Record keeping and reporting;
- Proper packaging to prevent leakage of hazardous waste during normal transport conditions and in potentially dangerous situations (e.g., when a drum falls out of a truck);

- Identifying the characteristics and dangers associated with the waste being transported through labeling, marking and placarding of the packaged waste;

- Preparing applicable Land Disposal Restriction (Land Ban) shipping notices.

It is important to note that these pretransport regulations only apply to generators shipping waste off-site.

In addition to the requirements outlined above, EPA and authorized states also developed pretransport regulations for accumulation of waste prior to transport. A generator can accumulate hazardous waste on-site for 90 days or less without a permit, as long as the following requirements are met:

- Proper Storage - The waste is properly stored in containers or tanks marked with the words "Hazardous Wastes" and the date on which accumulation began. The waste must also be inspected at least weekly and inspections records maintained.

- Emergency Plan - A contingency plan and emergency procedures to use in an emergency must be developed.

- Personnel Training - Facility personnel must be trained in the proper handling of hazardous waste.

- Preparedness and Prevention Measures - Providing adequate security measures, signage, and communication systems.

The 90-day period allows a generator to collect enough waste to make transportation more cost-effective; that is, instead of paying to haul several small shipments of waste, the generator can accumulate waste until there is enough for one large shipment.

THE HAZARDOUS WASTE MANIFEST

The manifest is the fundamental element of the hazardous waste tracking system. The uniform hazardous waste manifest is the document which accompanies shipments of waste and tracks the material from the generator (the cradle) to the ultimate disposal facility (the grave). The RCRA manifest requires the following information:

- Name and EPA identification number of the generator, transporter(s) and the facility where the waste is to be treated, stored or disposed;

- U.S. DOT description of the waste being transported;

- Quantities of waste being transported; and

- Address of the treatment, storage or disposal facility to which the generator is sending the waste.

- 24-hour emergency contact telephone number.

It is especially important for the generator to prepare the manifest properly, since the generator is responsible for the hazardous waste produced and its ultimate disposition.

Waste Minimization

When Congress passed the Hazardous and Solid Waste Amendments (HSWA) in 1984, it established a framework aimed at eliminating specific forms of waste management such as land disposal, in favor of more technologically advanced, permanent destruction methods, such as incineration.

Among its complex and far reaching provisions, the HSWA contained a statutory provision which initiated waste minimization criteria. Sections 3002(a)(6), regarding the preparation of biennial waste reduction reports, and 3002(b) of HSWA, entitled, "Waste Minimization," require generators of hazardous waste to practice and report on waste minimization activities. It requires generators of hazardous waste to sign a specific certification on the manifest indicating that they are doing all that is "economically practicable" towards reducing the volume or quantity and toxicity of the hazardous waste generated at a facility. It is a signed certification that generators are in full compliance with HSWA waste minimization criteria.

Section 3002(b) of HSWA, entitled "Waste Minimization," reads as follows:

> "(b) Waste Minimization - Effective September 1, 1985, the manifest required by subsection (a)(5) shall contain a certification by the generator that -
>
> (1) the generator of the hazardous waste has a program in place to reduce the volume or quantity and toxicity of such waste to the degree determined by the generator to be economically practicable; and
>
> (2) the proposed method of treatment, storage, or disposal is that practicable method currently available to the generator which minimizes the present and future threat to human health and the environment."

With regard to the requirement for biennial reporting of waste reduction efforts to regulatory agencies, Section 30021(a)(6) reads as follows:

> "(6) submission of reports to the Administrator (or the State agency in any case in which such agency carries out a permit program pursuant to this subtitle) at least once every two years, setting out -

(A) the quantities and nature of hazardous waste identified or listed under this subtitle that he has generated during the year;

(B) the disposition of all hazardous waste reported under subparagraph

(C) the efforts undertaken during the year to reduce the volume and toxicity of waste generated; and

(D) the changes in volume and toxicity of waste actually achieved during the year in question in comparison with previous years, to the extent such information is available for years prior to enactment of the Hazardous and Solid Waste Amendments of 1984."

In addition to these enforceable waste reduction mandates brought about by the HSWA manifest certification, many states have already passed additional statutes and regulations to address pollution prevention and waste reduction.

For example, in August 1990, New York State passed a law requiring facilities that generate and have the potential to release hazardous wastes and toxic substances into the environment reduce, to the maximum extent possible the volume or quantity and toxicity of wastes, whether emitted into the air, discharged into the waters, or treated and disposed of in a permitted facility. The waste reduction may be achieved by implementing technically feasible and economically practicable waste reduction technology, process or operation changes. The legislature declared that implementing such measure will help the State achieve an overall reduction in the generation and release of hazardous waste of fifty percent over the next ten (10) years.

This law requires generators of hazardous wastes to prepare, implement and submit a Hazardous Waste Reduction Plan (HWRP) to the New York State Department of Environmental Conservation (NYSDEC). The HWRP, which is reviewed for acceptance by NYSDEC, must be updated biennially and annual status reports must be submitted. Failure to submit an acceptable plan precludes the generator from signing the hazardous waste manifest certification.

The requirements of the Hazardous Waste Reduction Plan include, but are not limited to, the following:

- Quantification of hazardous waste(s)
- Description of hazardous waste source(s) of generation and disposal method(s)
- Indices of hazardous waste generation to production (i.e., output from, or input to, the process generating the waste stream)

- Submission of a hazardous waste generator summary
- Cost estimate(s) for managing each waste
- Evaluation of technical feasibility and economical practicability of implementing waste reduction options
- Listing of technically feasible and economically practicable waste reduction measures and schedule for implementing identified waste reduction measures
- Description of corporation's and facility's waste reduction policy
- Identification of party responsible for implementation of waste reduction plan
- Identification of waste reduction measurement(s)
- Identification of employee training programs
- Estimate of anticipated hazardous waste reduction
- Estimate of anticipated transference of hazardous waste into other environmental media
- Submission of Hazardous Waste Reduction Program Summary (HWRP)
- Biennial updates of HWRP
- Annual status reports

In addition, to the state statute, EPA has published its interim final rule regarding waste minimization program requirements. Although published in the Federal Register as an interim final rule, the guidance puts "additional enforcement teeth" behind the hazardous waste manifest certification requirements mandated by the Hazardous and Solid Waste Amendments.

TAX ASSESSMENT/REGULATORY FEES

In addition to the regulatory/compliance implications discussed above, there is an additional liability when hazardous waste is generated at your facility and properly managed via a manifest, or a nonhazardous waste is accompanied by a manifest. That liability is a special assessment and regulatory fee. In New York State, these assessments and fees are administered by the New York State Departments of Taxation and Finance and Environmental Conservation, respectively. The "bottom line" is that the generation

of hazardous waste in New York State can affect your "bottom line." Another good reason to make sure your hazardous waste is in fact, *hazardous*. Let's briefly review the two revenue programs.

As mentioned above, the first tax, entitled, "Special Assessments on Generation, Treatment or Disposal of Hazardous Waste in New York State" is administered by the Department of Taxation and Finance and is self reported by generators and TSDFs within the state on Form TP-550. This self reporting program is managed comparable to other state taxes, that is, it is prepared and reported by the generator and subject to review and audit by the Department of Taxation and Finance. In its simplest form, the Special Assessment, or "waste end assessment" as it is commonly referred to, is calculated by generators based on the tons of hazardous waste generated in New York State that received on site treatment or disposal or that were designated for removal or removed from the site of generation for treatment or disposal or for storage prior to such treatment or disposal during the reporting period. With regard to treatment and/or disposal facilities, these entities are only required to report the tons of hazardous waste received from generators outside New York State for treatment disposal or for storage prior to such treatment or disposal (this avoids double counting.)

In accordance with the Environmental Conservation Law (§27-0923 Special Assessments on Hazardous Wastes Generated) the following assessment rate schedule currently applies:

Category	Assessment Rate (in dollars per Ton)
Tons disposed of in landfill on-site of generation.	$27
Tons designated for removal or removed from the site of generation for disposal in a landfill or designated for removal or removed from the site prior to disposal in a landfill	$27
Tons designated for removal or removed from the site of generation for treatment or disposal (except by landfill or incineration), or for storage prior to such treatment or disposal	$16
Tons designated for removal or removed from the site of generation for incineration or for storage prior to incineration .	$9
Tons incinerated on the site of generation	$2
Tons received from out-of-state for landfill disposal or for storage prior to such disposal	$27

Tons received from out-of-state for treatment or disposal other than landfill or incineration, or for storage prior to such treatment or disposal	$16
Tons received from out-of-state for incineration or for storage prior to incineration.	$9

As can be seen from the table above, the rates are structured to provide an incentive for disposal/treatment of waste by incineration and discourages disposal via landfilling. A deduction may be taken for waste that is reclaimed.

These special assessments are paid quarterly and are due to the Department by the 20th day of the month after the end of each calendar quarter. While the fees may not seem onerous at first glance, it does not take much material to achieve a ton of waste. For instance, a 55 gallon drum of water (the density used to calculate the fee) weighs approximately 459 lbs or approximately .23 of a ton. So one can see how quickly the special assessments can take a bite of your bottom line.

The second financial implication of generating hazardous waste is the Regulatory Fee, which is administered by the New York State Department of Environmental Conservation pursuant to 6 New York Codes, Rules and Regulations Parts 480 through 486 (Revised 1991).

Unlike the "waste end assessment" discussed above, the Hazardous Waste Program Fee prescribed in Part 483 is an invoice prepared and sent by the Department based on data from annual generator reports and manifest documents submitted.

Basically, for generators of hazardous waste, the hazardous waste program fee is currently determined as follows:

- $1000.00 for generators of equal to or greater than 15 tons per year and less than or equal to 100 tons per year of hazardous waste,
- $6,000.00 for generators of greater than 100 tons per year and less than or equal to 500 tons per year of hazardous waste,
- $20,000.00 for generators of greater than 500 tons per year and less than 1,000 tons per year of hazardous waste, and
- $40,000.00 for generators of greater than 1,000 tons per year.

In addition to the above, generators of equal to or greater than 15 tons per year of hazardous *wastewater* are assessed $3,000.00.

The use of a manifest New York State should only accompany shipments of hazardous waste as defined under Part 371. In fact, Part 372.2(b)(6) states ..."Use of a Uniform Hazardous Waste Manifest constitutes a determination by the generator that the solid waste is a hazardous waste in New York and/or the state of generation."

Therefore, the utilization of a manifest accompanying a waste material that is clearly not a hazardous waste material may be interpreted as a violation of New York State hazardous waste regulations and therefore could be enforceable.

SUMMARY

We have just reviewed a number of regulatory and financial requirements that generators of hazardous waste in New York State and elsewhere across the country are obligated to comply with in order to protect human health and environment. Presentations such as this are typically offered to assist hazardous waste generators in achieving and maintaining regulatory compliance... and thereby... *minimize* liability from regulatory violations and associated fines.

However, as we stated at the outset, the objective of this presentation is quite the opposite. The focus here is to identify how one's liability is actually increased by utilizing the same regulatory system discussed above (i.e., manifest document, etc.) when it simply is not required because the waste is not truly a *hazardous* waste.

Example. Facility A uses a water soluble alkaline powdered product to aid in degreasing engine electric motors and transmission parts prior to rebuilding as part of its scheduled maintenance program. Rather than establish a proper waste characterization program with appropriate data quality objectives and quality assurance/quality control program, the facility manager characterizes the spent solution as a characteristic hazardous waste and ships it off-site via a licensed transporter with a signed manifest. The waste is characterized as corrosive (D002). This practice continues for a number of years, with manifests documenting ten's of thousands of gallons of "hazardous waste" being generated at the facility. (In fact, subsequent analytical data and proper waste characterization determined the material not to be hazardous.)

What are the liabilities associated with this scenario?

First, the use of a manifest signifies that the entity is a hazardous waste generator and, as such, is required to comply with appropriate federal and state generator requirements. Most important among these requirements is obtaining an EPA ID number. The ID number *must* be obtained by the generator in order to use a manifest. Now that you have declared generator status, the following enforceable requirements are applicable:

- compliance with specific procedures for handling waste

- record keeping and reporting
- proper labeling, marking and placarding
- develop and implement an emergency plan
- personnel training
- Preparedness and prevention measures
- annual generator report.

The above requirements are enforceable and may be subject to fine if determined not to be satisfactory to government inspectors. However, if the generator manifests wastes as "non-hazardous," the above requirements are not applicable.

Remember, the signature box on the manifest provides for a certification indicating that the generator has a program in place to reduce the volume and toxicity of waste, and that the method of treatment, storage or disposal minimizes present and future threats to human health and the environment. While these are commendable objectives, they are not applicable for a small manufacturing facility that does not generate hazardous waste in the first place.

There are also hazardous waste reduction plan requirements. Hazardous waste manifest documents are utilized to quantity the amounts of hazardous waste being generated at a facility. This process can include an otherwise non hazardous waste generator on the list of *hazardous* waste generators required by state law to prepare a Hazardous Waste Reduction Plan. The use of manifests and the submission of annual generator reports at a facility that does not generate hazardous waste in the first place can be an unnecessary regulatory burden. It costs resources to develop, submit and implement a hazardous waste reduction plan.

Last but not least, there are the "waste end assessments" reportable and payable to the Department of Taxation and Finance in New York State and regulatory fees assessed directly by the Department of Environmental Conservation. While perhaps not perceived as an overwhelming burden, when taken as a whole in consideration with the other prescribed regulatory requirements, improper hazardous waste characterizations can take a bite from your bottom line.

In short, the time, money and resources spent up front in proper waste characterizations including the development and implementation of clear data quality objectives and a quality assurance/quality control program, can go a long way toward reducing environmental compliance and financial liability.

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INORGANICS

A Comparison of Methods of Measurement of Cr^{+6} in Wastewaters, Soils and Sediments: UV-Visible Spectrometry and Ion Chromatography

10th Annual Waste Testing and Quality Assurance Symposium
Arlington, Va. July 1994

Stuart J. Nagourney, NJDEPE, and John Birri and Leonard Vu,
USEPA, Region II

Cr is one the most interesting and chemically diverse elements in the periodic table. It routinely exists in the environment in inorganic compounds or organometallic complexes in several oxidation states. The most common species are the +3 and +6 forms; in its trivalent form, Cr is often a nutrient while Cr^{+6} is well recognized as a probable agent of lung cancer in man[1] as well as having been reported to produce gastrointestinal disorders, dermatitis and ulceration of the skin.[2]

From the 1900's to the early 1970's, it is estimated that more than 2 million tons of chromite ore processing residue were created by a variety of manufacturing processes in Hudson County, New Jersey. Some of this material was used as fill material. Cr^{+6} is also a by-product of several industrial processes and is present at low concentrations in some commercial products. Public concern about the possible health affects associated with skin contact and inhalation from soluble and inhalable Cr^{+6}-containing media has driven efforts to enhance the understand of how Cr behaves in the environment and ways to accurately measure its speciated forms. The measurement of Cr^{+6} is now required as part of many NJ Pollution Elimination Discharge System (NJPDES) permits.

Any study to accurately assess the levels of speciated Cr in ambient air, waters, soils, sediments or other media requires an understanding of several contributing factors: the ability to obtain a representative sample, the means to quantitatively remove the Cr from the media of interest without altering its indigenous oxidation state and the capability to accurately measure specific ionic forms. The sampling and sample preparation aspects have been studied by many investigators. USEPA Method 7196a[3] is a colorimetric method originally designed for water and wastewaters that is routinely used to measure Cr^{+6} in non-aqueous extracts. USEPA Method 218.6 was originally designed to utilize Ion Chromatography for the measurement of Cr^{+6} in emissions from incinerators burning municipal sludge; it has been applied to drinking, ground, waste and seawaters with considerable success.[4]

Most users of the colorimetric method report few problems with its applicability when Cr^{+6} sample concentrations are high or when there are limited concentrations of organic material present in the matrix. At lower Cr^{+6} concentrations, the ability to quantitate Cr^{+6} may be difficult; this is exacerbated when matrix components of non-aqueous samples produce darkly colored extracts, making comparison of sample and blank often next to impossible.

This paper compares the results obtained by Methods 7196a and 218.6 on two types of samples that offer the greatest challenges to detection and quantitation of Cr^{+6}. These sample types are:

- effluents from industrial and domestic treatment plants where permit limits require accurate measurements to insure regulatory compliance
- sediments and soils from New Jersey which contain variable levels of Cr^{+6} and organic material and where the oxidation state of Cr may have been altered over time due to natural processes.

The samples were prepared for measurement and aliquots analyzed by both methods. The comparison of the results by both methods will offer new insight on options and limitations for the increasingly-important determination.

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Hexavalent Chromium Methodology for Soils: Results of Extraction Comparison Research and Multi-Laboratory Holding Time Study

R. Vitale, Quality Assurance Specialist/Principal, G. Mussoline, Senior Quality Assurance Chemist, Environmental Standards, Inc., Valley Forge, Pennsylvania 19482; J. Petura, Principal, Applied Environmental Management, Inc., Malvern, Pennsylvania 19355; and B. James, Ph.D., Associate Professor, University of Maryland, College Park, Maryland 20742

ABSTRACT

Hexavalent Chromium [Cr(VI)] analysis has been performed on a significant number of soil samples suspected of being contaminated with chromite ore processing residue (COPR) using a modified version of the SW846 (2nd Edition) Method 3060 followed by Method 7196A as the extraction and analysis procedures, respectively. The authors previously evaluated Modified Method 3060 using eight different soil materials, including field-moist and dried COPR. More recently, Modified Method 3060 has been compared to four alternate extraction techniques -- (1) distilled deionized water, (2) phosphate buffer extraction (pH 7), (3) Modified Method 3060 alkaline extraction (without heat), and (4) alkaline extraction with sonication (without heat) -- to compare the recoveries of soluble and insoluble Cr(VI) matrix spikes in four different soil types. For each sample type, Modified Method 3060 extracted the largest quantity of Cr(VI).

Additionally, a study was performed to establish a suitable holding time for soil samples prior to the analysis of Cr(VI) using Modified Methods 3060/7196A. Thoroughly homogenized, well-characterized samples of COPR were analyzed over a one-month period after collection by one commercial laboratory and subsequently over an eight-month period by four different commercial laboratories. The results of the round-robin testing over time revealed that Cr(VI) is stable in both field moist and dried COPR samples for at least one month after collection. Complementary testing showed that Cr(VI) is stable in the Method 3060 alkaline solution for at least 96 hours after digestion prior to analysis.

This paper summarizes the study design and performance results obtained from the five different extraction solutions that were used as the preparatory step for Cr(VI) analysis. It will also present and discuss the data obtained from the holding time study with regard to (1) comparison of results using Modified Methods 3060/7196A among the four commercial laboratories, (2) the stability of Cr(VI) in COPR as a function of holding time after soil sample collection, and (3) the stability of Cr(VI) in the Method 3060 alkaline digestate (extract) prior to analysis with respect to holding time.

INTRODUCTION

Quantification of hexavalent chromium [Cr(VI)] in soils without inclusion of Cr(III) has significant relevance due to the difference in the toxicity of the +6 and the +3 valence states. An effective and reliable means of extracting Cr(VI) from soil samples is required. A novel aspect of this requirement is that the media used to extract Cr(VI) from soil samples not only has to be an efficient extraction media, it must also be conducive to maintaining Cr in the +6 valence state. The maintenance of Cr in the +6 valence state necessitates the use of an extraction medium that does not influence both the reduction of Cr(VI) and the oxidation of Cr(III). This study evaluated the use of five different extraction methods in the preparation of soil samples for Cr(VI) analysis by SW846 Modified Method 7196A. Both soluble and insoluble Cr(VI) matrix spikes were used to evaluate the extraction efficiency of each method.

The extraction methods included: (1) an extraction using water, (2) a phosphate buffer extraction solution, (3) an alkaline extraction solution employing the use of sonication, (4) a modified version of SW846 Method 3060 employing heat, and (5) a modified version of SW846 Method 3060 without heat. These five different extractions were tested with the same four soil matrices; (1) quartz sand, (2) Cr(VI) chromite ore processing residue (COPR), (3) anoxic sediment and (4) loam soil. Soluble and insoluble Cr(VI) matrix spike compounds, as well as Cr(III) matrix spike compounds, were used to evaluate the extraction media on the different soil types. The Cr(VI) recoveries of the matrix spike compounds after sample digestion and analysis were assessed to evaluate the efficacy of each solution for extracting Cr(VI), minimizing the reduction of Cr(VI) to Cr(III), and inhibiting the oxidation of Cr(III) to Cr(VI). The results of this portion of the study were evaluated to determine (1) the best of the methods evaluated for extracting all Cr(VI) (both soluble and insoluble) from soils, (2) if oxidation and/or reduction of Cr occurs during the extraction process and (3) if a sparingly-soluble form of Cr(VI) is dissolved and recovered from soils.

Additionally, a study was performed in an attempt to evaluate and establish a suitable holding time for soil samples prior to the analysis of Cr(VI) using SW846 Modified Methods 3060/7196A. Thoroughly homogenized, well-characterized samples of COPR and laboratory-prepared synthetic chromium-bearing soil were analyzed over a one-month period after collection by one commercial laboratory and subsequently over an eight-month period of time by four different commercial laboratories.

EXPERIMENTAL

Extraction Comparison

For each of the soil materials, 2.5 g of oven-dry soil material (sand, COPR, anoxic sediment and air-dried loam) was weighed into 60, 250-mL beakers. The beakers were then divided into five groups of twelve beakers for the five extraction media, and each group of 12 beakers was divided into four groups of three each for the four soil matrices. For each group of 12 beakers, the following four spikes of Cr were added in triplicate:

(1) None

(2) Cr_2O_3: (36.8 mL of 1.00 g Cr_2O_3/L suspension per beaker; equivalent to a spike of 10,000 mg Cr(III)/kg soil material)

(3) $BaCrO_4$: 0.0100 to 0.0200 g of solid compound was added to each beaker and the exact weight recorded; equivalent to a spike of approximately 1000 mg Cr(VI)/kg soil.

(4) K_2CrO_4: 1.25 mL of 2000 mg Cr(VI)/L solution was added to each beaker; equivalent to a spike of 1000 mg Cr(VI)/kg soil.

To each group of 12 beakers prepared with the four spikes, 50 mL of the following extracting solutions were added:

(1) Distilled water (pH 5.7)

(2) Phosphate buffer: 0.005 M K_2HPO_4/0.005 M KH_2PO_4 (pH 7)

(3) 3060 Extraction Solution: 0.28 M Na_2CO_3/0.5 M NaOH (pH 11.8) Added to two sets of 12 beakers; one to be heated and the other to remain at room temperature.

(4) Sonication Solution: 0.1 M NaOH

All suspensions were swirled and allowed to stand for 60 $\pm$ 5 minutes before further treatments were applied as follows:

(1) One-half of the soil suspensions in the Method 3060 solution was heated at 90-95° C on a hot plate, with stirring, for 60 minutes, and the other half was allowed to stand at 25 ±2°C.

(2) The water and phosphate buffer suspensions were stirred for 60 minutes at room temperature.

(3) The suspensions in 0.1 M NaOH were placed in a sonicating bath for 30 minutes, and allowed to stand at room temperature for an additional 30 minutes.

At the end of these treatments, all beakers were brought to a total solution volume of 120 mL of water by weight (assuming the density of water to be 1.0 g/mL) using distilled deionized water. After centrifuging a portion of the suspensions (25°C, 10 min., 10,000 × *g*), which is equivalent to the filtration step in Method 3060, the diphenylcarbazide (DPC) colorimetric method (SW846 Method 7196A) was used to measure Cr(VI) in the centrifugates after making appropriate dilutions using distilled water.

Holding Time Study

Three different soil types [a high-level Cr(VI) COPR sample (field moist and dry), a moderate-level Cr(VI) COPR sample and a synthetic moderate-level Cr(VI) sample] were analyzed over a period time to determine a time frame over which Cr(VI) remains stable from sample collection to sample preparation and analysis. In addition to this, the soil types were evaluated to determine a time frame over which Cr(VI) remains stable in the alkaline digestate after sample preparation, prior to analysis.

All of the sample types were prepared and analyzed following Modified Methods 3060/7196A.

RESULTS AND DISCUSSION

Extraction Comparison

Absorbance readings were measured at 540 nm (as specified in Method 7196A) to determine the concentration of Cr(VI) in each extract, including samples spiked with soluble and insoluble forms of chromium. Table I shows the results of these analyses readings.

Table 1

Sample Type		Sand		COPR		Sediment		Loam	
Extraction Media		Mean Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Percent Recovery	Mean Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Percent Recovery	Mean Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Percent Recovery	Mean Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Percent Recovery
Water Solution	a	< 1¥	0	992	0	< 1	0	< 1	0
	b	< 1	0	925	0	< 1	0	< 1	0
	c	31.3	2	916	-6	< 1	0	105	5
	d	1100	110	1760	77	< 1	0	1070	107
Phosphate Buffer Solution	a	< 1	0	1120	0	< 1	0	< 1	0
	b	< 1	0	1090	0	< 1	0	< 1	0
	c	10.3	1	1130	1	< 1	0	37	3
	d	1100	110	2110	100	< 1	0	1100	110
3060 Solution with Heat	a	< 1	0	1400	0	< 1	0	< 1	0
	b	< 1	0	1400	0	< 1	0	< 1	0
	c	1260	82	2220	64	< 1	0	512	39
	d	1100	110	2500	110	< 1	0	1070	107
3060 Solution without Heat	a	< 1	0	1250	0	< 1	0	< 1	0
	b	< 1	0	1260	0	< 1	0	< 1	0
	c	180	12	1500	22	< 1	0	206	18
	d	1090	109	2290	104	< 1	0	1100	110
Sonication	a	< 1	0	1190	0	< 1	0	< 1	0
	b	< 1	0	1160	0	< 1	0	< 1	0
	c	126	9	1430	18	< 1	0	419	35
	d	1070	107	2250	106	< 1	0	1080	108

Notes:
¥ - All values are means of three replications
a - Unspiked
b - Spiked with Cr(III)
c - Spiked with insoluble Cr(VI)
d - Spiked with soluble Cr(VI)

None of the extraction procedures was able to extract any Cr(VI) from the unspiked sand, loam and sediment. The soluble Cr(VI) spikes that were added to the sand and loam were recovered completely by all four extraction procedures and zero percent recovery was observed in the anoxic sediment, as expected, due to its strongly reduced condition. The water and phosphate buffer solutions extracted Cr(VI) from the COPR samples; however, the water extraction procedure recovered only 71% and the phosphate buffer solution recovered only 79% of the Cr(VI) that was extracted by Modified Method 3060 (with heat). The alkaline digestion solution using sonication (without heat) and Modified Method 3060 (without heat) also extracted Cr(VI) from the COPR sample; however, the alkaline digestion solution with sonication recovered only 85% and Modified Method 3060 (without heat) recovered only 89% of the Cr(VI) that was extracted by Modified Method 3060 (with heat). Figure 1 shows a comparison of the amount of Cr(VI) extracted from the unspiked COPR by the five different extraction techniques.

Figure 2 presents the Cr(VI) percent recoveries observed from the five extraction techniques following the addition of soluble and insoluble forms of Cr(VI) to the four different soil types. Modified Method 3060 (with heat) was capable of removing the greatest amount of Cr(VI) [both soluble and insoluble forms of Cr(VI)]. Another noteworthy item from Figure 2 is that in all instances, the anoxic sediment displayed 0% recovery. This 0% recovery was observed despite the extraction technique that was used. This indicates that the soil type (i.e. sediment), and not the extraction technique, was responsible for the reduction of the Cr(VI) spikes.

Holding Time Study

Thoroughly homogenized, well-characterized samples of COPR (both field moist and dried) were analyzed over a one-month period after collection by one commercial laboratory and subsequently over an eight-month period by four different commercial laboratories. An additional sample of COPR (passed through a 0.85μm sieve) and a soil sample (passed through a 0.85μm sieve) spiked with Cr(VI) by a commercial laboratory have been repeatedly analyzed by three different commercial laboratories over time. The results of the round-robin testing over time revealed that Cr(VI) is stable in both field moist and dried COPR samples for at least one month after collection, indicating that a holding time of at least one month for Cr(VI) is appropriate. Figure 3 shows the results of the Cr(III) analysis over the eight-month period.

Complementary testing showed that Cr(VI) is stable in the Method 3060 alkaline solution for at least 96 hours after digestion, prior to analysis. The commercial laboratories involved in the study were requested to analyze each sample for Cr(VI)

Figure 1

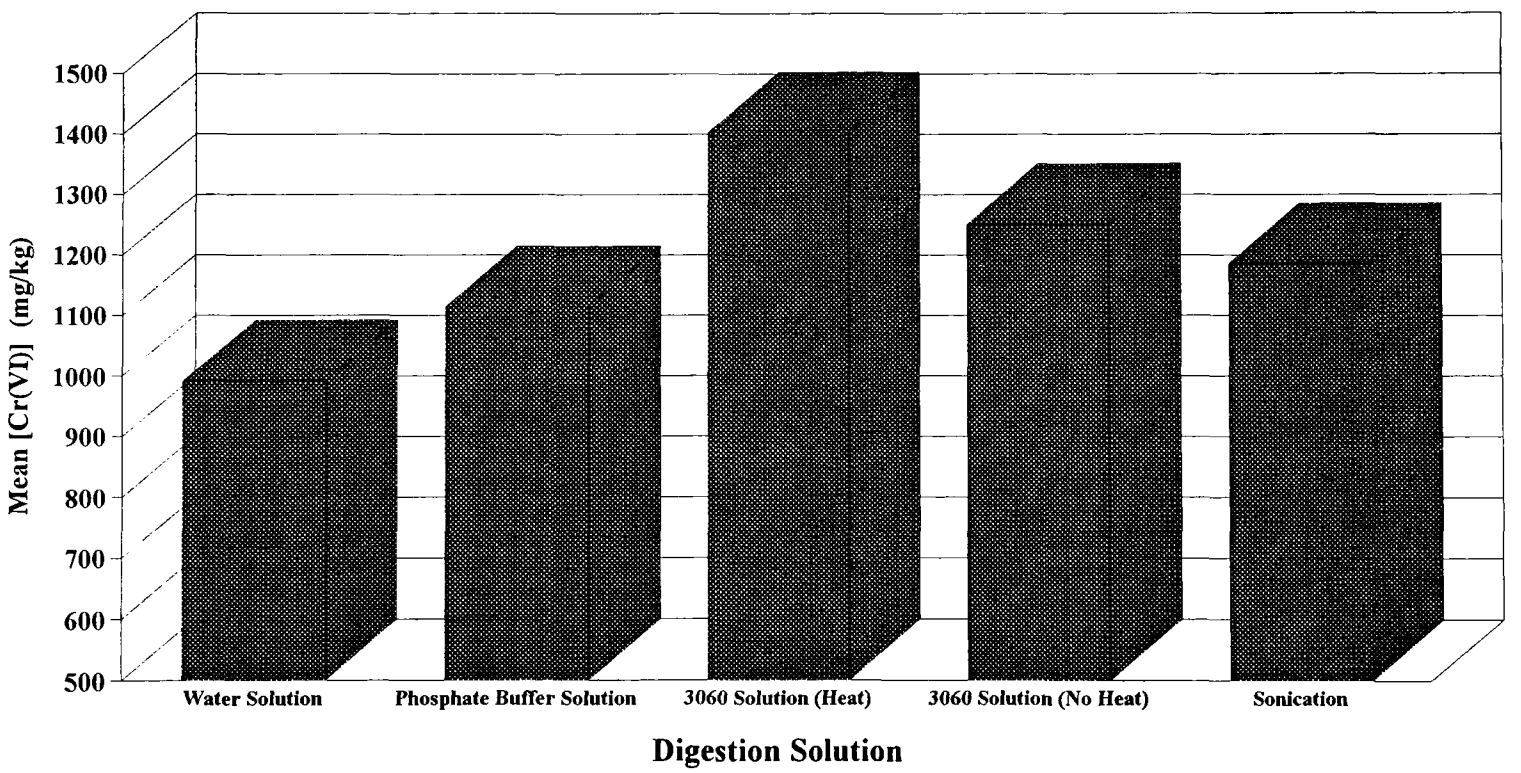
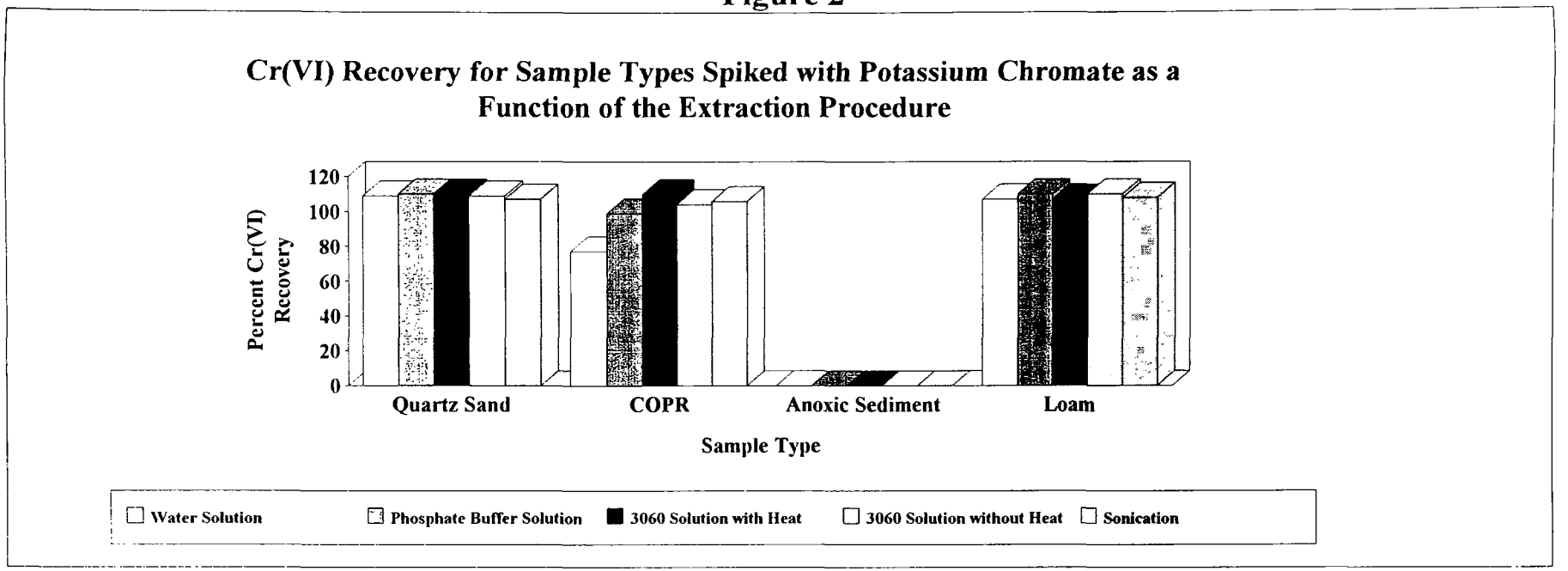

Cr(VI) Concentrations for COPR Using Different Digestion Solutions
Mean [Cr(VI)] (mg/kg)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
Water Solution
Phosphate Buffer Solution
3060 Solution (Heat)
3060 Solution (No Heat)
Sonication
Digestion Solution

Figure 2


Cr(VI) Recovery for Sample Types Spiked with Potassium Chromate as a Function of the Extraction Procedure
Percent Cr(VI) Recovery
120
100
80
60
40
20
0
Quartz Sand
COPR
Anoxic Sediment
Loam
Sample Type
Water Solution
Phosphate Buffer Solution
3060 Solution with Heat
3060 Solution without Heat
Sonication

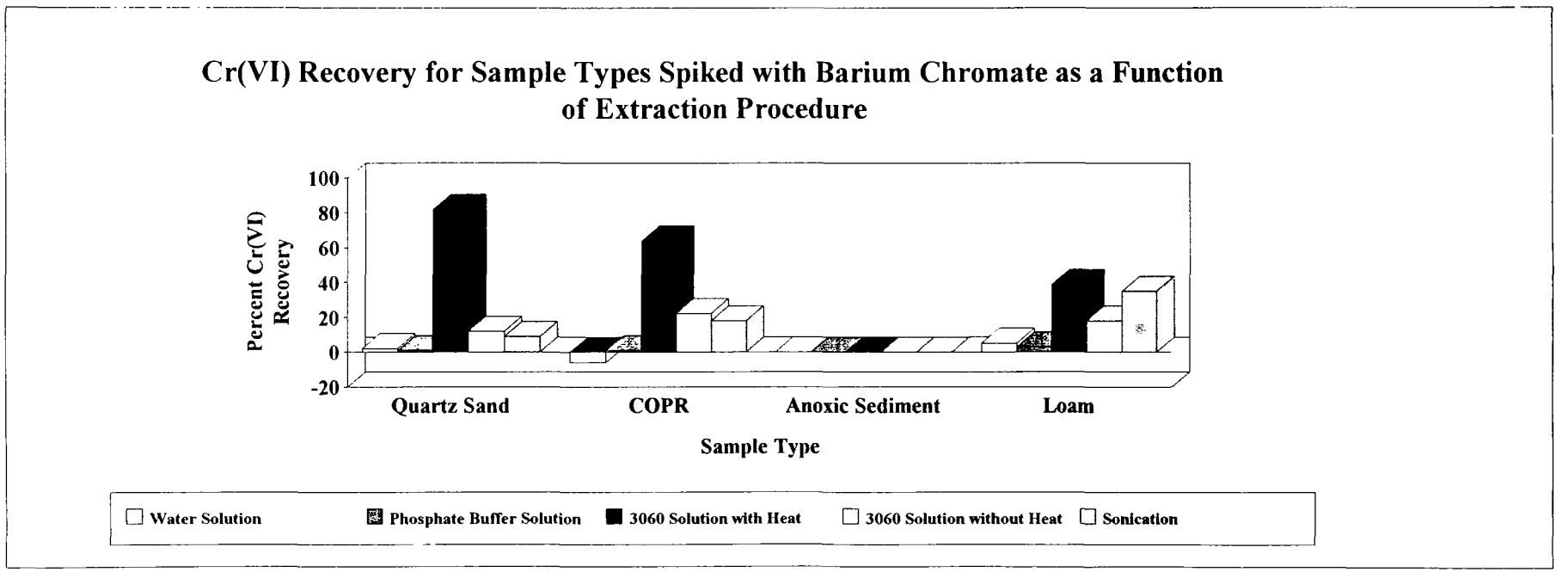
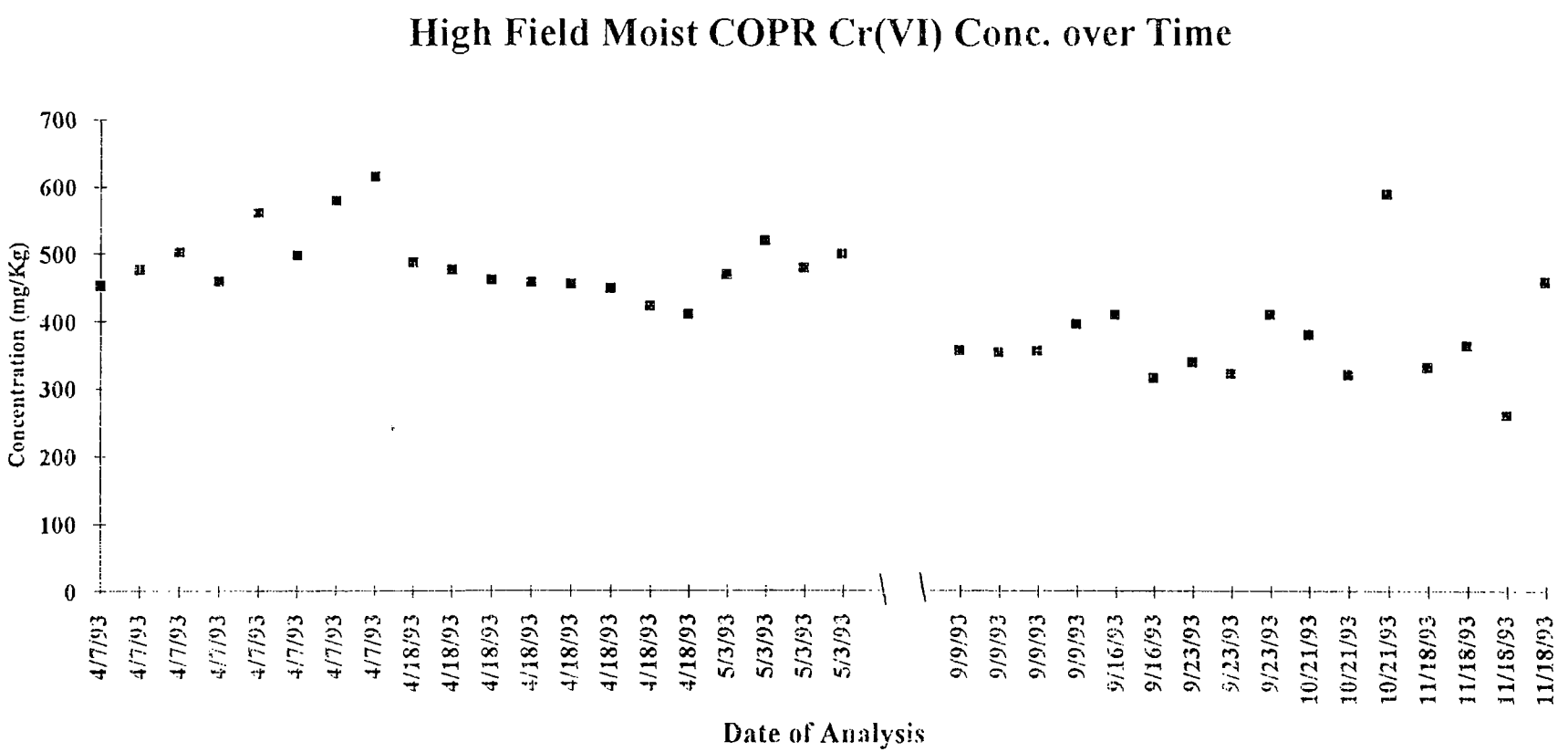

Cr(VI) Recovery for Sample Types Spiked with Barium Chromate as a Function of Extraction Procedure
Percent Cr(VI) Recovery
100
80
60
40
20
0
-20
Quartz Sand
COPR
Anoxic Sediment
Loam
Sample Type
Water Solution
Phosphate Buffer Solution
3060 Solution with Heat
3060 Solution without Heat
Sonication

Figure 3


High Field Moist COPR Cr(VI) Conc. over Time
Concentration (mg/Kg)
700
600
500
400
300
200
100
0
4/7/93
4/7/93
4/7/93
4/7/93
4/7/93
4/7/93
4/7/93
4/7/93
4/18/93
4/18/93
4/18/93
4/18/93
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5/3/93
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5/3/93
9/9/93
9/9/93
9/9/93
9/9/93
9/16/93
9/16/93
9/23/93
9/23/93
9/23/93
10/21/93
10/21/93
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11/18/93
11/18/93
Date of Analysis

upon receipt and again at varying time periods from the initial analysis. This testing, as summarized on Figure 4, revealed that the Cr(VI) concentration did not change over time once the sample had been digested by the alkaline digestion procedure (Modified Method 3060). The longest holding period for the digestates was 96 hours, and consistent results were obtained among the participating laboratories.

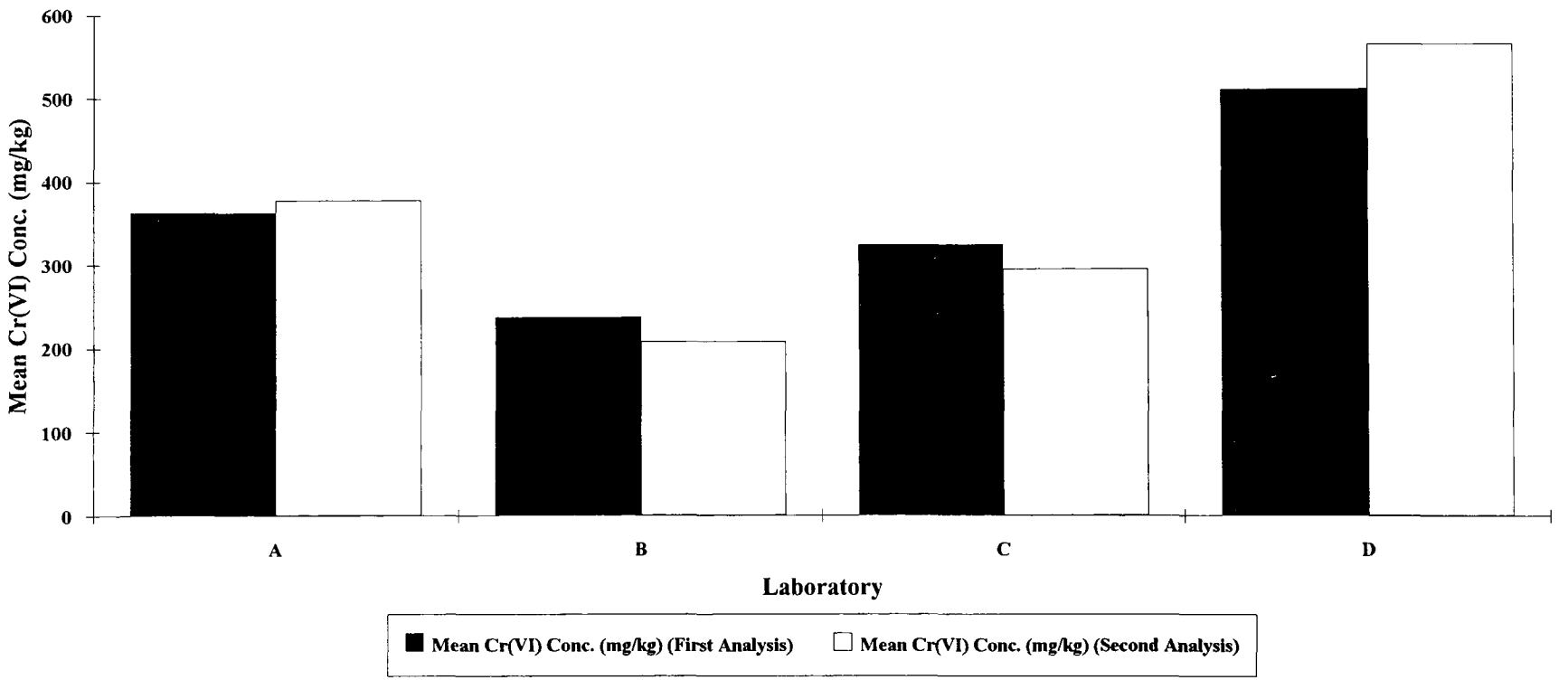
CONCLUSIONS

The results of this study demonstrated that a modified version of SW846 Method 3060 (with heat) was the most effective procedure for removing Cr(VI) from the four soil types investigated. The results also confirmed that Modified Method 3060 (with heat) was the most capable method of extracting all forms of Cr(VI) (soluble and insoluble) of the extraction methods investigated. Matrix spike recoveries also revealed that this method is capable of maintaining Cr(VI) in the +6 oxidation state.

Further study has revealed that Cr(VI) in COPR samples is stable for up to a one-month period from collection. Subsequent studies have shown that Cr(VI) is stable in the alkaline 3060 Solution (after digestion) for at least 96 hours.

Figure 4

Mean Cr(VI) Concentrations Observed by Four Commercial Laboratories



Notes:
Laboratory A reanalyzed after 96 hrs.
Laboratory B reanalyzed after 72 hrs.
Laboratory C reanalyzed after 48 hrs.
Laboratory D reanalyzed after 24 hrs.

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ENZYME-LINKED IMMUNOASSAY (ELISA) FOR THE DETECTION OF MERCURY IN ENVIRONMENTAL MATRICES

Craig Schweitzer, Product Development Manager, BioNebraska, Inc., Lincoln, Nebraska, 68524, L. Carlson, Scientist, BioNebraska, Inc., Lincoln, Nebraska, 68524, B. Holmquist, Vice President of Research and Development, BioNebraska,Inc., Mal Riddell, Managing Director, BioNebraska, Inc., D. Wylie, Consultant, BioNebraska, Inc.

ABSTRACT

Immunochemical-based analytical methods are widely used in the medical diagnostic field, but they have only recently been adapted for field-portable environmental applications. BioNebraska has developed such an immunoassay for the detection of mercury in environmental samples. The assay allows for real-time, user-friendly generation of data at a fraction of the cost of traditional methods. The assay is available in two formats, a microplate format for large volume, quantitative analysis of samples in the laboratory and a tube format for rapid semi-quantitative analysis in the field.

The environmental sample, typically 5 grams of soil or sediment, is extracted for ten minutes with a mixture of hydrochloric and nitric acids. A buffer is added and the sample is filtered and diluted by means of a dropper bottle with an enclosed filter. The samples are then ready for analysis by the immunoassay. NIST traceable reference samples are included for extraction and comparison with the test samples. After extraction, the assay itself can be done in less than twenty-five minutes and consists of four reagents, each of which is added for a 5-minute incubation. The reagents include the extracted sample, a monoclonal antibody specific for mercuric ions, a secondary enzyme-conjugated antibody specific for the monoclonal, and a substrate solution which is oxidized by the enzyme on the secondary antibody. The enzymatic reaction which produces the color development is terminated, and the mercury concentration is determined relative to the reference standards by means of battery-operated, field-portable, differential photometer available from BioNebraska. The dilutions and additions of reagents are facilitated by dropper bottles provided in the kit. The short times required for extraction and immunoassay allows the user to produce real-time data in less than 40 minutes. The convenience and rapidity of the assay allow field testing of multiple samples to be analyzed in a short time frame, resulting in lower site evaluation and clean up costs, and fewer samples that require analysis by slower, more expensive methods. Based on in-house and independent field results, the assay appears to be well-suited for low-cost, real-time, user friendly field screening of mercury in the environment. Other substances present in environmental matrices do not appear to interfere with the assay, and the results correlate well with traditional analytical methods. In addition, preliminary data suggests that the immunoassay can be applied to the measurement of mercury in seafood and animal tissues, so that potential problems resulting from biomagnification of mercury can be identified before the contaminated food sources are used for human consumption. In summary, the

results show that the BiMelyze mercury immunoassay is a reliable alternative to more expensive, time-consuming analytical methods.

INTRODUCTION

Heavy metal contamination in the environment is recognized as a serious danger to humans and wildlife. Accordingly, the use of toxic heavy metals has become more strictly regulated; but careless practices in the past have led to massive deposits of these toxins in the environment. Metals are of special interest because they bioaccumulate up the food chain and have long half-lives in biologic tissues. Mercury, one of the most toxic heavy metals, causes severe behavioral, reproductive and developmental problems (1). Although a significant portion of the mercury present in the environment is caused by the natural degassing of the earth's crust (2), most mercury derives from anthropogenic sources, including mining, smelting, chloralkali industries, electrical equipment, paint industries, military applications, agriculture, and medicine (3). Mercury is also directly released to the environment by the burning of fossil fuels and from municipal waste incinerators.

Analytical tools that can measure environmental contaminants in the field are central to the ability to regulate, manage, and decontaminate sites. Conventional analytical methods, such as atomic absorption and X-ray fluorescence, although very precise, can be used only in a laboratory setting. Immunochemical techniques provide sensitive and specific methods capable of measuring analytes of interest in complex biological matrices. The medical laboratory community has long recognized these qualities in immunoassays, but only in the last few years have they been adapted for use in detecting environmental contaminants.

BioNebraska has developed an immunoassay for the detection of mercury in environmental samples. The assay exists in two formats: a plate format which is quantitative and best suited for laboratory analyses, and a tube format which can be used for semi-quantitative measurements in the field. The immunoassay can specifically and quantitatively detect mercuric ions in several different environmental matrices. Analyses of laboratory and field samples using either format gives results that are in good agreement with those obtained by more conventional analytical methods, such as cold-vapor atomic absorption, neutron activation analysis, and X-ray fluorescence. The assay is not affected by other metals at concentrations likely to be encountered in environmental samples.

EXPERIMENTAL

Monoclonal antibodies.

The production and characterization of the mercury-specific monoclonal antibodies used in these analyses were described previously (4,5).

Extraction of samples for immunoassay

Before the BiMelyze® immunoassay can be used for environmental analysis. The mercury is extracted from the sample using a kit available from BioNebraska. The procedure requires digesting a 5-gram sample, representative of the area being tested, in a solution of hydrochloric acid, nitric acid, and water (2:1:1) for ten minutes with intermittent, gentle agitation. The acid for the extraction is provided by the end user or, alternatively, is available from an independent supplier. After extraction, the sample is buffered, filtered, and diluted by means of filter-tipped dropper bottles provided in the soil extraction kit, then analyzed by the immunoassay. National Institute of Standards and Technology (NIST)-traceable standards are included in the kit and are extracted at the same time as the unknown samples to provide comparisons for semi-quantitative determination of mercury in the field.

BiMelyze Mercury Assay

The assay has been developed in two formats: a quantitative 96-well, plate method for analyzing large numbers of samples in the laboratory, and a semi-quantitative, field-portable tube method. Both formats consist of sequential addition of four reagents, with a five-minute incubation period for each. The BiMelyze immunoassay is based on the initial binding of the mercuric ion from a sample to the mercaptan of glutathione that has been covalently linked to bovine serum albumin and bound to a solid support (Figure 1). After a water rinse, a mouse anti-mercury antibody is added which binds to the mercury. The tubes/wells are washed with a detergent then rinsed with water to remove unbound antibody. The amount of anti-mercury antibody bound is detected by binding horseradish peroxidase-labeled rabbit secondary antibodies to the mouse antibodies. After washing as above, substrate, which is oxidized by the peroxidase-labeled antibodies, to produce a green chromogen is added. The amount of color that develops is a function of the amount of mercury in the initial sample. Color development is terminated by addition of stop solution, and the tubes are read anytime within an hour. The absorbance of the color in the tubes/plate is measured at 405 nanometers. Microplate readers, present in most larger laboratories, are used to read the color development of the plate assay. A field-portable, battery-powered, differential photometer, available from BioNebraska, allows the absorbance in the tube assay to be quantified.

Metal specificity

Standard assays were performed as above except that various concentrations of additional metal salts were added to the samples prior to assay, and their effect on color development in the assay was monitored.

RESULTS

The lower limit of quantitation of mercuric ions with the BiMelyze immunoassay in an aqueous sample is 0.25 parts per billion (ppb) for both the tube and plate assays. Figure 2

shows a dose-response curve in which Mercury Standard Reference Material 3133 from the National Institutes of Standards and Technology was diluted to various concentrations in 0.1 M HEPES buffer, pH 7.0, and analyzed with the tube assay. The results demonstrate that the absorbance in the ELISA is linear and reproducible over the range from 0.25 to 25 ppb with all coefficients of variation below 8%. Similar results have been reported previously for the mercury-specific plate assay (5).

Since the soil samples must be acid extracted and neutralized before assay, it was necessary to know the pH dependence of mercury binding to the ligand-coated tubes. This was tested by using a three-point standard curve with mercury concentrations of 0, and 1 ppb in buffers at pH 2, 4.75, 6, 7, 8, 8.75, 10, and 11.8 (Figure 3). Samples of 0.5 ml were assayed according to the tube protocol. The assay is essentially unaffected over the pH range 4.75 to 8.75. Consequently, the pH of the samples is adjusted to between 6-8 for routine analysis.

Because many metals are ubiquitous in the environment, their effect on the reliability of the mercury-specific assay was characterized in detail using several approaches. First, a standard curve was constructed in which known concentrations of mercury were diluted in a multi-metal mixture and measured in the immunoassay. The composition of this mixture corresponded to that of the EPA extract metals quality control sample formerly available from the Environmental Protection Agency. It contained 100 mg/L barium nitrate, 1 mg/L cadmium sulfate, 5 mg/L lead nitrate, 5 mg/L silver nitrate, and 5 mg/L chromium trioxide. Solutions of mercury at concentrations of 20, 2, 0.5 and 0.2 ppb were prepared in the metal mixture and used in the immunoassay. The results obtained with these samples were compared to a standard with mercury at the same concentrations in a buffer at pH 7.0 which did not contain the other metals. The standard curves obtained with mercury in these two diluents (Figure 4) are essentially identical, indicating that none of these metals has an effect on the mercury immunoassay.

The potential interference by individual metals was examined over a wide concentration range, to a level higher than would normally be present in field samples (Figure 5). Standard curves were constructed in which mercury at 100, 50, 10, 5 and 0.5 ppb was diluted into solutions containing the indicated concentrations of these metals. According to the experimental design, for each metal there were five separate mercury-specific standard curves, each containing 1 mM, 10 μM, 100 nM, 10 nM and 1 nM of a potentially interfering metal. A control standard curve was also included in which the mercury was diluted to the same concentrations in an equal volume of metal-free buffer. The metals examined were: arsenic trioxide, barium nitrate, cadmium chloride, chromium nitrate, cupric chloride, gold trichloride, iron sulfate, lead chloride, nickel chloride, silver nitrate, sodium bicarbonate, sodium chloride, strontium nitrate, thallium nitrate and zinc chloride.

Barium nitrate (Figure 5a), which gave results typical of most metals, shows no interference even at the highest concentrations employed. Only three of the metals tested affected mercury detection, but they did so only at high concentrations. Gold trichloride inhibited the response at the two highest concentrations (Figure 5b). The highest

concentration of gold trichloride caused a purple precipitate when added to the tube in the first step of the assay (data not shown). Silver nitrate produced an increase in absorbance at the two highest concentrations (Figure 5c), which might be related to silver salt precipitation. An increase in signal was also seen with 1 mM chromium nitrate (data not shown).

Finally, the mercury content of several soil samples containing certified amounts of various metals was measured. The descriptions of these samples and their metal compositions are shown in Table 1. Triplicate samples were extracted according the BiMelyze protocol, and analyzed with the BiMelyze Mercury Tube Assay. By comparison with soil standards containing either 4 ppm or 15 ppm, the results were interpreted as less than 4 ppm, between 4 and 15 ppm, and greater than 15 ppm. As shown in Table 2, the immunoassay correctly predicted the mercury concentrations of these samples in almost all cases. The only incorrect determination was in experiment #3 with soil sample #4.

The reproducibility of the soil assay was examined with five-gram aliquots of reference soils containing 0, 1, 2, 3.2, 4, 4.8, 6, and 8 ppm mercury, as determined by cold-vapor AA. Seven replicate analyses were done of each. The results (Table 3) are presented as the differential absorbance of each mercury concentration relative to a 4-ppm standard. The data demonstrate the ability of the test to distinguish between small differences in mercury concentration in soils. They also show the reliability of the assay, since only one false-negative and one false-positive were obtained in these analyses.

To demonstrate the usefulness of the assay under field conditions, the BiMelyze Mercury Tube Assay was used to analyze ten environmental samples, whose mercury concentrations were also measured by both neutron activation analysis (NAA) and X-ray fluorescence (XRF). The general format of the study was to compare the unknown soil samples to the 5 and 15 ppm mercury-in-sediment standards. The data for the tube assay were interpreted as <5, 5-15, or >15 ppm by comparison of the absorbance of each sample to that of the standards. The tube assay gave excellent agreement with the reference methods, differing from neutron activation analysis in only two samples (#3 and #5). However, X-ray fluorescence analysis of sample #5 agreed with the immunoassay rather than with NAA. Sample #3 was not analyzed by XRF.

Another field study was conducted by an environmental testing company who collected samples and analyzed them with the BiMelyze Mercury Tube Assay. and by cold-vapor AA. The description of the samples, along with the results of the analysis (Table 5) indicate a good agreement by both methods, showing a disparity with only one sample. However, even with that sample, the difference was not large, since the AA value was 14 ppm and the BiMelyze results were >15 ppm. This independent analysis tested matrices which have not been tested by BioNebraska (e.g., paint, cinderblock, and sludge), but suggests the versatility of the method. The matrices for which the BiMelyze assay is applicable appears to be limited only by the ability of the acid mixture to disassociate and oxidize mercury to the mercuric form.

DISCUSSION

The BiMelyze mercury tube immunoassay provides an accurate, reliable method for detecting mercury in a variety of matrices. Under laboratory conditions the assay is quantitative for mercury in aqueous solution (Figure 2). The tube assay was designed as a field test that could be used for on-site evaluation of environmental samples. Under these conditions, the assay is semi-quantitative. The mercury concentration is determined by direct comparison to a standard with a known amount of mercury. When used with both field samples and NIST-traceable soil standards, the tube assay results agreed with those obtained by a reference method (either NAA or AA) in at least 20 of 22 various samples (Tables 4 and 5). The importance of determining the mercury concentration by comparison to a standard analyzed at the same time as the unknown samples must be emphasized. The mercury assay is an enzyme-linked immunosorbent assay (ELISA) whose interpretation depends on the absorbance obtained by enzymatic conversion of a colorless substrate to a colored product (Figure 1). The absorbance obtained with samples having the same mercury concentration can vary from day to day (Table 2), since the enzyme activity of the assay is affected by ambient conditions. Analysis of a reference standard at the same time as the unknown samples controls for this variability.

With environmental samples, acid digestion is needed to extract total mercury from constituents of the matrix. This treatment oxidizes mercury to mercuric ions, for which the antibody is specific. The extraction method used here consists of treatment of the sample with a mixture of hydrochloric acid, nitric acid and water (2:1:1) for ten minutes. This extraction method is as efficient as E.P.A. Method 7471 for extracting most forms of mercury, except for methylmercury (data not shown). Excellent correlation has been reported previously when the plate assay was used for analysis of environmental samples and compared to other analytical methods (6). The reliability of the results obtained in the previously reported study led to the inclusion of the BiMelyze Mercury Plate Assay into the Department of Energy Methods Compendium as Method MB 100. The results from analyses of environmental samples with the BiMelyze Mercury Tube Assay, as reported here, are equally reliable. The method can accurately measure mercury in a variety of environmental samples. Independent organizations have tested cinder block and paint chips in addition to various soils, and it is likely to be applicable to other matrices which have not previously been assayed successfully (Table 5). We are currently working on an efficient, rapid, and user friendly extraction technique for methylmercury, which would have implications for measurement of mercury in biological samples, such as fish tissue.

In the past, accurate testing of environmental samples for mercury has been limited by the availability of analytical methods, such as AA, that utilize expensive equipment requiring highly trained personnel for proper operation. Another disadvantage of these procedures is the lag time between sample collection and acquisition of the results, and problems arising from the instability of the sample, since, in most cases, the samples must be sent off to reference laboratories for analysis. In contrast, the BiMelyze mercury assay provides a convenient, cost-effective, real-time method for monitoring and surveying environmental sites for mercury that can be performed in the field by personnel with minimal training. Its

use can thus reduce the number of samples that must be analyzed by more expensive, traditional methods. The real-time data acquisition reduces potential re-mobilization costs which can occur if initial remediation is insufficient. The method is ideal for measurement of mercury in remote areas where sample storage, inventory and transportation present logistical problems. The kit is stable for at least six months at 4°C and for shorter periods of time at elevated temperatures. The only instrumentation required is a field-portable spectrophotometer that is inexpensive (<$1,000) compared to the instrumentation needed for traditional analytical methods. The method has a high selectivity for mercury and is not affected by metals likely present in environmental samples (Figure 5).

With increased awareness on the part of both the general public and various governmental regulatory agencies concerning toxic chemicals in the environment, the demand for convenient, reliable methods for their detection will certainly increase. Although environmental immunoassay technology is relatively new, it provides an excellent way for local, state, and federal agencies to implement effective monitoring programs on increasingly tight budget constraints. Immunoassays can be used in conjunction with traditional analytical methods to allow a larger number of samples to be analyzed at a lower total cost.

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Table 1.- Metal compositions of certified reference soils.

	Sample metal composition, ppm					
METAL	1[a]	2[b]	3[c]	4[d]	5,6,7[e]	8[f]
Aluminum	4090	7.5%[g]	6.11%	6000	6.1%	4090
Antimony	<12	7.9	3.79	27.8	na	<12
Arsenic	<2	17.7	23.4	67.7	7.3	<2
Barium	50.3	968	414	187	360	50.3
Beryllium	<1.0	na	na	57.5	na	<1.0
Cadmium	<1.0	0.38	3.45	110	na	<1.0
Calcium	1190	1.89%	2.6%	2040	na	1190
Chromium	6.63	130	135	189	88	6.63
Cobalt	<5.0	13.4	14.0	87.0	19	<5.0
Copper	<5.0	34.6	98.6	141	na	<5.0
Iron	8710	3.5%	4.11%	10800	2.6%	8710
Lead	8.01	18.9	161	100	80	8.01
Magnesium	1100	1.51%	1.2%	2050	na	1100
Manganese	167	538	555	294	1400	167
Mercury	<0.10	1.4	1.47	2.36	107	122
Molybdneum	na	2.0	na	124	na	na
Nickel	<8.0	88	44.1	79.6	na	<8.01
Potassium	1310	2.03%	2.00%	2130	1.5%	1310
Selenium	<1.0	1.57	1.12	99.1	na	<1.0
Silver	<2.0	0.41	na	124	5	<2.0
Sodium	<260	1.16%	0.55%	527	1200	<260
Thallium	<1.0	0.74	1.06	67.9	na	<1.0
Vanadium	15.4	112	95	84.8	60	15.4
Zinc	23.6	106	38	197	160	23.1

[a] Environmental Research Associates Inorganics Blank Soil.
[b] NIST Standard Reference Material (SRM) 2709 San Joaquin Soil.
[c] NIST SRM 2704 Buffalo River Sediment.
[d] Environmental Research Associates Priority Pollutant/CLP Lot # 216.
[e] NIST-SRM 8408 Mercury in Tennessee River Sediment.
[f] Environmental Research Associates Custom Mercury Standard.
[g] weight percent basis.

Table 2. Analysis of certified reference soils using BiMelyze Mercury Tube Assay.

Soil Sample	[Mercury] (ppm)	A_{405}[a] Exp. 1	Exp.2	Exp.3	Interpretation
1	<0.10	0.12	0.05	0.08	-----[b]
2	1.40	1.01	0.64	0.47	<4
3	1.47	0.78	0.41	0.19	<4
4	2.36	1.54	0.84	0.925[c]	<4
5	4[d]	1.76	1.01	0.83	-----[b]
6	15[d]	1.99	1.45	1.59	-----[b]
7	50[d]	2.04	1.73	2.02	>15
8	122	2.55	2.55	2.55	>15

[a] Absorbance at 405 nanometers with the BiMelyze Differrential Photometer
[b] Standard reference point, no interpretation
[c] Only value which gives incorrect conclusion
[d] NIST-SRM solid phase diluted from an initial concentration of 107 ppm.

Table 3. Reproducibility of BiMelyze Mercury Assay Tube Kit with extracted soil samples

Seven replicate extractions of 5 gram soil samples with a 4 ml mixture of 2:1:1 hydrochloric, nitric acid and water. The samples were then analyzed by both the tube assay and cold vapor atomic absorption. CVAA data represents an average of the seven analysis and the immunoassay data are presented as the difference relative to a 4 ppm standard.

[Hg] ppm	[AA] ppm	TUBE ASSAY EXPERIMENTS 1	2	3	4	5	6	7
0.0	0.0	-1.38	-1.32	-1.02	-0.57	-1.05	-0.98	-1.03
1.0	1.05±.07	-0.63	-0.62	-0.57	-0.34	-0.69	-0.51	-0.41
2.0	2.08±.12	-0.25	-0.38	-0.40	-0.16	-0.47	-0.37	-0.08
3.2	3.27±14	-0.06	-0.26	-0.17	+0.28	-0.22	-0.05	-0.04
4.0	4.16±.24	-----[a]	-----	-----	-----	-----	-----	-----
4.8	4.93±.31	+0.26	+0.05	+0.03	+0.46	+0.16	+0.15	+0.02
6.0	6.11±.32	+0.23	-0.10	+0.07	+0.66	+0.21	+0.22	+0.21
8.0	7.97±.36	+0.23	+0.15	+0.30	+0.92	+0.25	+0.37	+0.19

[a] 4.0 ppm used as standard

Table 4. Analysis of mercury in soils using the BiMelyze Mercury Assay Tube Kit.

Sample	Concentration by NAA ppm	Concentration by XRF ppm	Absorbance at 410 nm	Interpretation
1	na	na	0.077	----[a]
2	na	na	0.131	----
3	na	na	0.216	----
4	116	90-116	0.357	>15
5	<3.3	na	0.104	0-5
6	11	na	0.293	>15
7	<2.1	na	0.096	0-5
8	<5.3	22-52	0.292	>15
9	<1.5	na	0.127	0-5
10	<7.7	na	0.088	0-5
11	87	150-159	0.337	>15
12	19	na	0.259	>15
13	121	118-122	0.264	>15

[a] Standard controls, no interpretation

Table 5. Independent analysis of mercury in samples using the BiMelyze Mercury Assay Tube Kit at an abandoned battery reclamation site.

SAMPLE DESCRIPTION	TEST KIT	CVAA[a]
Process Room	< 5 ppm	0.83 ppm
Dust from process room	< 5 ppm	> 4.5 ppm
Groundwater -unfiltered	< 0.5 ppb	< 0.4 ppb
Soil, alkaline	< 5 ppm	0.93 ppm
Sludge from tank	> 15 ppm	4,400 ppm
Sump sludge	5 >15 ppm	14 ppm
Cinderblock	< 5 ppm	3 ppm
Cinderblock- duplicate	< 5 ppm	
Soil	5 >15 ppm	14 ppm
Paint	> 15 ppm	34 ppm
Backround cinderblock	< 5 ppm	1.4 ppm
Backround paint	> 15 ppm	14 ppm
Debris from CO_2 blast	> 15 ppm	19 ppm

[a] Cold Vapor Atomic Absorption

FIGURE LEGENDS

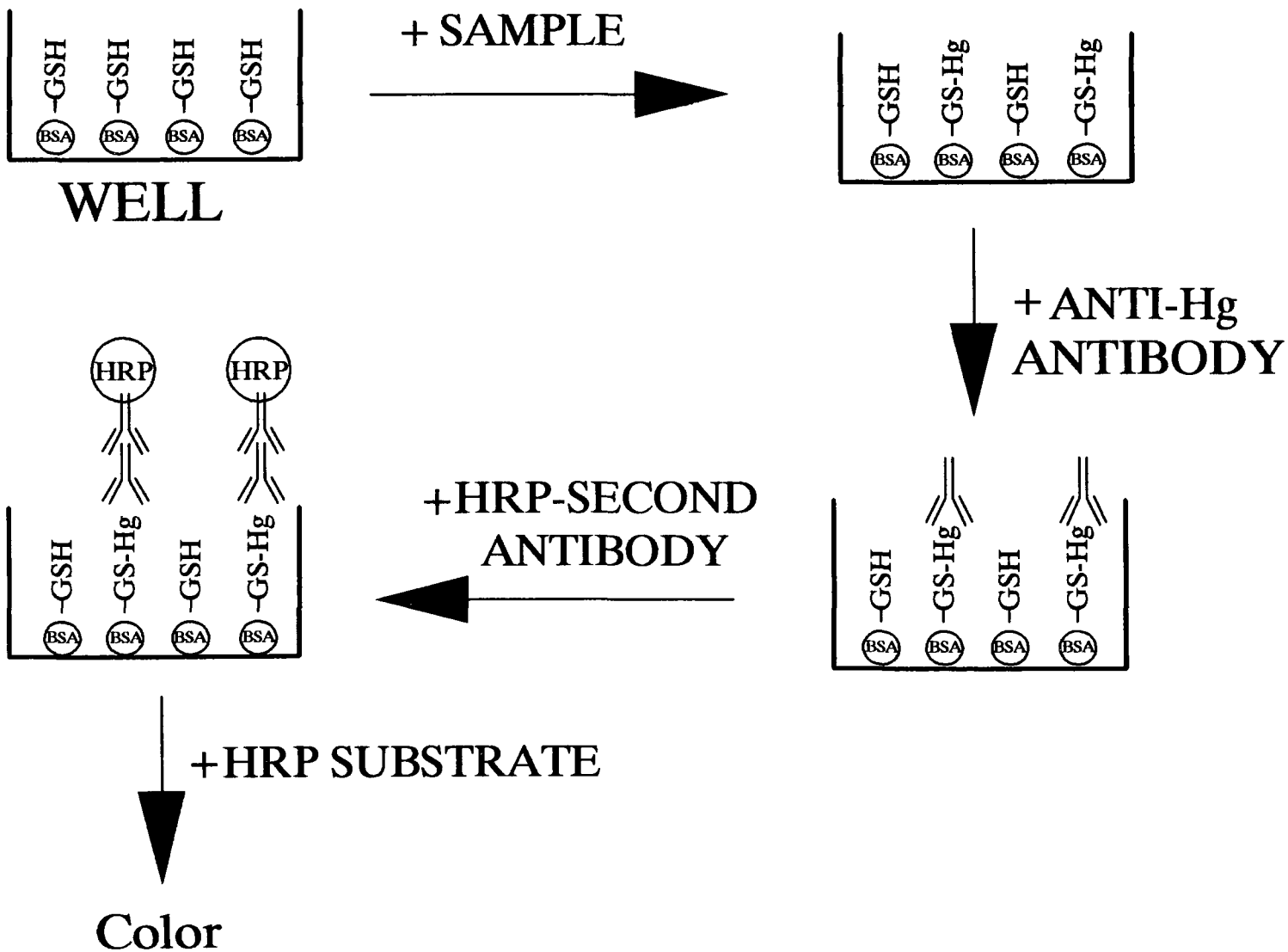
Figure 1. Basis of the BiMelyze Mercury Immunoassay "ELISA". The schematic shows the major steps and the reagents used to perform the assay.

Figure 2. Dose response curve for mercury detection by the BiMelyze Mercury Tube Assay. Mercuric nitrate was diluted to final concentrations of 0, 0.25, 1, 5, 10, and 25 ppb in pH 7.0 buffer. The mercury solutions were then analyzed by ELISA as described in the Experimental section, with six replicates for each concentration. The results demonstrate both the linearity and reproducibility of the assay for mercury concentrations between 0.25 and 25 ppb when graphed as the ELISA absorbance versus the log of the mercury concentration.

Figure 3. Effect of pH on mercury detection by ELISA. Solutions containing either 0 or 1 ppb mercuric nitrate in buffer adjusted to the indicated pH with either 1 N HCl or 1 N NaOH. The solutions were then used in the ELISA as described in the Experimental section.

Figure 4. Detection of mercury in EPA Extract Metals Quality Control Sample. Mercuric nitrate was diluted to final concentrations of 0, 0.2, 2, or 20 ppb in a solution containing metals at the concentrations present in the EPA Extract Metals Quality Control Sample(■), as described in the Experimental section. A standard curve was then obtained by analysis of these solutions in the ELISA and compared to that obtained with mercury diluted to the same concentrations in 0.1 M HEPES buffer, pH 7.0(●). A sample containing metals at the same concentrations as in the EPA quality control sample but without mercury was also included in the assay(▲).

Figure 5. Effect of non-mercury metal salts on mercuric ion detection by ELISA. Standard curves of mercury concentrations ranging from 0.5 to 100 ppb were assayed in solutions containing potentially interfering metals at final concentrations of 1 nM(O), 10 nM(×), 100 nM(▲), 10 μM(■), and 1 mM(●). A control curve in which the mercury was diluted into pH 7.0 buffer was also included(□) These solutions were then used in the ELISA as described in the Experimental section. For each concentration of metal salt, a control point containing the same concentration of metal salt but with no added mercury was included and is represented by the bottom-left points. Figure 5a represents typical results obtained with the listed metals. Figure 5b shows the inhibition by gold trichloride, and Figure 5c shows the increase in signal with silver nitrate.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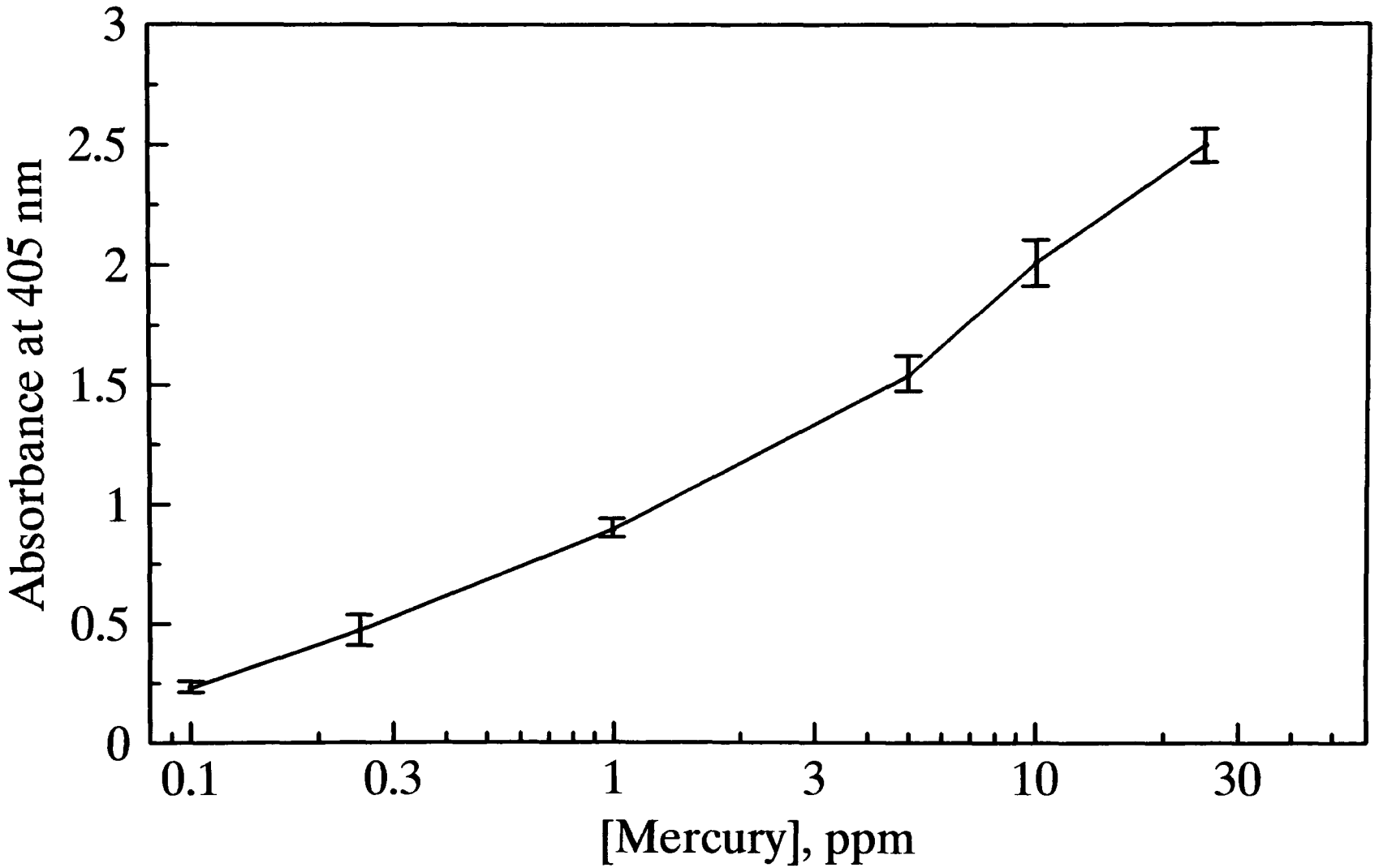
Absorbance at 405 nm
3
2.5
2
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1
0.5
0
0.1
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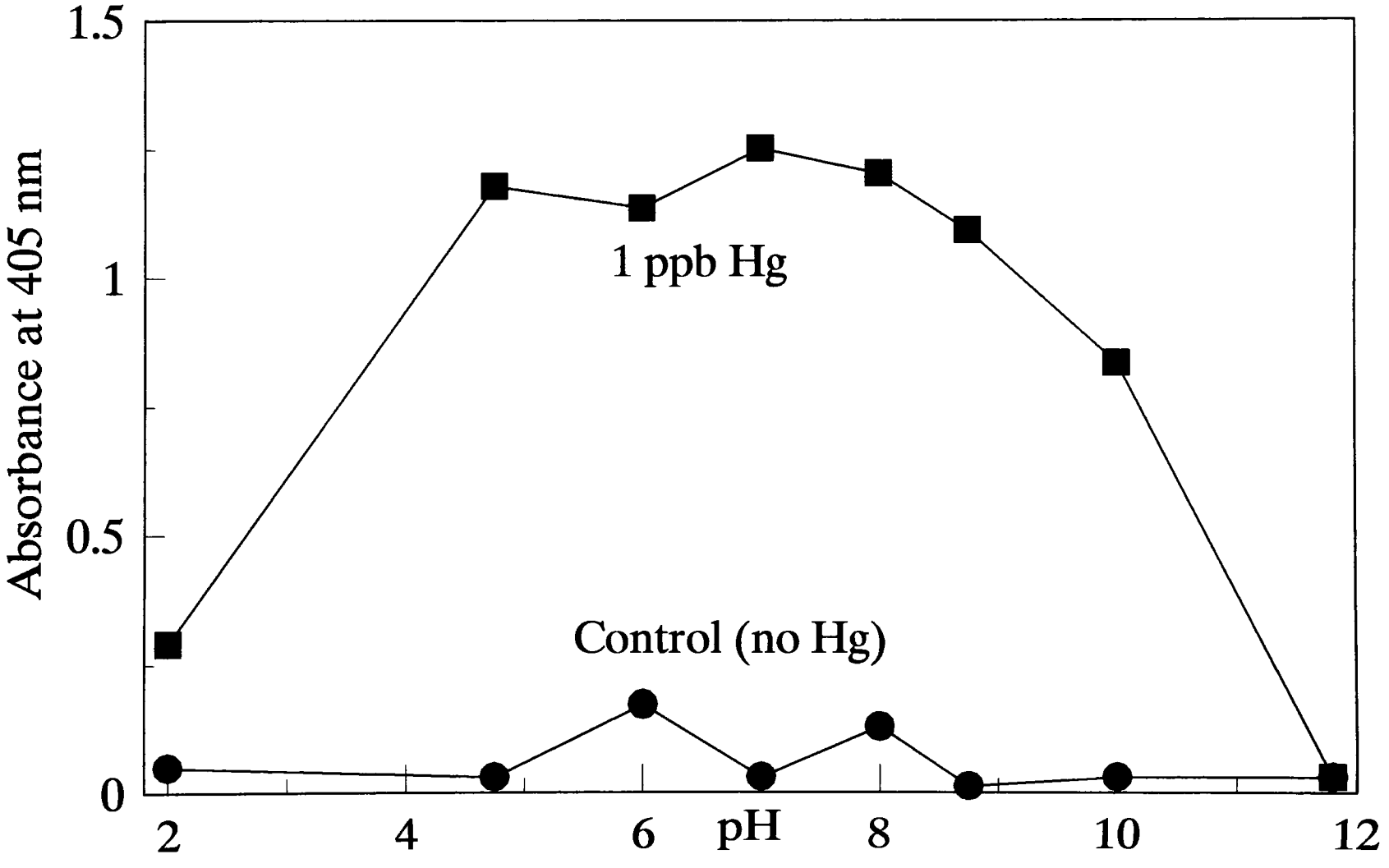
1
3
10
30
[Mercury], ppm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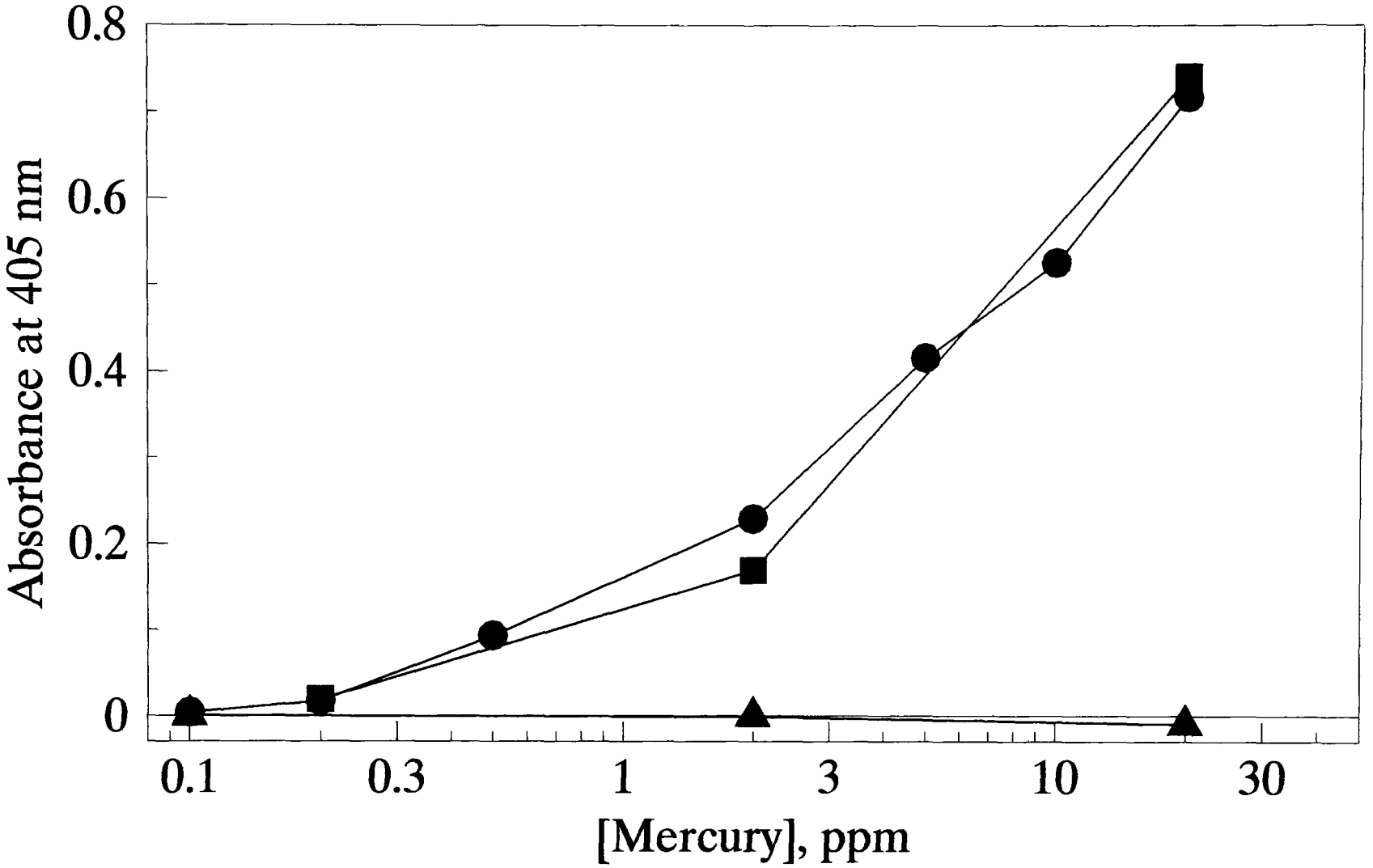
0.8
0.6
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Absorbance at 405 nm
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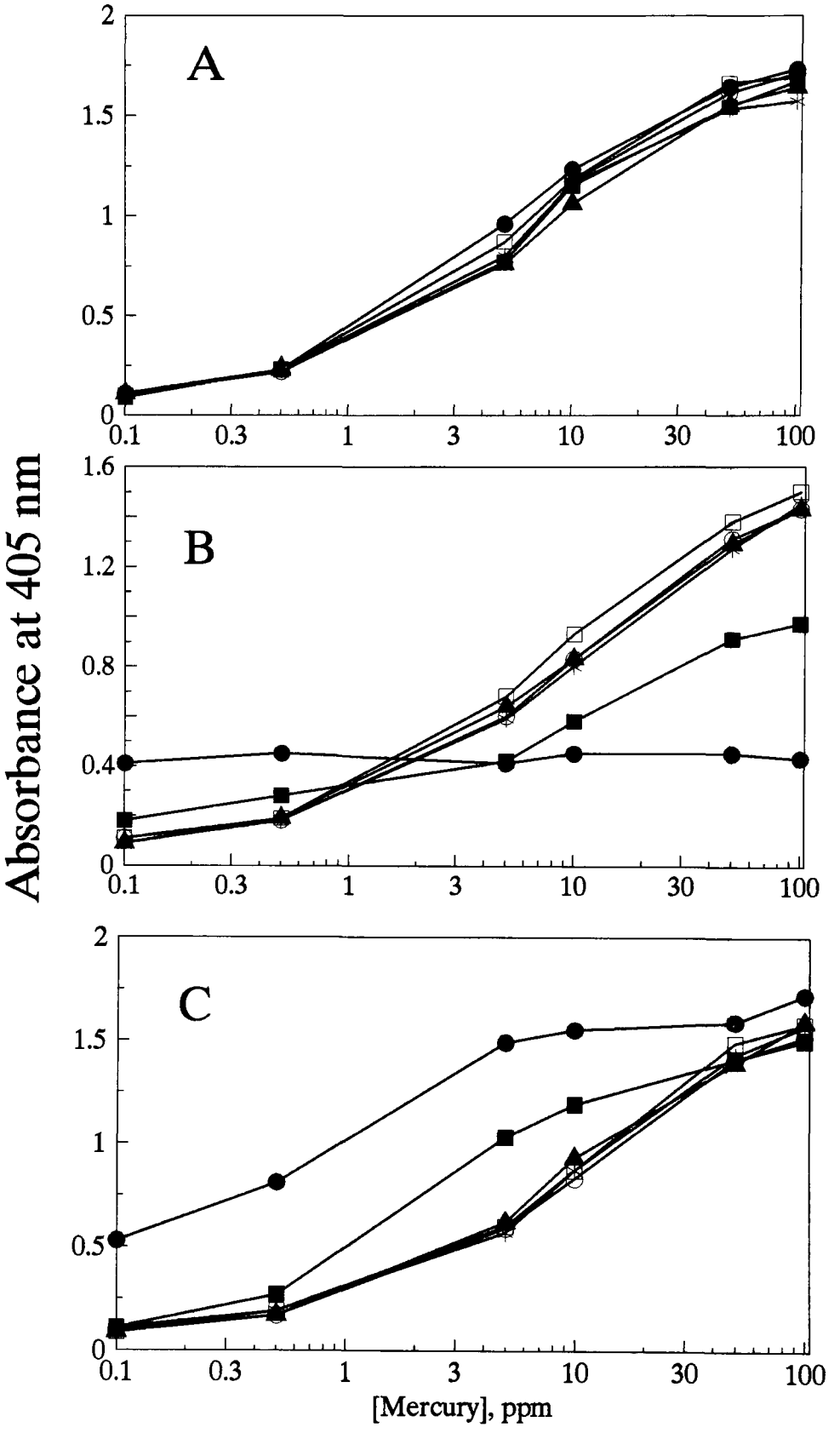
0.3
1
3
10
30
[Mercury], ppm


A
B
C
Absorbance at 405 nm
[Mercury], ppm
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0.5
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0.1
0.3
1
3
10
30
100

APPLICATION OF A NEW MERCURY SPECIATION TECHNIQUE TO SAMPLES FROM SITES HEAVILY CONTAMINATED WITH MERCURY

Eric L. Miller, *David E. Dobb*, and *Dolf Cardenas*, Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada 89119; and *Edward M. Heithmar* and *Ken W. Brown*, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119.

ABSTRACT

Mercury contamination in the environment poses a serious health risk, especially when the contaminants are in a toxic form (such as organomercury compounds) that can accumulate in organisms. Other species (such as mercury sulfide) are geologically stable and are of less concern. Mixtures of these compounds can occur naturally or anthropogenically at a given site. Therefore, an accurate method for speciating between types of mercury compounds is an absolute necessity for obtaining proper risk assessment data. EPA's Environmental Monitoring Systems Laboratory at Las Vegas is developing methods for speciating mercury and other metals to enable the Agency to make better risk-based decisions. In the work described here, a method has been developed and applied to soil and sediment samples from three sites heavily contaminated with mercury. The samples were analyzed for total mercury and for five types of mercury compounds.

Separation of the mercury types was based on sequentially leaching the soil samples with a series of increasingly acidic and oxidizing extraction solutions. Specifically, the types of mercury compounds and their associated extractants (as applied in sequential order) included: organic (soluble in toluene in the presence of chloride, e.g., CH_3Hg^+); "water soluble" (soluble in 0.01M K_2SO_4 and 0.01M KCl, e.g., $HgCl_2$ and soluble Hg^{2+} salts); dilute-acid soluble (soluble in 0.2M HNO_3, e.g., HgO); concentrated-acid soluble (soluble in 3.9M HNO_3, e.g., free and amalgamated elemental mercury); oxidizing concentrated-acid soluble (soluble in 3.9M HNO_3, 0.7M HCl, e.g., HgS and Hg_2Cl_2). Concentrations of mercury in total mercury extracts and specific mercury compound extracts were measured by inductively coupled plasma-mass spectrometry (ICP-MS), with confirmatory determinations by anodic stripping voltammetry (ASV), cold vapor atomic absorption spectrophotometry (CVAAS), and X-ray fluorescence (XRF).

Samples from the sites were found to contain total mercury concentrations ranging from < 1 mg/kg to 3000 mg/kg. At one site where samples were taken from two depths, deeper samples contained higher total mercury concentrations than shallow samples. In shallow samples, about 80 to 90 percent of the mercury was extracted as elemental mercury. In deeper samples, mercury was present predominantly as a mixture of elemental mercury and mercury sulfide in approximately equal concentrations. Minor amounts of dilute-acid soluble mercury (HgO) were present in most of the samples. Water soluble mercury compounds were typically < 1 mg/kg, but detectable. Organic mercury compounds were typically undetectable at < 0.005 mg/kg. The new speciation procedure offers significant improvements in accuracy and throughput over previous methods, enabling analysis of many samples at low cost.

NOTICE: Although the research described in this presentation has been funded wholly or in part by the U.S. Environmental Protection Agency through Contract 68-C0-0049 to Lockheed ESAT, it has not been subjected to the Agency's review. Therefore, it does not necessarily reflect the views of the Agency. Mention of any trade names or commercial products does not constitute endorsement or recommendation for use.

"Almost Digestions" or Hot-Acid Leaches with Continuous Flow Microwave Sample Preparation

by
Edward E. King, David A. Barclay, J. Douglas Ferguson, Lois B. Jassie,
CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28105.

Abstract

An important advance in sample preparation for atomic spectroscopy is the use of flow injection coupled with microwave digestion to produce a continuous flow microwave sample preparation system. This approach automates the most time consuming step in the analytical process: sample preparation. The SpectroPrep™ system embodies this hybrid technique and has been applied to the preparation of environmental samples prior to metals analysis.

Introduction

In environmental analyses for determination of metals, total digestion of the matrix is not practical nor always needed. Partial digests, or leaches, have the ability to extract analytes of interest, however, reproducibility of these extractions is not well documented. Because reaction conditions in the SpectroPrep™ system are reproducible through consistent temperatures, the analyst has the ability to tailor the leaching procedure to the matrix and to the elements of interest. The broad applicability of the SpectroPrep™ system for achieving needed consistency is demonstrated in the preparation and analysis of soils, sludges, and other solids at slurry concentrations to 1% in a variety of acid media.

The objectives of this study were to

- Demonstrate the comparability of hot-acid leaching continuous flow microwave sample preparation to EPA SW-846 Method 3051 (batch) for the analysis of metals in environmental samples

- Assess the reproducibility of hot nitric acid leaching for the preparation of soils, sediments, sludges, and oily wastes, and

- Evaluate the distribution of analytical results for extractable metals in a set of solid environmental samples over their dynamic range

These objectives have been accomplished by implementing the following strategy:

- Use of Standard Reference Materials (SRMs) to assess the accuracy and precision of both methods
- Use of mixtures of known materials (SRMs) to establish the dynamic range of the techniques

- Real life testing with subset of real world and certified reference material samples

Experimental Protocol

Materials

Materials selected for this study were drawn from a variety of sources to simulate a realistic environmental laboratory's sample distribution. Such solids might constitute the bulk material in a hazardous waste sample. In addition to wet soil, fuel-soaked soil, clay, and dewatered sludge, five reference materials representing three types of matrices were included. Two sediments- SRM 2704, BCSS-1; two soils-SRM 2710 and SRM 2711; and one rock, CANMET MRG-1 were analyzed. Average particle size was reduced to < 250 microns to allow passage through the tubing and filters in the continuous flow system.

All samples were analyzed routinely for twenty elements; Al, Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, V, and Zn.

Leach reagent (acid) to sample ratio for batch Method 3051 is 10 mL of concentrated nitric acid (HNO_3) for 0.5 g of solid. Continuous flow sample to reagent ratio is 0.5 g of solid in 50 mL of 20 % nitric acid. This represents a slurry concentration of 1%. A 10 ppm yttrium standard is incorporated into the acid reagent to track the continuous flow dilution factor.

Methodology

Method detection limits were established for the SpectroPrep™device in 20% acid solution to match the final concentration of the analyzed solutions from both the continuous flow and from the diluted batch digested samples. Six samples was the normal complement for Method 3051. Four replicates of every material were prepared for analysis and method blanks were included in the batches to round out a complement. On average, one blank was analyzed for every 4 samples. For the continuous flow, 2 replicates of each material were weighed out and each replicate was sampled twice. One blank was analyzed for every 10 samples run through the system.

Temperature and pressure conditions for the two methods were matched as closely as posssible. Method 3051 stipulates the following performance criteria: 1) reach 175 °C in 5.5 minutes, and 2) remain between 170-180 °C for the balance of ten minutes. Under these conditions, the pressure varies from 140 psi in a completely inorganic material like the CANMET rock, to 175 psi for a fuel-soaked soil which contains ~ 8% organic material. In the continuous flow system the estimated temperature of ~ 200 °C is achieved by maintaining a backpressure of 175 psi at the last pump. For the normal 10 mL sample loop the average residence time of this sample stream is 2 minutes and 15 seconds.

Metal concentrations were determined by inductively coupled atomic emission spectroscopy (ICP-AES) on an ARL model 3560 sequential spectrometer equipped with a mini-torch and Meinhard nebulizer. In continuous flow, 8-9 mL are normally collected from the 10 mL sample loop which represents a 1.3 dilution. All of the batch samples are diluted to 50 mL so that the acid concentration presented to the ICP instrument is 20%.

Assessment of the dynamic range was achieved by carefully mixing two of the SRMs containing low and high concentrations of the metals of interest according to the proportions in Table I. This resulted in samples whose Mn concentration, ranged from ~ 20-8000 ppm with similar ranges for Zn, Cu and Pb. Only the managanese data will be presented here.

Table I. Mixture Composition for Dynamic Range Study

	Composition, %	
Material	SRM 2710	SRM 2711
Low	0	100
Mix I	25	75
Mix II	50	50
Mix III	75	25
High	100	0

Results and Discussion

Comparability of leaching by the two microwave methods is shown by the generally good agreement between the elemental values obtained by continuous flow and the batch reactor as seen in Table II.

Table II. Elemental Concentrations in Mixture II of Montana Soil SRM 2710 and SRM 2711 (1:1) Prepared by Microwave Leaching with Nitric Acid

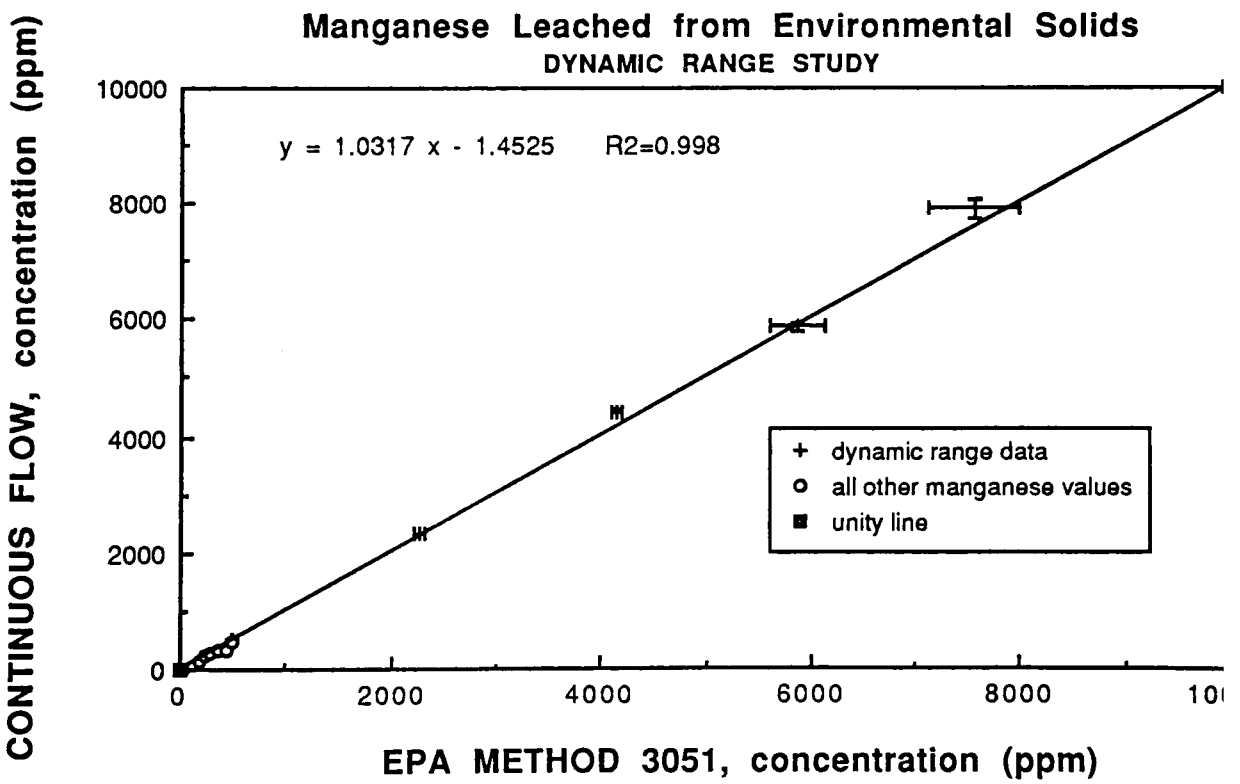
	concentration, ppm				
	continuous flow		Method 3051		
Element	mean	% RSD	mean	% RSD	Exp Range
Al	23500	0.51	17772	5.09	12000-24500
As	373	0.72	337	0.73	289-355
Ba	292	0.65	258	1.11	235-330
Ca	12980	0.26	12615	0.54	11900-14900
Cd	40.1	0.37	36.3	0.25	22.6-36
Co	10.4	1.21	8.57	8.02	6.65-12
Cr	24.2	1.29	21.9	3.66	15-24
Cu	1478	0.47	1420	0.49	1245-1755
Fe	23272	1.00	23581	1.66	19500-29000
K	6562	0.60	4876	3.02	3200-5200
Mg	6913	0.47	5997	1.76	5800-7500
Mn	4426	0.23	4153	1.04	3300-4810
Na	861	0.64	398	4.98	345-455
Ni	20.3	1.15	19.8	2.01	11.4-17.5
P	866	0.45	787	1.89	830-1000
Pb	3207	0.38	3081	0.42	2615-4250
V	54.6	0.37	40.4	4.38	35.5-50
Zn	3276	0.85	3303	1.88	2745-3620

For many of the elements, the continuous flow data are ~ 3% high on average. For vanadium at 55 and 44 ppm and cobalt at 10.4 vs 8.6 ppm respectively, the bias is ~ 20% for SpectroPrep™ values. Individual manganese values obtained for the reference materials that make up the mixture are in good agreement however, with leach values published in a certificate addendum issued by NIST, as Table III demonstrates.

Table III. Manganese Leached by Nitric Acid from SoilsReference Materials Prepared by Microwave Sample Preparation

	concentration, µg/g		
material	Method3051	continuous flow	NIST range
2710	7570	7895	6600-8900
2711	496	501	470-570

Despite this bias in favor of the SpectroPrep™ results, inspection of Figure 1 demonstrates that the dynamic range for managanese is linear over nearly four orders of magnitude.



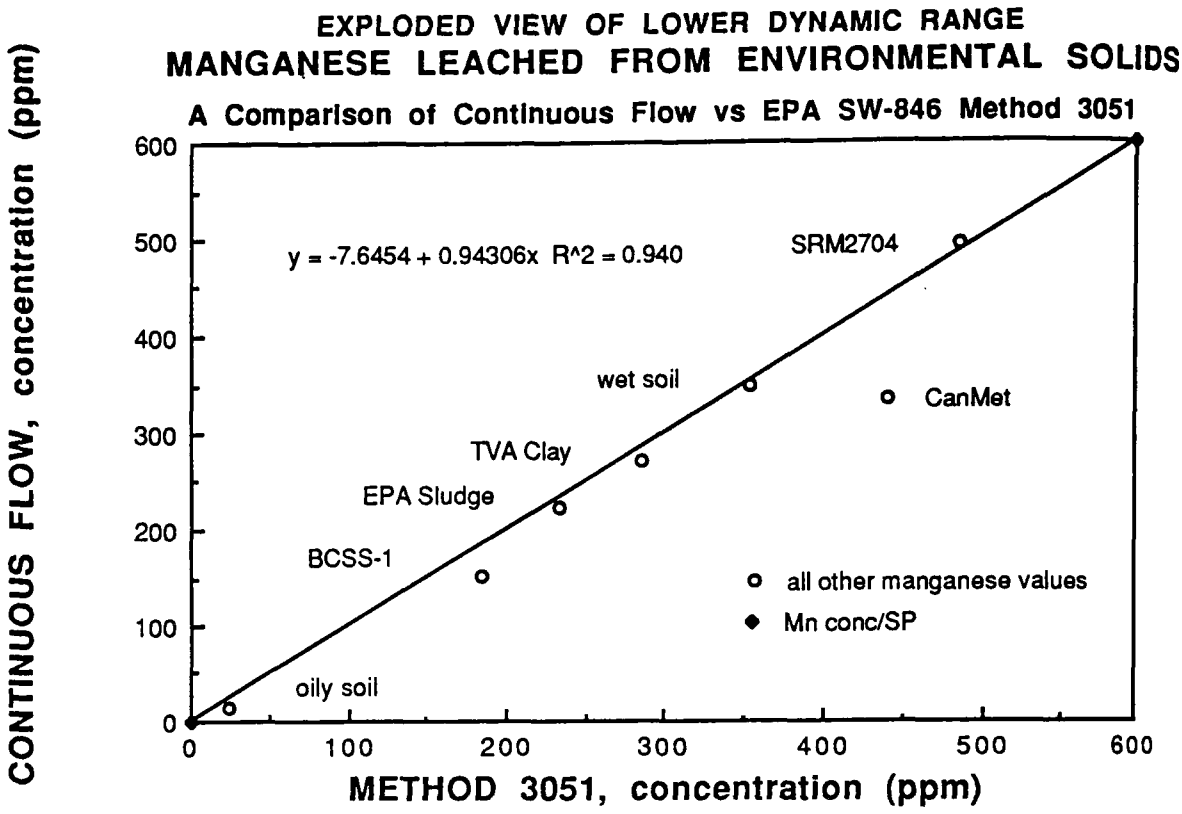


Figure 2 demonstrates that the linearity is as good between 25 and 500 ppm as it is between 500 to 8000 ppm.

For *all samples* prepared by continuous flow the average relative standard deviation (RSD) is 4.43 % compared to 5.15 % RSD for EPA Method 3051. The RSD ranges from 0.82% to 10.37 % for SpectroPrep™ where the smallest value is for MIX II and the highest was for the CANMET material. For the batch method, the lowest value is for Montana Soil SRM2710 and the highest imprecision is for the oily soil matrix. For *all elements* the %RSD for continuous flow is 4.37 % compared to 5.26 % RSD for EPA Method 3051. %RSD ranges were 2.19-8.61% for the continuous flow and 2.50-8.71% for the batch method.

Conclusions

Both continuous flow and batch microwave hot acid leaching are comparable sample preparation methods for the determination of metals in soils, sediments, sludges, and oily wastes. Data using Standard Reference Material mixtures whose concentrations span 4 orders of magnitude show the validity of the continuous flow procedure. Average < 5% RSDs for acid leaching procedures indicate that the goal of reproducibility has indeed been achieved.

An Inter-Laboratory Comparison of Instruments Used for the Analysis of Elements in Acid Digestates of Solids

David Eugene Kimbrough, Public Health Chemist II, Janice Wakakuwa, Supervising Chemist, California Environmental Protection Agency, Department of Toxic Substances Control, Southern California Laboratory, 1449 W. Temple Street, Los Angeles, California, 90026-5698

Abstract

This paper presents data from an inter-laboratory study of 160 accredited hazardous materials laboratories comparing the accuracy and precision of four different analytical instruments, inductively coupled plasma - atomic emission spectroscopy, inductively coupled plasma - mass spectroscopy, flame atomic absorbance spectroscopy, graphite furnace atomic absorbance spectroscopy, and hydride generation atomic absorbance spectroscopy. Each laboratory performed a mineral acid digestion on five soils spiked with different concentrations of arsenic, cadmium, molybdenum, selenium, and thallium. The resulting digestates were analyzed on one of the above instruments. Results show that at most concentrations that ICP-AES has significantly better precision and accuracy than the other techniques but had the highest rates of false positives and negatives. HGAAS and GFAAS consistently showed the poorest precision and accuracy. FAAS better precision and accuracy than either HGAAS or GFAAS but performed poorer than ICP-AES. FAAS however had fewer false positives and negatives than ICP-AES.

AN EVALUATION OF INTERELEMENT CORRECTION FACTORS: USES AND LIMITATIONS

Guy A. Laing, L.J. Ottmar, D.E. Dobb, F.C. Garner, J.T. Rowan, Lockheed Environmental Systems & Technologies Company, Las Vegas, NV 89119, and *L.C. Butler*, U.S. Environmental Protection Agency, Las Vegas, NV 89119.

Abstract

The Environmental Monitoring Systems Laboratory in Las Vegas, under the Office of Research and Development, is continually evaluating and improving quality assurance parameters so as to obtain more reliable data from EPA methods. One quality assurance parameter associated with the data received from an inorganic Statement of Work (SOW)is the interelement correction factors (IECs) used by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). IECs are a procedural and contractual requirement for the use of ICP-AES in the Contract Laboratory Program (CLP), and are used to remove the spectral interferences that are present in the ICP-AES method. A similar type of correction is also performed for Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS), which is being considered for use in future SOWs. In both methods the analytical data are subject to corrections to the analytical signal based upon responses from interfering constituents. These correction factors are based upon measured or known relationships between non-analyte peak intensities and the corresponding magnitude of interference on an analyte peak. This study evaluates correction factors in both ICP-AES and ICP-MS to determine their uses and limitations. Real data are examined in order to illustrate the impact of error in interelemental corrections as well as to suggest methods for detecting inappropriate corrections. Limitations on the use of corrections are considered and alternative methods for applying corrections are proposed. A detailed statistical evaluation of the errors is presented, along with an evaluation of the limitations of the interferences based upon the amount of interferant present. Each of the sources of error are examined and statistical models were evaluated which manipulate the relevant factors and evaluate their relative importance as sources of error.

INTRODUCTION

In the CLP's Inorganic SOW(1) one of the areas that would benefit from increased quality control is the determination and application of IECs. The current SOW stipulates only that IECs must be determined for spectral interferences due to aluminum, calcium, iron, and magnesium at all wavelengths used for each analyte reported by the method. Other IECs must be reported only if they are applied. The SOW makes no requirements as to how the IECs should be determined, what the basis for their determination is, and does not stipulate a standardization procedure for the factors themselves. The only other reference to interferences states that the laboratory must assume responsibility for verifying the absence of

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NOTICE

Although the research described in this article has been funded wholly by the U.S. Environmental Protection Agency through Contract 68-C0-0049 to Lockheed Environmental Systems & Technologies Company, it has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

spectral interferences from interfering elements that may be present in a sample but for which there is no channel in the instrument array. Because no requirement for evaluation of those spectral interferences exists in the SOW, they are generally ignored, as evidenced historically by a lack of statements about spectral interferences in case narratives supplied to the EPA.

A related quality assurance parameter that is designed to test the IECs is the Interference Check Solution (ICS). Although there is not a direct contractual link between the ICS and the IECs, the QC requirements associated with the ICS require that the IECs have values that will allow the ICS QC criteria to be met. The results of this study demonstrate that the ability to pass the ICS criteria does not evaluate the IECs sufficiently.

IECs can be error prone requiring a greater measure of quality assurance criteria than is currently felt necessary. In fact, the IECs incorporate error from each measurement included as part of the final analytical determination, and the total error depends on the number of measurements, the amount of interferant, the accuracy and magnitude of the correction factor(s), and the precision of the individual measurements.

Although ICP-AES and ICP-MS are similar in the use of IECs, ICP-MS does offer some advantages over the ICP-AES primarily because the number of interferences is greatly reduced in ICP-MS(2). Additionally, the IECs themselves are generally based upon different properties than in ICP-AES. In ICP-AES the IECs are a result of spectral interferences which are affected by spectrometer settings and plasma conditions, as well as by relative concentrations between the analyte and the interferant(3). Therefore, the exact relationship between the analyte and interferant can vary from day to day. In ICP-MS on the other hand, the IECs (called elemental expressions) are primarily determined by the naturally occurring abundances of the isotopes of the elements(4). Because the abundances of the isotopes are independent of the plasma conditions, are constant, and are well defined, they can be applied independently of the exact instrument make or model used. These isotope ratios are also applicable even if the interference is due to a molecular interference. In order to determine if a molecular correction is required, it is only necessary to examine for the presence of the elemental constituents.

EXPERIMENTAL

A Fisons ARL Model 3560 ICP-AES was used to evaluate the IECs for ICP-AES. The linearity of the IECs was tested by running a single element solution of iron at six different concentrations a total of three different times. The curves of apparent analyte concentration were plotted against the iron concentration for a number of different analytes. The plots were examined for linearity and noise associated with each individual measurement.

The same ICP was used to evaluate the presence of interferants which are not typically examined by laboratories performing work for the CLP. These interferences were assessed by evaluating single element solutions of cerium, copper, manganese, titanium, and zirconium. A spectral scan was obtained for each solution around the silver 328.070 nm wavelength and the apparent silver concentration was evaluated. Additionally, each solution was screened for the presence of silver using a Perkin-Elmer 5000 ICP-MS to validate the absence of silver in the single-element solutions.

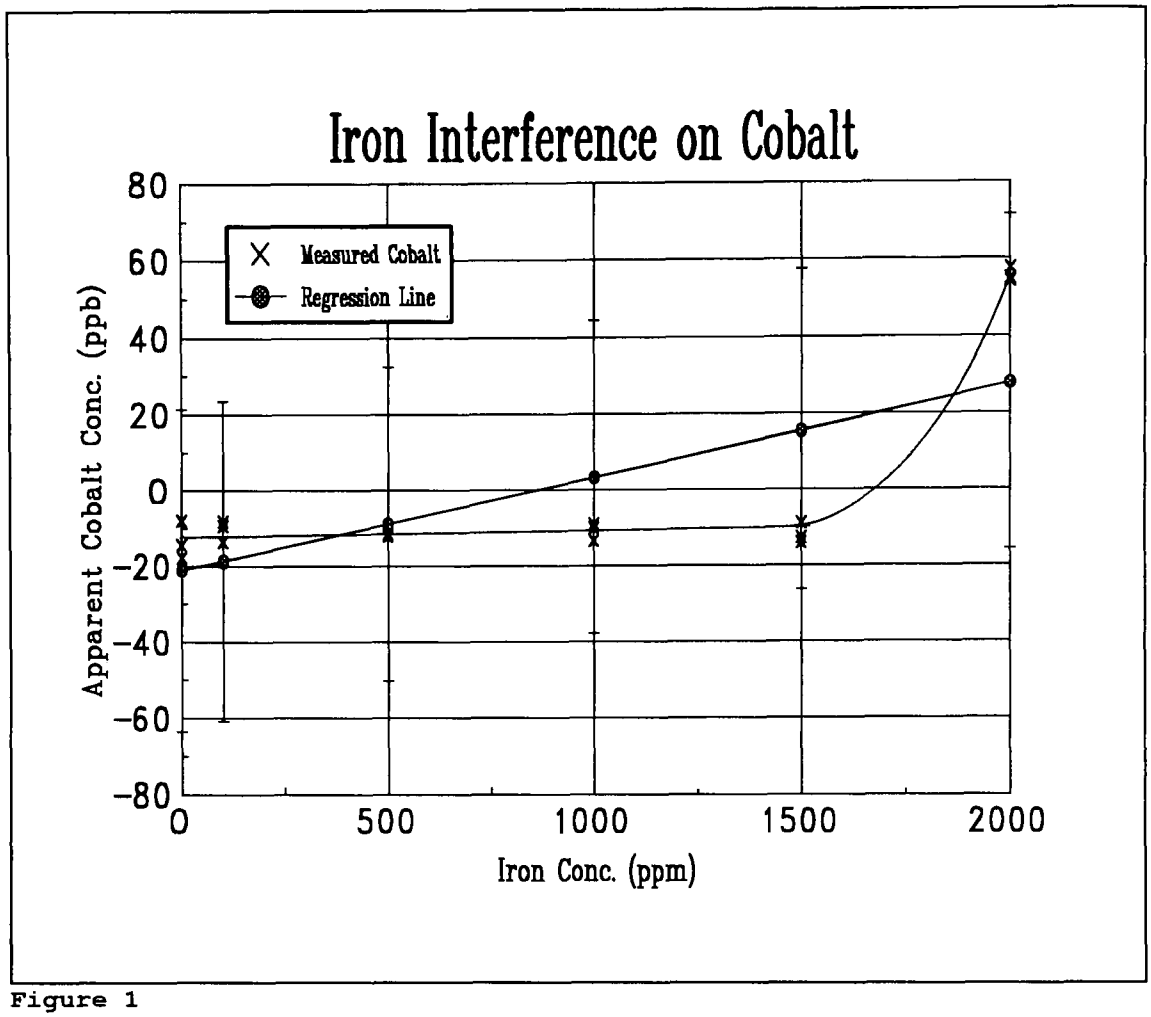

Figure 1

RESULTS AND DISCUSSION

To evaluate the use of IECs, the linear relationship between the analyte peak intensity and the magnitude of the interference was tested. The assumption that a linear relationship exists may often be false, as demonstrated by Figure 1 which represents the cobalt interference from iron. It is clearly seen that the cobalt interference does not occur at all until sometime after the iron concentration exceeds 1,500 ppm in solution and peak broadening causes it to be detected. Therefore it would clearly be inappropriate to use the IEC which would be determined when the iron concentration is less than 1,500 ppm for iron concentrations greater than 1,500 ppm. Likewise it would also be incorrect to use an IEC derived from the iron solution at 2,000 ppm for iron concentrations less than 1,500 ppm. To evaluate the relevance of interferences of this type, additional information needs to be available to assess the frequency with which samples are subject to interferences of this type. The levels at which the interferences are tested should then be evaluated. Table 1 contains results of the CLP Analysis Results Database (CARD) which show the concentrations at the listed rankings typically found in various matrices.

Table 1. Statistical ranking of iron concentration in the CLP by matrix (Concentration is reported in mg/L of the solution after digestion).

matrix	25th Pct.	50th Pct.	75th Pct.	95th Pct.	Maximum
ground water	0.1	1.21	13.2	105	35,500
other water	.034	.086	.675	53.6	2,050
soil/sediment	33.9	72	126.5	309.5	17,200
other soil	16.5	39.3	61.5	98.5	1,160

Tables like these may be useful, once the interferant curve has been determined, in evaluating the frequency that errors in quantitation occur due to the presence of interferants. This information will be essential for those who make policy to determine the extent of potential problems, which will be relevant as quality assurance procedures are evaluated.

Another situation in which the interferant level can be demonstrated to have a deleterious effect on data quality, is when the interferant exceeds the capacity of the detector. The resulting correction would be inappropriate in two scenarios. First, if the instrumentation does not notify the operator of detector saturation, then the saturated signal would be applied to the IEC and the result would be biased high because the interferant was not properly quantified. Modern instrument software systems generally notify the operator of this situation, but as recently as 1989 this interference was observed in the Multilaboratory Evaluation of Method 6020 CLP-M(2). The second scenario occurs when the operator identifies the presence of a large interferant and performs a dilution to correctly quantitate the interferant but does not apply the correction to the original undiluted sample. This procedure would have to be performed manually, and should be identified in the case narrative. This has rarely been identified in case narratives and therefore the extent of this problem cannot be determined.

Another error that may occur in the use of IECs is the failure to make a correction when one is needed. This may take two forms. The first is demonstrated in ICP-AES by the interference of manganese on silver. This interference was observed in data presented in the Multilaboratory Evaluation of Method 6020 CLP-M Inductively Coupled Plasma - Mass Spectrometry(2) when the ICP-AES instruments found silver levels present at levels in one sample which were 4 times greater than the CRDL and 8 times greater than the typical IDL. The failure to perform an interelement correction was due to an unidentified spectral interference. Not only can this happen when a channel for the interferant is present in the spectrometer, but could also happen when a channel for the interferant is not present in the spectrometer. Table 2 demonstrates this by evaluating the interference on silver by a variety of interferants. The absence of silver contamination in the single-element solutions were verified by the use of ICP-MS.

Table 2. Interference effects on silver.

Interferant	Interferant Concentration (ppm)	Apparent Silver Concentration (ppb)
Cerium	100	-59.68
Copper	100	-2.83
Manganese	10,000	1,316
Titanium	100	800
Zirconium	75	196

Several observations from the data in Table 2 can be made. First is that the correction for silver from titanium is quite high. This demonstrates when an interference is typically not determined even though the capability to perform the correction is usually available. Secondly, the interference from zirconium is also high but because an optical channel is generally not available, the interference cannot be assessed. Third is the negative interference from cerium, which means that the spectral interference is actually at the background correction point, not at the analytical wavelength. Fourth, the interference from copper appears to be negligible even though there are two copper emission lines in the vicinity of the analytical line. One line at 327.40 nm is below the silver analyte line at 328.07 nm, and the other is at 328.27 nm, just above the silver line. This raises the possibility that the background correction point circumstantially corrected for the copper interference and if the copper concentration had varied, the IEC of zero would not have worked. Finally, the data in Table 2 identifies a manganese correction that would need to be applied to the silver data once the manganese level was correctly measured. Most laboratories do not correct for this interference when the amount of the analyte in solution greatly exceeds the linear range for the analyte.

Another example of when an interelement correction is not performed is when the interference is difficult to measure. The chromium interference on antimony using ICP-AES has long been known, but many laboratories still fail to correct for it. This has consistently resulted in false-positive reports for antimony in samples with high levels of chromium. Table 3 presents the data from one of the samples evaluated in the Multilaboratory Evaluation of Method 6020 CLP-M(2). The data demonstrate that even though each of these laboratories used identical wavelengths to perform the analysis, not only is the interelement correction performed inconsistently between laboratories, but the magnitude of the correction varies widely. It can also be seen from the data that the results varied widely and were not dependant upon the application or non-application of an interelement correction.

Table 3 - Antimony Results Comparing ICP-MS and ICP-AES

ICP-MS Laboratory	Sb Result	Duplicate Sb Result	ICP-AES Laboratory	Sb result	Duplicate Sb Result	Cr IEC value
A	50.6	54.4	M	245	252	.00515
B	45	52.6	O	81.3	93.8	none
C	51.2	48.7	P	3150	3140	none
E	46.11	47.76	Q	1100	1020	.006717
F	41.8	50.1	R	1190	1000	none
G	53.6	58.6	S	4580	4980	.255
H	54.2	55.7	U	864	623	none
J	53.5	59.8	V	926	979	none
			X	1920	1810	none
Mean	51.48			1553		
Std. Dev.	4.84			1473		
Percent RSD	9.4			94.8		

Note - Results were excluded if they were either less than the IDL, or the laboratory significantly missed the calibration QC requirements.

Another issue not addressed by the quality assurance for IECs, is the

assumption that the solutions used to determine the IECs are free from contamination. In the course of this investigation it was noted that several laboratories were using interelement correction factors which could not be substantiated by any spectral interferences listed in the reference wavelength tables. One of the most striking examples was a manganese interference on nickel. In this particular case it is difficult to chemically separate the nickel from the manganese and most manganese will contain some nickel as an impurity. This would lead to the use of a correction factor because of a nickel impurity in the single element manganese solution, not because of a spectral interference. If the solution being evaluated to determine the IEC for an analyte is contaminated, then the use of the solution would lead to the use of an IEC when one is not warranted. The ICP-AES method is particularly prone to this error because generally no additional checks on the validity (i.e. spectral verification of contamination) of the correction factor are performed. Currently the SOW does not specify that any additional checks must be performed, therefore the extent of the problem can not be determined at this time. In ICP-MS this problem is not as widespread due to the less empirical nature of elemental expressions.

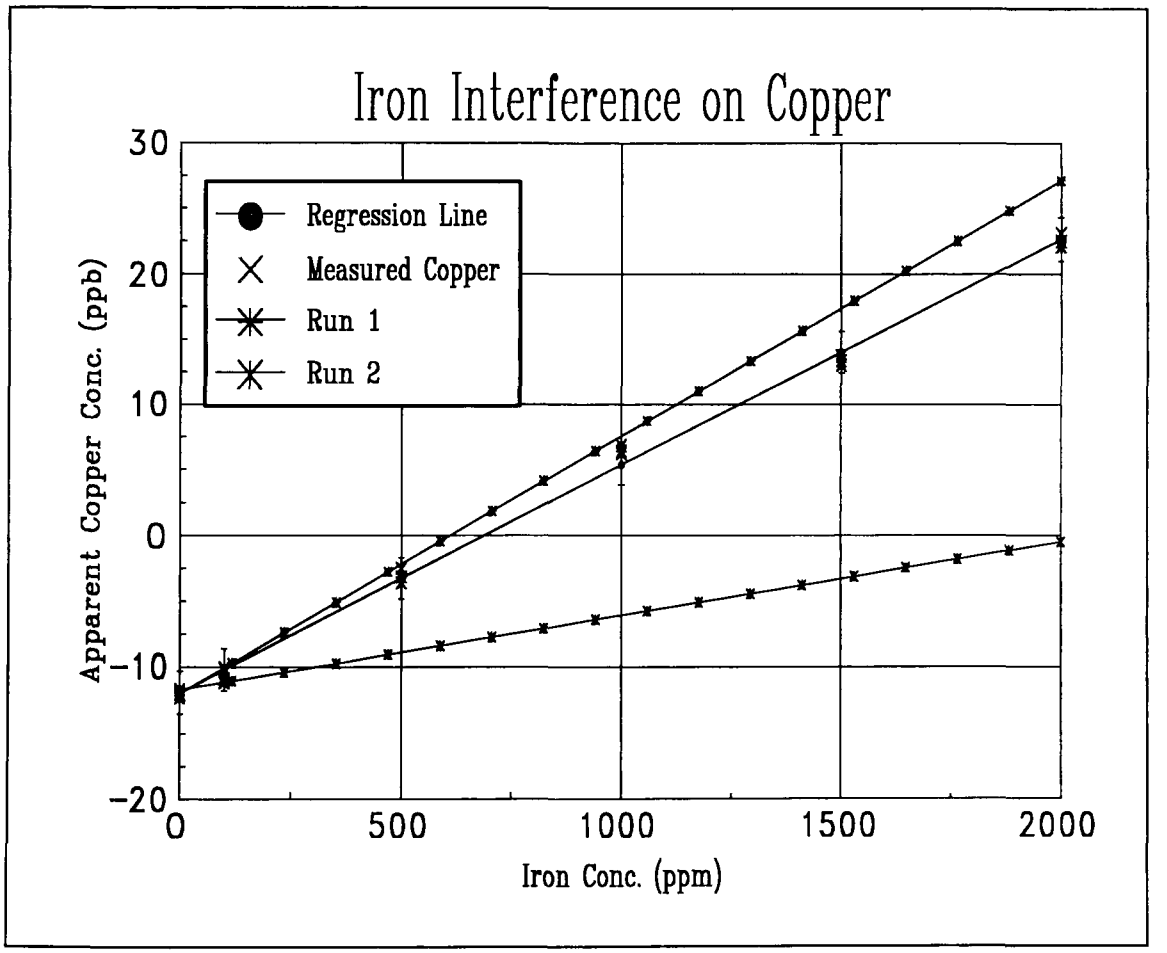

Figure 2

Another problem that can affect data quality is the assumption that the relationship between the interferant and the interference is linear.

Figure 2 demonstrates the fallacy of making that assumption. It can be clearly seen that when the iron concentration is 100 and 1,500 ppm, the apparent copper concentration is less than the apparent copper concentration when the iron concentration is 1,000 ppm. This may be due to the iron interfering primarily with the background correction point (the background correction would be abnormally high which, when subtracted, would result in a negative contribution on the part of iron to copper). At a iron concentration higher than 1,500 ppm the wing of an iron line interferes with the analytical wavelength giving an apparently high copper value. Figure 2 also demonstrates the difference that two different determinations would make on the IEC. In fact simply using the three data points from the 100 ppm iron concentration, the slope varies from 0.00559 to 0.01956, representing differences of a factor of three between the determinations.

Figure 2 also shows that a single point evaluation of the interference would have a negative intercept. Without a thorough evaluation of the intercept of the regression line, the copper interference would have a negative slope, which would clearly be incorrect.

Finally, even when the relationship between an interferant and the interference has been accurately defined, then errors are still contributed by the imprecision associated with the measurements of each associated peak. This error is dependant upon the size of the correction terms and the magnitude of the interferant.

Because the IECs in ICP-AES and ICP-MS are mathematically similar, an evaluation of how the factors used for IECs could be applied independently of the method used was studied. A statistical model was developed to evaluate the effects of the magnitude of the correction terms in IECs on the analyte signal. The model consists of the following.

If
X = the concentration of the target analyte
Y_i = the concentration of the ith interferant

and
Z = is the observed response at the primary mass or wavelength of the target analyte

where
a = the calibration slope
a_i = the correction factor, and
b = the coefficient of variation (%RSD) in intensity measurement
k = the number of potential interferants
$\hat{Y}$ is the estimate of Y_i
then

$$Z = aX + a_1Y_1 + a_2Y_2 + \ldots a_kY_k + \epsilon.$$

We have estimates of Y_i, a, and a_i

The estimate of X is

$$\hat{X} = \frac{Z - \sum a_i\hat{Y}_i}{a}$$

and the variance of the estimate is

$$V(\hat{X}) = \left(\frac{1}{a^2}\right) (V(Z) + \sum a_i^2 V(Y_i)$$

If the relative standard deviation of the response measurement is approximately constant for all responses,

i.e. RSD = 100 * b
then

$$V(\hat{X}) = \left(\frac{b^2}{a^2}\right)\left(Z^2 + \sum a_i^2 \hat{Y}_i^2\right)$$

This assumes that Z *and* $\hat{Y}_i$ are all independent measurements.

Once these factors are determined then the errors can be estimated by the above equation. As the equation demonstrates, the magnitude of the interferant peak contributes error to the analytical peak.

CONCLUSIONS

Based on the observations cited above, a need exists for the definition of additional quality assurance requirements on the interelement corrections factors used for ICP-AES. It is apparent that the traditional reliance upon the ICS criteria to fully evaluate the IECs does not evaluate the interferences that have been mentioned. Requirements for IECs should also be used for ICP-MS when that technique becomes commonly used in the CLP. The factors which should be defined consists of criteria which evaluate the ruggedness of the IEC terms being used. These include, an evaluation of the solutions used to determine the IECs to prevent assigning IECs that are simply due to contamination, a precedure to obtain better estimates of the IEC factors by running replicates of the IEC determinations, a procedure to standardize the factors so that comparisons can be made between instruments, and means by which a more thorough evaluation of the spectral characteristics and limitations of the IECs is performed.

The use of an error analysis statistic may also be useful either in data review or data validation. The statistic presented here appears to describe the analytical system quite well for ICP-AES and ICP-MS, but before it receives widespread use, its characteristics should be more thoroughly examined.

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IMPROVED DETECTION LIMITS WITH AXIAL PLASMA

Vincent J. Luciano, Thermo Jarrell Ash Corporation, 8E Forge Pkwy.,
Franklin, MA 02038

ABSTRACT:

The last year has seen a switch away from the conventional side on viewing of the ICP to axial viewing as a direct result of improvements in detection limits for all elements capable of ICP determination. With the proper optical configuration, detection limits improvements of up to 20x can be achieved with conventional pneumatic nebulization. Alternative nebulization devices (ultrasonic, thermospray, electrospray) reduce these limits even further. The axial design has now been incorporated into both simultaneous and sequential photomultiplier instruments and into solid state detector systems. Data will be presented in several matrices for each instrument type and a summary comparison given between conventional and axial viewing.

ANALYSIS OF ENVIRONMENTAL SAMPLES USING THE TJA 61E TRACE ICP

Dr. Ruth E. Wolf, Inorganic Technology Manager, Enseco-Rocky Mountain Analytical Laboratory, Debra K. White, Chief Inorganic Scientist, Enseco Inc., 4955 Yarrow Street, Arvada, Colorado 80002

ABSTRACT

For many years, the inability of most commercial ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) instrumentation to achieve the detection levels for arsenic, lead, selenium, and thallium needed for environmental decision making has resulted in the routine use of graphite furnace atomic absorption spectroscopy (GFAAS) for the analysis of these four elements. The use of both ICP-OES and GFAAS on environmental samples requires the preparation of each sample by two separate digestion methods for CLP work and up to three separate digestion methods for SW-846 Methods, increasing both analysis costs and waste generation. Since GFAAS is a single element technique, each sample must be analyzed independently for each desired element. This makes GFAAS analysis both time and labor intensive. In addition, GFAAS is prone to matrix interferences which in many cases affect the quality of the data and the quality control sample burden for CLP GFAA analyses is also high due to the post-digest analytical spike required on every sample.

The introduction of the 61E Trace ICP by the Thermo Jarrell Ash Corporation (Franklin, MA) represents an opportunity to decrease the use of GFAAS for the analysis of arsenic, lead, selenium, and thallium. The 61E Trace ICP is capable of achieving detection levels comparable to GFAAS for As, Pb, Se, and Tl allowing the use of ICP-OES for quantitation of these elements at levels of environmental concern. The elimination of the separate GFAAS sample digestion procedures and the individual analyses of these elements by GFAAS should result in an increase in sample throughput and a decrease in analysis costs, turnaround time, and waste generation.

There were, however, some concerns about the comparability of the data from the ICP-OES analysis to results generated by traditional GFAAS analyses. Clients with extensive historical data based on GFAAS methodology have been especially concerned. In order to evaluate the impact of the Trace ICP on data quality, data comparability, and analysis costs an extensive study was undertaken at Enseco-RMAL. Client and reference samples were analyzed using conventional ICP-OES and GFAAS methods as well as with the new TJA 61E Trace ICP. Data from both ICP and GFAAS preparation methods were also generated and compared. Finally, analysis time and costs were tracked and compared to evaluate the financial impact of the Trace ICP on a large production environmental laboratory such as Enseco-RMAL. The results generated from these studies will be presented and discussed as well as several technical considerations that must be addressed when using the 61E Trace ICP.

INTRODUCTION

Although the use of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) has become widely used in the environmental industry since the late 1970's, only recently has it become possible to analyze for the low levels of arsenic, lead, selenium, and thallium that are environmentally important using ICP-OES. These four elements have routinely been analyzed by environmental laboratories using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), since the levels of regulatory concern are typically in the 1-2 parts per billion range, a detection level that is routinely achieved using GFAAS. The use of GFAAS for arsenic, lead, selenium, and thallium and ICP-OES for elements such as aluminum, antimony, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, sodium, silver, vanadium, and zinc has lead to a highly labor intensive analysis scheme. In a typical laboratory following SW-846 methodology this would require two separate sample digestions for GFAAS analysis: 1) for As and Se and 2) for Pb and Tl. In addition a third sample preparation must be performed for the ICP-OES analysis of the remaining elements. Once the samples are prepared, arsenic, lead, selenium, and thallium must be analyzed individually using GFAAS. This results in a total of three sample preparation procedures and a minimum of 5 analyses to provide analytical data on the metals content of a single sample.

Other disadvantages of the GFAAS technique include its susceptibility to matrix interferences which require the use of matrix modifiers and its comparatively narrow linear range (typically 1-100 ppb) which can lead to many sample dilutions. Furthermore, most laboratories perform analytical spikes on each sample when GFAAS is used in order to assess the effect of the matrix on the sample result. This leads to a relatively high Quality Control sample burden as well.

In March of 1993, the Thermo Jarrell Ash Corporation (Franklin, MA) introduced an ICP-OES instrument that could routinely meet detection levels comparable to those of GFAAS for arsenic, lead, selenium, and thallium. This would allow the use of ICP-OES for the quantitation of these particular elements at levels of regulatory concern. The TJA ICAP 61E Trace is an improved version of the TJA 61E ICAP that has long been used by the environmental industry. The specifications of the TJA ICAP 61E Trace are given in Table 1.

Use of ICP-OES for the analysis of all the environmentally important metals including arsenic, lead, selenium, and thallium would eliminate the need for the two separate GFAAS sample digestions and the four separate GFAAS analyses for these elements. Overall, the ability to use ICP-OES for all metals analyses would lead to advantages for both the environmental laboratory and the client (e.g. government agencies, engineering firms, regional EPA offices, and remediation programs). These advantages include the following: reduction in analysis costs, reduction in waste generated by the sample preparation procedures, decreased analytical turnaround times, and decreased data validation costs.

There were, however, some concerns about the comparability of the data from ICP-OES analysis to results generated by traditional GFAAS analyses. Clients with extensive historical data were especially concerned. There were also questions on the performance of the instrumentation including its ability to meet regulatory detection levels, linear ranges, ease of use, and if there were any operational difficulties not observed in the traditional horizontally viewed ICP-OES instrumentation. To answer these questions, Enseco performed an extensive evaluation of the 61E Trace ICAP with the cooperation of Thermo Jarrell Ash over a period of about 3 months. The results of these studies will be discussed.

EXPERIMENTAL

Materials and Instrumentation: A TJA 61E Trace ICP with the analytical lines listed in Table 2 was used for the study. Additional lines were installed to compensate for interferences and a yttrium line was also installed to be used as an internal standard. Standard ICP stock solutions were used from several different commercial standards vendors as well as actual client samples and NIST Standard Reference Materials (SRMs) 1643c and 2711. A commercially available reference soil from Environmental Resource Associates was also used in the study.

RESULTS AND DISCUSSION

Detection Limits and Linear Ranges: Detection limits studies were performed by analyzing a low level standard (10 ppb) with rinsing in between for a total of 7 measurements per day for three non-consecutive days. The average of the daily standard deviations was then multiplied by 3 to obtain the Instrument Detection Limit (IDL). Linear ranges were obtained by analyzing standards of successively higher concentrations until the highest standard was found where the result read within ±5% of the true value. The results of the detection limit and linear range studies are listed in Table 3. It should be noted that these were obtained with the use of an internal standard to compensate for any viscosity differences.

The IDLs obtained following the protocol from the Environmental Protection Agency's (EPA) Contract Laboratory Program (CLP) Statement of Work (SOW) as described above were generally within a factor of two of those obtained using the same CLP IDL methodology for GFAAS. The linear ranges obtained using the Trace ICP are however, much higher - generally by a factor of one hundred.

Physical interferences/viscosity effects: It has long been known that greatly differing acid concentrations between samples and standards in ICP-OES analysis can bias sample results. Most regulatory methods suggest that users matrix match all samples and standards to avoid such biases. In order to determine whether such viscosity effects were a significant

problem on the Trace ICP a simple study was conducted. The instrument was calibrated with a standard prepared in a 10% nitric/10% hydrochloric acid matrix. Standards containing 100 ppb of As, Pb, Se, and Tl were then prepared in differing acid combinations and concentrations and the measured concentration recorded. Under SW846 Method 6010A a ±10% control is established on the calibration. As a result, any biases seen in this study that were greater than ±10% of the true value were deemed significant. The results shown in Tables 4 and 5 indicated that significant biases can occur if the sample acid content differs from that of the standards. The largest differences occurred when the acid content was 2% or less and when only hydrochloric acid was used. A further study, in which yttrium was used as an internal standard to compensate for nebulization changes caused by differing acid content showed that the use of such an internal standard element can significantly reduce or eliminate this type of bias completely in most cases.

Dependance of IDLs on Nebulizer and Conditions: It was also shown that the Instrument Detection Limits obtained are highly dependant on the nebulizer used and the optimization conditions of the nebulizer. The original Meinhard K Type nebulizer installed with the instrument was replaced with a new Meinhard K Type nebulizer obtained from Thermo Jarrell Ash and the IDLs determined using the argon and solution flow rates established with the previous nebulizer. It was found that for some elements the IDL obtained nearly doubled, as is illustrated in Table 6. The new nebulizer was able to achieve similar detection limits to the original nebulizer only after an optimization of argon flow rates was undertaken (about 4 hours are required for this procedure). As a result of this study, IDL checking procedures were incorporated into Enseco's Standard Operating Procedures as part of the optimization routine that must be followed whenever a new nebulizer is installed.

Data Comparability Studies: Tables 7-9 illustrate results obtained by Trace ICP, regular ICP-OES, ICP-MS, and GFAA results on a variety of water and soil samples. For the most part the GFAA and Trace ICP results for the aqueous samples compare well. The less than symbol indicates that the measured value was less than the reporting limit. In the case of the GFAA analyses the Reporting Limits were raised by a factor of 50 due to dilutions because of poor analytical spike recovery. The ICP-MS results for Se on the aqueous samples are higher than the GFAA results due to the presence of Br in the samples that was not corrected for at the time of analysis.

The results by Trace ICP for NIST SRM 1643C in Table 9 are all generally within ±10% of the certified value, which is within the limitation imposed by the calibration verification criterion of Method 6010A of ±10%.

The soil results for client samples show some differences in the lead and arsenic results, depending on whether the ICP or the GFAA digestate from Method 3050 was analyzed for some samples. This difference is a result of the different sample preparation method and not a result of the

instrumentation differences.

The results for the PriorityPollutnT - CLP Soil, Lot 213 compare well and are within the advisory ranges established by the manufacturer for all elements under any sample preparation conditions. The certified values were established by a round robin study of 8-15 laboratories performing SW-846 Method 3050 and Method 6010A for analysis.

The results obtained for NIST SRM 2711 compare very well, generally within ±10%, with the average results obtained from a NIST Interlaboratory Study of 17 U.S. EPA CLP laboratories.

SUMMARY

The TJA 61E Trace ICP did perform up to the expectations established by the manufacturer of: 1) IDLs comparable to GFAA, 2) wide linear range, 3) data comparable to GFAA analysis for most samples, and 4) realization of decreased analysis costs and turnaround times.

Several recommendations can be made after the 3 month evaluation of the TJA 61E Trace ICP. First of all, since the IDLs were found to vary with the individual nebulizer used and that each nebulizer must be independently optimized to achieve the best IDLs, IDL optimization and checking procedures should be included in any laboratory Standard Operating Procedures describing the operation of this instrument.

In addition, the use of an internal standard element, such as Yttrium, to compensate for acid viscosity effects that can contribute to result bias due to differing acid concentrations is highly recommended. Although the study showed that the internal standard could not entirely negate the problem at vastly different acid concentrations, in the vast majority of acid concentrations seen in analyses done under SW-846 protocols, the problem could be alleviated.

Data comparability with traditional GFAA and ICP-OES results was generally good with real client samples and certified reference materials. Some differences were observed that appear to be caused by the change in sample preparation method, rather than due to the change in the analysis technique

Table 1. TJA ICAP 61E Specifications

- 3/4 meter Rowland Circle, Paschen-Runge Mount
- Vacuum Optics
- 2400 groove/mm Holographic Grating
- 10 micron entrance and exit slits

  Resolution: 0.008 nm 2nd order
  0.016 nm 1st order

- Axial plasma viewing
- Cyclone spray chamber
- Meinhard concentric nebulizer
- 27.12 MHz crystal controlled RF generator
- Crawford/Kunselman noise reduction technique

Table 2. Configuration of 61E Trace ICAP used in the study.

Element	Order	Line (nm)	Use
As	2	189.042	Analytical
Se	1,2	196.026	Analytical
Pb	1,2	220.353	Analytical
Tl	2	190.864	Analytical
Sb	1,2	206.838	Analytical
Cd	2	226.502	Analytical
Al	1	308.215	Interference
Ca	1	317.953	Interference
Mg	1	279.078	Interference
Fe	1	271.441	Interference
Mn	1	257.610	Interference
V	1	292.402	Interference
Cr	1	267.716	Interference
Mo	1	202.030	Interference
Y	1	371.030	Internal Standard

Table 3. Detection Limits and Linear Ranges

Element	CLP Detection Limit	Linear Range
As	3.0 ppb	10 ppm
Pb	2.0 ppb	30 ppm
Se	3.7 ppb	20 ppm
Tl	2.5 ppb	30 ppm
Sb	2.3 ppb	10 ppm
Cd	0.5 ppb	10 ppm

Table 4. Physical interference effects caused by acid concentration

Nitric Conc.	Hydrochloric Conc.	Arsenic Recovery (%)	Lead Recovery (%)	Selenium Recovery (%)	Thallium Recovery (%)
1%		110.9	111.6	114.2	116.3
5%		105.9	109.1	102.3	106.7
10%		101.2	109.4	94.7	101.9
20%		94.5	105.7	85.9	90.7
1%	1%	109.3	111.7	117.2	116.4
5%	5%	105.4	108.5	106.9	116.4
10%	10%	100.7	106.5	98.4	102.0
	5%	111.1	110.7	121.9	120.7
	10%	110.3	107.9	121.6	117.8
	20%	106.4	105.7	120.9	115.2

Notes:

1. Measurements are percent recoveries of a 100 ppb spike in the listed acid concentration.

2. No Internal Standard was used.

3. Instrument was calibrated at 1 ppm in 10% nitric/10% hydrochloric acid.

Table 5. Use of Internal Standard to correct for physical interference effects caused by acid concentration

Nitric Conc.	Hydrochloric Conc.	Arsenic Recovery (%)	Lead Recovery (%)	Selenium Recovery (%)	Thallium Recovery (%)
1%		101.9	102.3	104.4	107.3
5%		96.9	99.5	93.1	98.1
10%		94.8	102.3	88.5	95.6
20%		91.0	102.0	82.9	87.2
1%	1%	101.2	103.2	108.1	108.1
5%	5%	98.1	100.7	99.2	99.8
10%	10%	95.0	101.0	93.3	96.8
	5%	101.3	100.5	110.5	110.5
	10%	102.4	99.9	112.4	109.5
	20%	99.1	98.3	112.3	107.6

Notes:

1. Measurements are percent recoveries of a 100 ppb spike in the listed acid concentration.

2. 2 ppm Yttrium was used as Internal Standard.

3. Instrument was calibrated at 1 ppm in 10% nitric/10% hydrochloric acid.

Table 6. Nebulizer Dependence on IDLs

	IDLs				
	As	Pb	Se	Tl	
Meinhard #1 (Ar @ 0.56 L/min)	2.1	1.1	2.0	1.9	(optimized)
Meinhard #2 (Ar @ 0.56 L/min)	3.9	0.8	4.8	4.0	(not optimized)
Meinhard #2 (Ar @ 0.60 L/min)	2.3	1.0	2.4	2.9	(optimized)

Table 7. Data Comparability - Aqueous Samples

	As Results (ppb)		Pb Results (ppb)	
Sample	GFAAS	Trace ICP	GFAA	Trace ICP
846-15	260	297	<50	<3
846-16	<500	243	<50	<3
846-17	240	251	<50	<3

	As Results (ppb)		Pb Results (ppb)		Se Results (ppb)	
Sample	ICP-MS	TRACE	ICP-MS	TRACE	ICP-MS	TRACE
3604-14	68	75	640	670	8.8	4.4
3604-15	42	42	150	150	4.0	<2
3604-16	32	35	300	320	5.7	<2
3604-16D	31	35	290	320	5.1	2.2
3604-17	47	49	400	520	7.4	4.2
3604-18	39	44	140	140	<3	<2

Note: Se values by ICP-MS are high due to a Br interference on ^{82}Se that was not corrected for during analysis.

Table 8. Data Comparability - Soil Results

	Arsenic Results (ppb)			Lead Results (ppb)		
		TRACE ICP			TRACE ICP	
Sample	GFAA	GFAA Prep	ICP Prep	GFAA	GFAA Prep	ICP Prep
155-01	8.6	15	28	78	78	98
155-02	12	25	34	138	116	271
155-03	5.6	11	15	90	94	94
155-04	<10	21	31	145	142	274
155-05	18	23	24	106	107	135
155-06	<10	29	32	73	156	170
155-07	7.4	12	46	82	83	113
155-08	33	42	54	140	130	145
DCS*	1450	1343	1308	1360	1464	1378
DCS*	1360	1274	1300	1360	1383	1361

* Environmental Resource Associates PriorityPollutnT - CLP Soil Lot 213

Table 9. Reference Material Results

Results for NIST SRM 1643C - Trace Elements in Water

Element	Trace ICP Average Results in ppb, (%RSD), n=2	NIST Certified Value Total Concentration in ppb, (± error)
As	88.6 (1.6)	82.1 (1.2)
Pb	31.2 (2.1)	35.3 (0.9)
Se	10.3 (1.1)	12.7 (0.7)
Sb	ND	ND
Tl	11.3 (0.9)	7.9*
Cd	13.1 (0.1)	12.2 (1.0)

* Result for information only, not certified.
ND = Not Detected

Results for NIST SRM 2711 - Montana Soil (EPA CLP Leach Study Results)

Element	Enseco-RMAL Trace ICP Method 3050 n=3 mg/kg, (%RSD)	NIST Interlab Leach Results Range mg/kg	NIST Average Method 3050 Leach Results mg/kg	Enseco-RMAL 61E Results mg/kg
As	89.0 (3.6)	88-110	90	102.6
Pb	1050.0 (0.4)	930-1500	1100	1100
Se	nr	nr	nr	nr
Sb	14.0 (0.8)	nr	<10	12.1
Tl	nr	nr	nr	nr
Cd	39.2 (0.2)	32046	40	37.8

nr = no recovery reported.

Results for Environmental Resource Associates PriorityPollutnT - CLP Soil Lot 213

Element	n=	GFAA Results mg/kg Avg (%RSD)	Trace ICP mg/kg GFAA Prep Avg (%RSD)	Trace ICP mg/kg ICP Prep Avg (%RSD)	Certified Value mg/kg	Advisory Range mg/kg
As	2	140 (4.5)	130 (3.8)	130 (0.5)	145	86-204
Pb	2	136 (0)	142 (4.0)	137 (1.0)	148	97-200
Se	2	158 (6.7)	123 (3.4)	120 (0.5)	143	97-189
Tl	2	86.7 (3.0)	81.9 (3.1)	80.0 (0.8)	85.1	44-126
Sb	2	89.2 (17)	85.9 (2.1)	74.2 (0.9)	55.2	10-200

ULTRASONIC NEBULIZATION AND ARSENIC VALENCE STATE CONSIDERATIONS PRIOR TO DETERMINATION VIA INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY.

Carol A. Brockhoff, US Environmental Protection Agency, Chemical Research Division, Environmental Systems Laboratory, Cincinnati, OH 45268.
John T. Creed, USEPA, CRD, EMSL, Cincinnati, OH 45268 and Theodore D. Martin, USEPA, CRD, EMSL, Cincinnati, OH 45268

Introduction

Arsenic is currently regulated under the National Primary Drinking Water Regulations (NPDWR) with a maximum contaminant level (MCL) of 50 ppb. The drinking water regulations associated with arsenic are in the process of being updated. This update will include a revised MCL for arsenic. If the revised MCL for arsenic is set below 2 ppb, the approved analytical methodologies for routine monitoring will need sub-ppb detection capabilities. This requirement alone will limit the number of acceptable analytical methodologies/techniques which could be utilized in routine monitoring. One technique which shows considerable promise for the detection of As in the low to sub-ppb range is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). One disadvantage of ICP-MS for the detection of Arsenic is an isobaric interference ($^{40}Ar^{35}Cl$) caused by chloride containing matrices. This sensitivity requirement in combination with the inherent isobaric interference may exceed the detection capability of ICP-MS if conventional nebulizers are utilized. The low dissolved solids associated with drinking water matrices could allow an ultrasonic nebulizer to be utilized to obtain the added sensitivity for monitoring arsenic in the sub-ppb concentration range.

Results and Discussion

An ultrasonic nebulizer is unlike a pneumatic nebulizer in that the aerosol is allowed to traverse a heated chamber followed by a condenser which desolvates the aerosol prior to its introduction into the plasma. This desolvation of the aerosol produces an arsenic response difference between the two predominate valence states of arsenic, As(III) and As(V). A 50ppb As(III) solution in 0.4% HNO_3 will produce a response which is approximately 40ppb if a 50ppb As(V) solution is used for calibration. This response difference observed in a nitric acid only matrix can be eliminated by adding 0.2% HCl to the 50ppb As(III) solution. This response difference between As(III) and As(V) as a function of HCl was further investigated by collecting samples at various points along the desolvation pathway of the ultrasonic nebulizer.

Figure 1 is a schematic of an ultrasonic nebulizer with four sampling points labelled. These sampling points are: 1.) prior to nebulization 2.) the spray drain 3.) the condenser drain 4.) the

aerosol exit from the condenser. Two sets of samples were collected at each of the four sampling points. One set of four samples was collected while nebulizing As in 0.4% HNO_3 and the other set of four samples was collected while nebulizing a mixed acid matrix of 0.4% HNO_3 and 0.2% HCl. The eight fractions collected at these four sampling points were then chromatographed [1] to separate the As(III) from the As(V). These chromatographic results are summarized in figure 1. The chromatographic results associated with the solution prior to nebulization indicated that equal amounts of As(III) and As(V) were found in both matrices. This indicates that the response difference initially observed was not induced by a preoxidation caused by the HCl prior to nebulization. The chromatographic results from the samples collected from the spray chamber drain indicate that the mixed acid sample contained a disproportionate amount of As(V). This may indicate that the heat from the transducer in combination with the HCl is causing some accelerated oxidation relative to the sample containing HNO_3 alone. The chromatographic results from the collection of the condenser drain indicate that after traversing the heating chamber and the condenser of the ultrasonic nebulizer all of the As(III) has converted to As(V) in the mixed acid matrix. While, the HNO_3 acid matrix showed very little additional oxidation. The As in the mixed acid sample is preferentially being oxidized as it traverses the heater tube and condenser. The final sample collected at the exit to the condenser was collected via a bubbler. The two samples collected at the exit to the condenser are essentially the same as those collected from the drain of the condenser. The As(III) from the exit of the condenser is completely oxidized in the presence of 0.2% HCl but is only partially oxidized in the presence of 0.4% HNO_3.

Conclusion

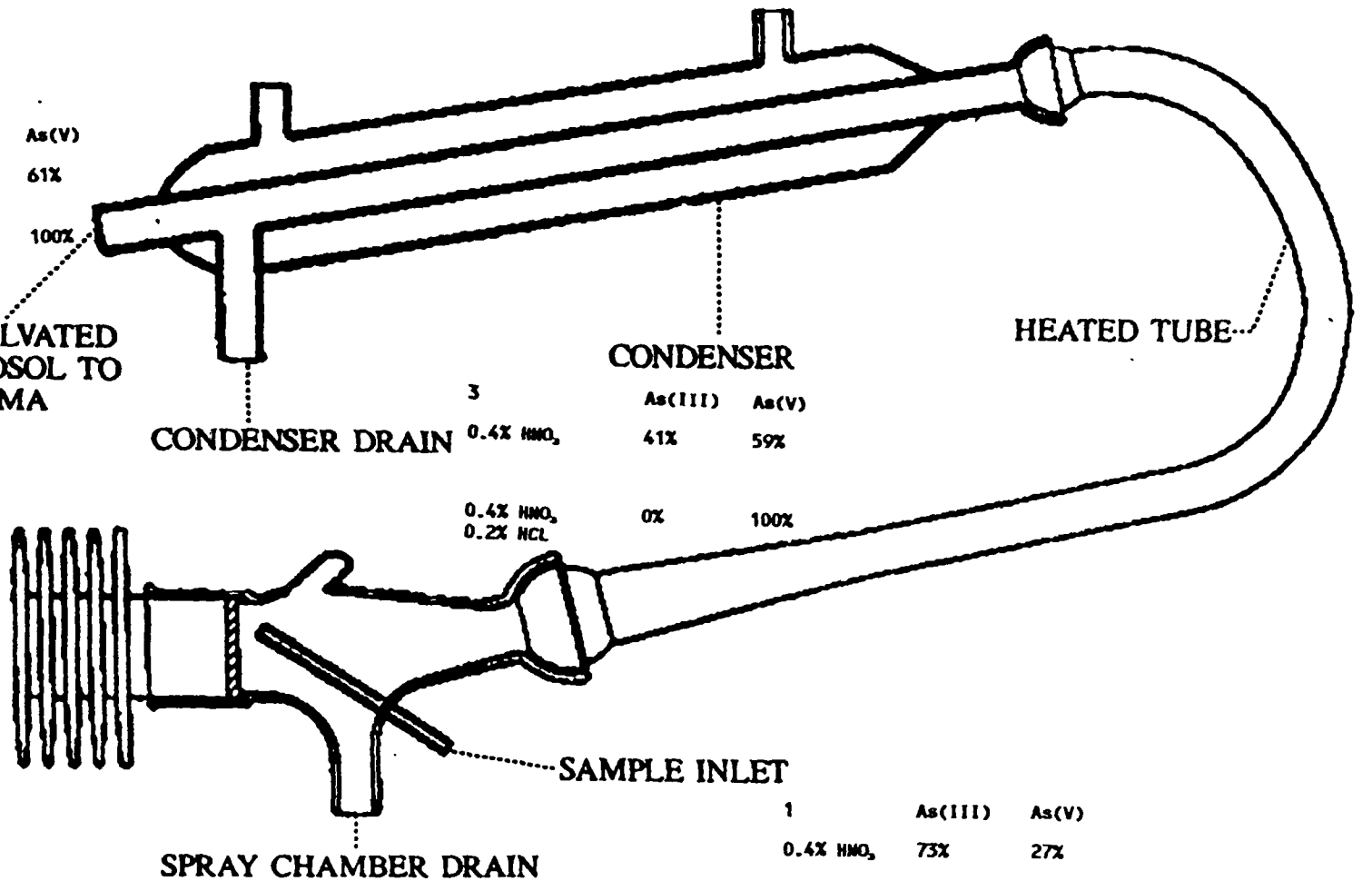
The ultrasonic nebulizer unlike a conventional pneumatic nebulizer, produces a response difference between As(III) and As(V) in a pure nitric acid matrix. This response difference can be eliminated by adding 0.2% HCl to both the As(III) and the As(V) solutions. The HCl does not oxidize the As(III) to As(V) prior to nebulization, but rather the As(III) is converted to As(V) as it traverses the ultrasonic nebulizer. In a pure nitric acid matrix this oxidation by the ultrasonic is not observed and therefore a response difference is observed.

References

1.) Raimund Roehl and Maricia M. Alforque, 1992 Winter Conference on Plasma Spectrochemistry, San Diego, Ca.

FIGURE 1

CHROMATOGRAPHIC SEPARATION AS A FUNCTION OF TRANSPORT



4	As(III)	As(V)
0.4% HNO_3	39%	61%
0.4% HNO_3, 0.2% HCL	0%	100%

3	As(III)	As(V)
0.4% HNO_3	41%	59%
0.4% HNO_3, 0.2% HCL	0%	100%

1	As(III)	As(V)
0.4% HNO_3	73%	27%
0.4% HNO_3, 0.2% HCL	73%	27%

2	As(III)	As(V)
0.4% HNO_3	42%	58%
0.4% HNO_3, 0.2% HCL	23%	77%

ALTERNATIVES TO THE USE OF ASTM TYPE II REAGENT GRADE WATER

Garabet H. Kassakhian, Manager, Quality Assurance, and Stephanie J. Pacheco, Assistant Manager, Quality Assurance, Tetra Tech, Inc., 348 West Hospitality Lane, Suite 300, San Bernardino, California 92408-3216

ABSTRACT

The American Society for Testing and Materials (ASTM) has established standard specifications for reagent grade water. ASTM Type II Reagent Grade water is often designated by quality assurance project plans (QAPjP) for use during field decontamination procedures, and for the preparation of trip and ambient blanks. The United States Environmental Protection Agency (USEPA) recommends its use in the preparation of reagents, and for general laboratory procedures, and it is also claimed by most laboratories as part of their quality assurance programs. The specifications of the most recent ASTM Type II (ASTM D-1193-91) for chlorides, sodium, total silica, and total organic carbon are inconsistent, incomplete and unattainable by routine analyses. A survey of laboratories engaged in federal Remedial Investigation/Feasibility Study (RI/FS) programs indicates that none can attain the quantitation limits stated in the ASTM specifications. It is recommended that an alternative standard specification for Reagent Grade Type II water by the American Public Health Association (APHA) be used. Although no commercially available purified water is certified to meet ASTM Type II specifications, the analyses of seventeen lots of purified water for project specific analytes of concern, namely metals, and volatile and semi-volatile organics, yielded results free of significant contamination. It is recommended that commercially available purified water be used *in lieu* of Reagent Type II water, on the condition that prior to use each lot of 100 to 200 gallons be tested to comply with the APHA specifications and be free of any analytes of concern.

INTRODUCTION

American Society for Testing and Materials (ASTM) Type II Reagent Grade water is widely recommended for use by the United States Environmental Protection Agency(USEPA) for use in laboratory analyses, and by other U.S. Government Departments, e.g. the U.S. Air Force, for use in field decontamination procedures[1,2]. Commercial procurement of ASTM Type II water is a challenge yet to be surmounted, while analyses for verification that the procured water indeed conforms to the ASTM Standard Specification for Reagent Water[3] has proved to be an impossible task.

The long standing ASTM Standard Specification for Reagent Water D-1193-77[4], that had been reapproved in 1983, was finally supplanted in 1991 by D-1193-91 (Table I). The current D-1193-91 standard specification requires that chlorides, sodium, total silica and total organic carbon be determined at very low detection levels. A close examination of the recommended test methods indicates that there is inherent inconsistencies in the recommended test methods, as indicated in Table II.

TABLE I
ASTM Specification for Type II Reagent Grade Water

Parameter	ASTM Recommended Test Method	Specification ASTM D-1193-77	Specification ASTM D-1193-91
Total matter, max. mg/L	Method B of Test Methods D-1888	0.1	Not applicable
Electrical conductivity, max μmho/cm (μS/cm) at 298°K (25°C)	D-1125	1.0	1.0
Electrical resistivity, min. MΩ-cm at 298°K (25°C)	D-1125	1.0	1.0
Minimum color retention time of potassium permanganate, minutes	D-1193-77, Section 7.4	60	Not applicable
Total Organic carbon (TOC), max. μg/L	D-4779	Not applicable	50
Maximum soluble silica	D-859	Not detectable	Not applicable
Total Silica, max. μg/L	D-4517	Not applicable	3
Sodium, max. μg/L	D-1428	Not applicable	5
Chlorides, max. μg/L	Under development per D-1193-91, footnote 6[3]	Not applicable	5

TABLE II
Status of ASTM Test Methods for ASTM Type II Water Analysis

Parameter/ ASTM Recommended Test Method (current)	**Specification per ASTM D-1193-91**	**Method Status**	**Reference**
Chlorides	5 μg/L	Method under development	Footnote no. 6[4]
Sodium/D-1428-82	5 μg/L	Method discontinued in 1990	p.591, 1992 Annual Book of ASTM Standards[5]
Total Silica/D-4517-85	3 μg/L	Method is not applicable; its range is from **25 μg/L** to **250 μg/L**	p.1, Section 1.2[6]
Total Organic Carbon/ D-4779-93	50 μg/L	New, unproven method, poor reproducibility. Type II water typically contains organic carbon in the range of 0.2 mg/L or less.	p.2, Section 8.2[7]

A number of nationally known laboratories currently engaged in federal RI/FS programs, were asked to supply their currently applicable methods and the relevant practical quantitation limits for the Table II analytes of interest, as presented in Table III.

Of the six laboratories surveyed none uses ASTM D-4779-93 to determine total organic carbon.

It is evident from Table III that detecting the ASTM required maximum permissible concentrations for chlorides, sodium, total silica, and total organic carbon is impossible under current analytical day-to-day operations of the laboratories. It comes as no surprise then that no commercial vendor of Type II water is able to provide lot or batch test certificates for their products.

During its RI/FS operations, Tetra Tech, Inc. chose to purchase commercially available purified water, and analyze each lot of 100 to 200 gallons for analytes of interest. The latter were selected on the basis of detected or suspected contaminants for the sites under investigation. Some or all of the following tests were conducted on the water samples, which were delivered to the laboratory unopened, and in their original containers.

Parameters	**Test Methods**
General Minerals	California Title 22
ICP Metals	SW6010
Arsenic	SW7060
Lead	SW7421
Mercury	SW7470
Selenium	SW7740
Total Organic Carbon	415.1
Silica as SiO_2	SW6010
Volatile Organics	SW8260
Semivolatile Organics	SW8270
Specific Conductance	E120.1

Four independent laboratories analyzed 17 samples of purified water. No analytes of interest as identified in past work were detected in the water analyzed. Although the purified water was supplied in heavy gauge 5 gallon polypropylene containers, the volatile and semivolatile organic tests did not indicate the presence of contaminants in the purified water traceable to the container material (Tables IV and V).

CONCLUSIONS

Since the current ASTM Type II reagent grade water specifications are difficult to adhere to and verify by readily available analytical means, it is recommended that commercially available purified water be used instead of ASTM Type II water, after testing a lot sample for analytes of interest.

It is also recommended that until ASTM clarifies the status of its Reagent Water Specification and the status of the related tests, a substitute specification be used, namely the one in use by the American Public Health Association (APHA).

Currently APHA, the American Water Works Association (AWWA), and the Water Environment Federation (WEF) use a less stringent Type II Reagent Water Specification[8], namely:

TABLE III
ASTM TYPE II WATER ANALYTE
PRACTICAL QUANTITATION LIMITS FOR SELECTED LABORATORIES

Parameter	**ASTM Specified Maximum Permissible Concentration in μg/L**	**Laboratory Suggested Method**	**Lab 1 located in EPA Region IX**	**Lab 2 located in EPA Region X**	**Lab 3 located in EPA Region IX**	**Lab located in EPA Region V**
Silica	3 μg/L	SW6010	200 μg/L	20 μg/L	200 μg/L	Not Applicable
Chlorides	5 μg/L	160.3	20 μg/L	1,000μg/L (Method 325.2)	Not applicable	100 μg/L (Method 300.0)
Sodium	5 μg/L	SW6010	2,000 μg/L	200 μg/L	not applicable	240 μg/L
Total Organic Carbon	50 μg/L	415.2	1,000 μg/L	500 μg/L (Method SW9060)	1,000 μg/L (Method 415.1)	5,000 μg/L (Method 415.1)

TABLE IV

Extraction Method: EPA Method 3520
Analytical Method: EPA Method 8270
Matrix: Water
Units: ug/L

Test Results of Semivolatile Organics in Purified Water
method 8270

Parameters	PQL	MDL	AUP-6	AUP-7	AUP-8	AUP-9	AUP-10	AUP-11	AUP-12	AUP-13	AUP-14
			4/6/93	6/17/93	8/11/93	9/9/93	12/16/93	12/16/93	2/17/94	4/7/94	4/7/94
Acenaphthene	10	8.8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthylene	10	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthracene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo (a) anthracene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo (b) fluoranthene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo (k) fluoranthene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo (g,h,i) perylene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo (a) pyrene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzyl alcohol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bis (2-Chloroethoxy) met	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bis (2-Chloroisopropyl) e	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bis (2-Chloroethyl) ether	10	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bis (2-Ethylhexyl) phthal	10	7	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Bromophenyl phenyl et	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Butyl benzyl phthalate	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Chloroaniline	10	5	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Chloronaphthalene	11	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Chlorophenyl phenyl et	10	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo (a,h) anthracene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzofuran	10	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Di-n-butyl phthalate	10	3	ND	ND	ND	ND	3.1J	ND	ND	ND	ND
1,2-Dichlorobenzene	10	8	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	10	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	10	10	ND	ND	ND	ND	ND	ND	ND	ND	ND
3,3'-Dichlorobenzidine	20	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethyl phthalate	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diethyl phthalate	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dinitrotoluene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,6-Dinitrotoluene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Di-n-octyl phthalate	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobutadiene	10	8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorocyclopentadie	10	10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachloroethane	10	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno (1,2,3-cd) pyrene	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Isophorone	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylnaphthalene	10	8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	11	11	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Nitroaniline	50	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Nitroaniline	50	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Nitroaniline	50	10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nitrobenzene	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
N-Nitrosodiphenylamine	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
N-Nitroso-di-n-propylami	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pyrene	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	10	9	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzoic Acid	50	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Chloro-3-methylphenol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Chlorophenol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dichlorophenol	10	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylphenol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,6-Dinitro-2-methylphen	50	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dinitrophenol	50	6	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylphenol (o-Cresol	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methylphenol (p-Cresol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Nitrophenol	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Nitrophenol	50	5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	30	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenol	10	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	50	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,6-Trichlorophenol	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND

J=DETECTED BETWEEN THE MDL AND PQL

TABLE V

Extraction Method: EPA Method 5030
Analytical Method: EPA Method 8260
Matrix: Water
Units: ug/L

Test Results ofVolatileOrganics in Purified Water
Method 8260

Parameters	PQL	MDL	AUP-6	AUP-7	AUP-8	AUP-9	AUP-10	AUP-11	Duplicate AUP-12A	AUP-13	AUP14
			4/6/93	6/17/93	8/11/93	9/9/93	12/16/93	12./16/93	3/9/94	4/7/94	4/7/94
Chloromethane	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromomethane	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl chloride	10	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	10	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylene Chloride	5	2	ND	19B	10	ND	ND	ND	ND	ND	ND
Acetone	10	10	ND	12	ND	ND	ND	ND	ND	10	12
Carbon disulfide	5	5	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethene	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,2-Dichloroethene	5	5	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,2-Dichloroethene	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl Ethyl Ketone	10	3	5J	ND	4J	4JB	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbon Tetrachloride	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl Acetate	10	10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloropropane	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethene	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibromochloromethane	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Chloroethyl vinyl ether	10	10	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Hexanone	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methyl Isobutyl Ketone	10	4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tetrachloroethene	5	3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorobenzene	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Styrene	5	2	ND	ND	ND	ND	ND	ND	ND	ND	ND
o-Xylene (1,2-Dimethylbenzene)	5	5	ND	ND	ND	ND	ND	ND	ND	ND	ND
m,p-Xylene (Sum of Isomers)	5	5	ND	ND	ND	ND	ND	ND	ND	ND	ND

APHA/AWWA/WEF Reagent Water Specification

Quality Parameter	Type II
Bacteria,CFU/mL	less than 1000
pH	not specified
Resistivity, megohm-cm at 25°C	greater than 1
Conductivity, μmho/cm at 25°C	1
SiO_2,mg/L	less than 0.1
Particulate matter	not specified
Organic contaminants	not specified

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IMPROVEMENTS TO EPA METHOD 335.2 FOR DETERMINATION OF TOTAL CYANIDE ACHIEVED BY OXIDATION OF INTERFERENCES

B.B. Potter, U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH 45268, *M Goldberg* and *A. Clayton*, Research Triangle Institute, Research Triangle Park, NC 27709

ABSTRACT

EPA Method 335.2 for the determination of total cyanide works well for simple cyanide salts in the absence of method interferences. However, industrial effluents may contain several interfering chemicals, including sulfide, thiocycanate, phenols, amines, oxidants, carbonates, aldehydes, sugars, fatty acids, and nitrite. Although other researchers have studied the effects of these interferences individually, no one has previously examined the effect of multiple interferences present simultaneously. We prepared test samples that simulated sewage treatment plant effluent and contained sulfide, thiocyanate, caffeine, nitrite, and hypochlorite. Samples were analyzed for cyanide content using Method 335.2 with a colorimetric endpoint. Results indicated that the relationship between measured cyanide concentration and the known amounts of cyanide and interferences is complex. Not only do the interferences exhibit a significant effect individually, they also exhibit significant interaction effects. Experiments performed using potassium permanganate and sodium vanadate indicated that either oxidant effectively removes most of the interference effects. However, an exact stoichiometric amount of permanganate was required for accurate cyanide; the presence of excess permanganate caused oxidation of cyanide. and thus low recovery. Excess vanadate was well tolerated by the method, and accurate analysis of cyanide was achieved even when sulfide, caffeine, nitrite, and p-cresol were present in the cyanide sample. However, neither oxidant was capable of removing the interfering effects of thiocyanate, and the use of vanadate can only be recommended in the absence of thiocyanate.

ANALYSIS OF As, Pb, Se and Tl IN SOLID WASTE USING THE TJA 61E TRACE ANALYZER ICP

Mark E. Tatro, Spectra, Inc., P.O. Box 1176, McAfee, NJ 07428; Larry Camp and Rick Christenberry, Progress Environmental Laboratory, 4420 Pendola Point Road, Tampa, FL 33619

ABSTRACT

The Thermo Jarrell Ash [TJA] 61E Trace Analyzer ICP has been claimed by the manufacturer to give detection limits comparable to Furnace AA for most elements. Typically most environmental laboratories use Furnace AA for the analysis of As, Pb, Se and Tl to meet the EPA Contract Laboratory Program (CLP) required detection limits of 10, 3, 5 and 10 ng/ml, respectively (1). We investigated the manufacturer's claims by developing methods for the analysis of As, Pb, Se and Tl in wastewater and solid waste to verify that the Trace Analyzer could replace Furnace AA analysis. Our results showed that with careful programming of background correction and inter-element correction factors, that method detection limits of 2.4, 1.4, 1.7 and 1.4 ppb for As, Pb, Se and Tl respectively can be obtained, that recoveries for these four analytes in the CLP ICP Interference Check Sample are in the 90% range, and that recoveries of these four analytes from real world spiked solid waste samples are very acceptable.

INTRODUCTION

Progress Environmental Laboratory [PEL] purchased a TJA 61E Trace Analyzer to fulfill the requirements of a contract to analyze solid waste samples for a number of analytes including As, Pb, Se and Tl. The manufacturer claims that the 61E Trace Analyzer can meet Furnace AA detection limits and PEL saw the obvious productivity advantages of analyzing for all elements by simultaneous ICP. PEL called in SPECTRA Spectroscopy & Chromatography Specialists, Inc. [SPECTRA] to develop the ICP methods for the 12 required contract elements including As, Pb, Se and Tl.

The problem with analyzing As, Pb, Se and Tl by ICP for environmental applications are typically twofold. One is that the signal to noise ratio is too low to meet the required detection limits; and, the other is that the emission from aluminum and iron, usually present at high concentrations, interferes with the analyte wavelength emission particularly for Pb and Se.

The 61E Trace Analyzer solves the signal to noise drawback by mounting the plasma torch horizontally so that the optical path is coincident with the plasma. This allows a larger segment of the plasma to be viewed than in the typical vertical mounted torch configuration. A redesign of the transfer optics improves the analyte signal intensitywithout increasing the background intensity (2).

The blank corrected signal for 1 ug/ml Cd using the conventional vertical torch configuration of the TJA 61 ICP is 703 intensity units as measured by SPECTRA during a previous methods development course. The blank corrected signal for 1 ug/ml Cd using the horizontal torch configuration of the 61E Trace Analyzer is 39,568 as measured here. Therefore, the 61E Trace Analyzer ICP provides a blank corrected signal enhancement of 56X for cadmium.

The 61E Trace Analyzer solves the background correction from aluminum and iron on Pb and Se by a simultaneous background correction technique where the analyte peak is measured at one wavelength order and the background is measured at another wavelength order simultaneously and by an improved wavelength resolution from the incorporation of a holographic grating. A dummy ''S'' channel is used to monitor the first and second order wavelengths of Pb and Se.

EXPERIMENTAL

The 61E Trace Analyzer ICP is equipped with a 2kW RF generator controlled at 27.12 MHz, built in peristaltic pump, concentric glass nebulizer, glass spray chamber and demountable quartz torch. The optics consist of a 0.75 m Rowland Circle with a Paschen-Runge mount 2400 grooves/mm holographic grating blazed at 500 nm. The system is interfaced to an IBM/ AT 386-33 computer using the ThermoSPEC software. The ICP conditions used for analysis are detailed in Table 1.

The logic followed by SPECTRA for setting ICP background correction intervals is to use the graphics capabilities to ''let the instrument speak for itself'' (3). Standards were prepared for setting background correction positions using 1,000 and 10,000 ug/ml plasma grade standards from J.T. Baker. The standards were (a) matrix blank; (b) 1 ug/ml As, Pb, Se and Tl; (c) 10 ug/ml Cr, Mn and V; and (d) 500 ug/ml Al, Ca, Mg and 200 ug/ml Fe. Since the samples would be in a matrix of 1% HNO_3 + 5% HCl following the SW-846 Method 3050 digestion procedure, all standards were prepared in this same matrix using J.T. Baker Instra-Analyzed grade acids. Scans were made using the four multi-element standards and overlayed to set the background correction positions for As, Pb, Se and Tl. The background correction positions chosen are detailed in Table 2. The two separate positions for Pb and Se represent the first and second order wavelength lines for these two elements.

To determine IEC's, the ICP was programmed with a series of four standards in a water matrix. We did not use the acid matrix to avoid contaminating the standards with Instra-Analyzed grade acids. The calibration standards used were (a) blank; (b) 1000 ng/ml As, Pb, Se, Tl; (c) 500 ug/ml Al, Ca, Mg and 200 ug/ml Fe; and (d) 10 ug/ml Cr, Mn and V. After calibration, the following standards were analyzed to calculate the IEC's: (a) 500 ug/ml Al; (b) 200 ug/ml Fe; (c) 500 ug/ml Ca; (d) 500 ug/ml Mg; (e) 10 ug/ml Cr; (f) 10 ug/ml Mn; (g) 10 ug/ml V.

We found it very useful to use the command function of the ThermoSPEC software to evaluate the effectiveness of the IECs. After the analysis of each standard, e.g. the 500 ug/ml Al, we saved the results that had not been corrected by IECs using the command function srd''500Al''. After entering the IECs for aluminum on the affected analytes into the program, we used the command function lrd''500Al''rdpv. This command applies the IECs to all the affected analytes and prints out a data sheet that shows the analytical results with the IECs applied. In this way we could estimate immediately if the IECs corrected interferences.

Table 3 details the IECs that were calculated from our study. We used the analyzed value for the interferent rather than the theoretical value. We were surprised to see IECs with values such as -2.4202 for the affect of V on Tl since we have been used to seeing IECs with values of 10^{-3} and 10^{-4}. The large IECs are due to the fact that for the traces such as As, Pb, Se and Tl the standards are programmed as ppb and the interferents are programmed as ppm. Therefore, the IEC for V on the Tl line was calculated as -24.71 ppb Tl/10.21 ppm V = -2.4202.

The proof of correct entries for background correction and IECs is the analysis of the EPA ICS [AB] standard. We prepared an ICS [AB] standard and spiked it with 500 ppb As, Se and Tl. The concentration of Pb in this standard is set at 1000 ppb. Table 4 details the recoveries obtained on the ICS [AB] standard. The EPA Contract Laboratory Program recommends recoveries between 80 to 120% for this standard. Our results were all well within these limits.

To determine method detection limits [MDLs] a multi-element standard was prepared containing all the elements of interest at a concentration of 3-5 times the reported instrument detection limit as required by EPA (4). Seven aliquots of the standard were digested using SW846 Method 3050 and analyzed as separate samples. Table 5 details the MDL concentrations determined from this study. The MDLs demonstrate that the 61E Trace Analyzer can meet EPA CLP detection limits for As, Pb, Se and Tl.

Over the course of one month, 20 individual 1.0 gram aliquots of different soil samples from the contract study at PEL were pre-digestion spiked with 250 uL of a 100 ug/ml multi-element standard and brought up to 100 mls following digestion by the staff at PEL. The spike levels were, therefore, 250 ng/ml in solution or 25 ug/gm on a w/w basis. Each soil sample was analyzed on a separate day and the recoveries calculated to formulate a Shewart Accuracy Control Chart. The average recoveries with 1 sigma standard deviations are detailed in Table 6.

SUMMARY

The TJA 61E Trace Analyzer ICP system is capable of replacing Furnace AA for the analysis of As, Pb, Se and Tl in solid waste samples. We found that the greatly improved sensitivity of this instrument providing MDLs at the < 1 ppb levels, requires the laboratory personnel to pay special attention to purity of standards and acids as well as contamination from the environment.

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TABLE 1

PARAMETER	SETTING
Number of Repeats	3
Integration	15 sec
Flush Time	45 sec
Torch Gas	High Flow
Auxilary Gas Flow	Low Flow
Nebulizer Pressure	30 psi
RF Power	950 W
Analysis Pump Rate	130
Flush Pump Rate	130
Relaxation Rate	0
Pump Tubing	Tygon-Orange

TABLE 2

ELEMENT	BGC OFFSET
As	- 15
Pb (1: +10 SS)	- 10
Pb (2: - 10 SS)	+10
Se (1: +10 SS)	- 10
Se (2: - 10 SS)	+10
Tl	- 15

TABLE 3

ANALYTE	INTERFERENT	k1
As1890	Fe2714	- 0.071890
	Al3082	0.008193
	Ca3179	0.026903
	Mg2790	0.004294
	Cr2677	0.165659
Pb2203-1	Fe2714	0.089876
	Al3082	0.394050
	Mg2790	0.003921
Pb2203-2	Fe2714	0.050755
	Al3082	- 0.185810
	Mg2790	0.004528
	Cr2677	0.244488
	V 2924	- 0.314890
Se1960-1	Fe2714	- 0.026270
Se1960-2	Fe2714	- 0.240540
	Mn2576	0.283170
Tl1908	Fe2714	- 0.212650
	Cr2677	0.220098
	Mn2576	0.215604
	V 2924	- 2.420200

"S" CHANNEL	WAVELENGTH	k1
Pb 2203	2203-1	- 0.333
	2203-2	- 0.667
Se 1960	1960-1	- 0.333
	1960-2	- 0.667

TABLE 4

ELEMENT	% R FROM ICS [AB]
As	94
Pb	92
Se	90
Tl	90

TABLE 5

ELEMENT	MDL (ppb)
As	2.4
Pb	1.4
Se	1.7
Tl	1.4

TABLE 6

ELEMENT	SOIL SPIKE RECOVERY (%)
As	92.9 ± 10.9
Pb	102.8 ± 7.4
Se	86.8 ± 16.7
Tl	102.8 ± 8.5

TRACE METAL VALENCE STATE CONSIDERATION WHEN USING ULTRASONIC NEBULIZER AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES).

Carol A. Brockhoff, U.S. Environmental Protection Agency, Chemistry Research Division, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268, Theodore D. Martin, U.S. EPA, CRD, EMSL-Cinti, Cinti, OH 45268, and John T. Creed, U.S. EPA, CRD, EMSL-Cinti, Cinti, OH 45268

ABSTRACT

In recent years there has been a need to measure trace metal concentrations in ambient and drinking waters at lower and lower concentrations. Under the Safe Drinking Water Act the maximum contaminant level (MCL) of some primary metal contaminants have been lowered to the exclusion of ICP-AES from the list of approved methodology for compliance monitoring of these analytes. New regulations based on water quality criteria have placed new sensitivity requirements on methodologies that can be used for the monitoring of ambient waters. Although widely used for many types analyses, ICP-AES has limited acceptance under these more demanding conditions. The utility of ICP-AES can be extended by utilizing an ultrasonic nebulizer to achieve improved sensitivity.

The 3-10 fold decrease in detection limits achieved with the ultrasonic nebulizer are not accomplished, however, without some analytical limitations. In this paper data will be presented demonstrating the limitation induced by the desolvation system on the determination of arsenic, chromium, and selenium in aqueous matrices. The desolvation step used in ultrasonic nebulization induces a different signal response for the two valence states of arsenic [As(III) vs As(V)] and chromium [Cr(III) vs Cr(VI)], a phenomenon which does not occur with pneumatic nebulization. For 1 mg/L solutions As(V) showed a 60% enhancement over As(III), while Cr(III) showed a 30% enhancement over Cr(VI). If hydrogen peroxide is added to a mixed acid (HNO_3 + HCl) solution of these analytes, As(III) is oxidized to As(V) and Cr(VI) is reduced to Cr(III). This simple addition of H_2O_2 to both sample and standard solutions alike brings these analytes to a common valence state and eliminates the difference in signal response.

In the case of selenium the enhanced analytical response is dependent on the presence of concomitant elements. The degree of enhancement is not only dependent on the particular element(s) in solution, but also their concentration. Different concomitant mixtures will produce different degrees of enhancement. A common drinking water matrix or a 1 mg/L solution of ICP-19 will produce ≈ 100% increase in signal over a 1 mg/L single element solution of selenium. One way to circumvent this matrix interference is to prepare a matrix matched calibration standard that approximates routine samples.

These analytical limitations are discussed in greater detail in the poster, a must stop on your poster paper tour.

Analysis of Silver and Other Elements by Toxicity Characterization Leaching Procedure (TCLP, SW 846 1311)

David Eugene Kimbrough*, Public Health Chemist II, Jayavant Patel, Public Health Chemist I, Janice Wakakuwa, Supervising Chemist, California Environmental Protection Agency, Department of Toxic Substances Control, Southern California Laboratory, 1449 W. Temple Street, Los Angeles California 90026-5698.

Abstract

Under Federal and State law a material is considered hazardous if exhibits the "characteristic of toxicity" as determined by the Toxicity Characterization Leaching Procedure, or TCLP, (SW 846 as method 1311). There are eight metals that can be tested by the TCLP which are silver, arsenic, barium, cadmium, chromium, lead, mercury, and selenium. This test using one of two acetic acid buffers to the amount of these elements which will leach in a landfill.

A study is presented on the solubility of silver and fifteen other elements using both of the TCLP buffers and a citric acid buffer used in similar leaching test mandated by California law (the Waste Extraction Test). The solubility of silver nitrate, silver chloride, and silver sulfate are all tested alone and with soils. Real world and laboratory control samples are also tested.

While reagent grade silver nitrate and sulfate are very soluble, silver chloride is high insoluble. During the extraction of real world materials, buffer silver nitrate and sulfate form highly insoluble silver salts. Thus, it is enormously unlikely for any real world material every to be determined to be hazardous using this test.

INTRODUCTION TO THE USEPA, METHOD 245.7, DETERMINATION OF MERCURY BY AUTOMATED COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY.

Billy B. Potter, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio; William H. McDaniel, Jenny Scifres, Michael A. Wasko, U.S. Environmental Protection Agency, Region 4, Athens, Georgia; Winslow J. Bashe and Miguel D. Castellanos, Technology Applications, Inc., Cincinnati, Ohio.

ABSTRACT

The U.S. Environmental Protection Agency (USEPA), Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) and Region 4, Environmental Services Division, Laboratory, Athens Ga., have developed EPA Method 245.7 for the determination of total and dissolved mercury found in water. The mercury method has an estimated method detection limit (MDL) that ranges between 0.3 ppt to 5 ppt of mercury. The MDL is made possible by digesting the sample using bromide/bromate reagent followed by detection of elemental mercury by cold vapor atomic fluorescence spectrometry at 253.7 nm.

INTRODUCTION

The METHOD 245.7, DETERMINATION OF MERCURY BY AUTOMATED COLD VAPOR, ATOMIC FLUORESCENCE SPECTROMETRY is written in the Environmental Monitoring Management Council (EMMC) method format. The EMMC format consists of the following sections:

1.0 SCOPE AND APPLICATION
2.0 SUMMARY OF METHOD
3.0 DEFINITIONS
4.0 INTERFERENCES
5.0 SAFETY
6.0 APPARATUS, EQUIPMENT, LABORATORY AND CLEANING REQUIREMENTS
7.0 REAGENTS AND CONSUMABLE MATERIALS
8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE
9.0 QUALITY CONTROL
10.0 CALIBRATION AND STANDARDIZATION
11.0 PROCEDURE
12.0 DATA ANALYSIS AND CALCULATIONS
13.0 METHOD PERFORMANCE
14.0 POLLUTION PREVENTION
15.0 WASTE MANAGEMENT
16.0 REFERENCES
17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Each section addresses the details of the method application, procedures and quality control issues necessary for the proper execution of the method.

Method 245.7 describes procedures for the determination of mercury (organic + inorganic) total recoverable or dissolved (filtered 0.45μ), in drinking water, surface and ground water, sea and brackish water, industrial and domestic wastewaters. The chemistry of sample digestion is based on the brominating reagent produces bromine monochloride:

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3KCl + 3H_2O$$

In the presence of excess bromide ions and acid, the bromine monochloride is then converted to free bromine[1]:

$$BrCl + \text{excess } KBr \rightarrow Br_2 + KCl$$

Mercury from inorganic mercury compounds are rapidly oxidized by bromine and organomercury species are degraded by the oxidizing properties of bromine releasing mercury (II)[2,3] as follows:

$$HgR_2 + Br_2 \rightarrow RHgBr + RBr$$

$$RHgBr + Br_2 \rightarrow HgBr_2 + RBr$$

The excess Br_2 reacts to oxidize mercury to form a complex. After the oxidation reactions are complete, excess bromine is removed by the addition of hydroxylamine hydrochloride.

The elemental mercury vapor is generated from the digested sample by reduction with stannous (tin II) chloride in the presence of hydrochloric acid[4]. High purity argon gas is used to purge the mercury vapor from a gas/liquid separator driving the equilibrium to the right as follows:

$$Sn^{+2} + Hg^{+2} \rightarrow (Ar\uparrow),\ Hg^{o}\uparrow + Sn^{+4}\downarrow$$

The excess $Sn^{+2}\downarrow$, $HCl\downarrow$, solution is discharged to a waste container and the mercury vapor is carried by the argon flow to the mercury concentrator or detector. The liquid containing spent reagents and sample are flushed continuously from the gas/liquid separator to a waste container. This waste contains tin and hydrochloric acid and does not contain mercury. The elemental mercury vapor is then purged from solution by a carrier stream of argon through a semi-permeable dryer tube[5] that removes water vapor.

For additional sensitivity mercury vapor may be concentrated on the optional gold amalgam concentrator. The concentrator is then heated rapidly to 450°C. The concentrated mercury vapor passes to the detector and is integrated as a peak. If the concentrator is not used, the vapor passes directly to the detector and is measured as a change in the rise (height) from the baseline. The mercury vapor concentration is determined by atomic fluorescence spectrometry at 253.7 nm[6,79]

The method was optimized using a statistically-based experimental design or chemometric approach as described by Deming and Morgan (1987)[10]. The chemometric experimental approach was applied to this mercury method to speed the process of method evaluation. The chemometric approach is dynamic (modifiable) and recursive (experiments may be repeated). During the execution of the experiments an evaluation of each "phase" of an experiment is required. When a modification of the experiment was required, it was strongly supported by the statistical evidence. The experimental design consisted of the following phases:

Phase 1 Familiarization Study.
Phase 2 Automated Instrument Optimization Study.
Phase 3 Automated Instrument Linearity Study.
Phase 4 Mercury Precision and Recovery Study.
Phase 5 Instrument Stability Study.
Phase 6 Initial Interference Study.
Phase 7 Sample Preservation Study.
Phase 8 Single Laboratory Validation Study.
Phase 9 Establish Instrument Control Charts.
Phase 10 Establish Clean Laboratory Protocol.

The automated instrument is generally configured as shown below. The gold amalgam accessory for the instrument system is not shown in this configuration. The gold amalgam accessory will be evaluated during the ruggedness testing part of the method development and is not part of the scope of this experimentation.

In the familiarization and optimization phase of the experiments, the mercury analyzer was optimized for maximum sensitivity and/or signal-to-noise ratio. The use of Simplex optimization was investigated using the carrier gas and sheath gas flow rates as selected variables. A range for optimized settings was found as described in Table 1. These settings may be changed periodically to optimize the instrument. Small changes, as long as they remain within the specified ranges, do not adversely effect the instruments performance. However one setting was made and procedures were held constant for the remaining experiments.

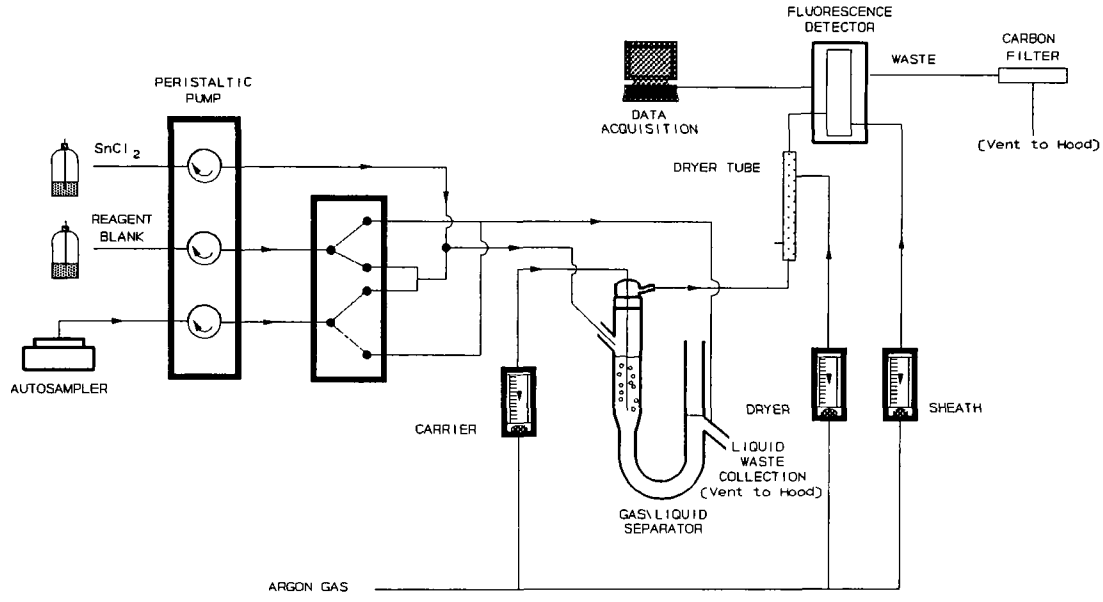

FIGURE 1: PSA AUTOMATED MERCURY FLUORESCENCE SYSTEM

INSTRUMENT CONTROL SETTING AND ARGON GAS FLOW SETTINGS	
Fluorescence Instrument Parameters	PSA *Merlin* Series AFS Range of Settings
Delay Time	5 to 15 seconds
Rise Time	20 to 30 seconds
Analysis Time	30 seconds
Memory Time	60 seconds
Argon Gas Control	Range of Settings
Gas Regulator	20 to 30 psi.
Carrier Flow	150 to 450 mL/minute
Drier Tube Flow	2.5 to 3.5 L/minute
Sheath Flow	150 to 250 mL/minute

The Method 245.7 procedure used is based on a method used by the Yorkshire Water Authority (YWA) in the United Kingdom[11]. The method procedure is simplified and summarized as follows:

1) Add 5 mL (1+1) hydrochloric acid and 1 mL 0.1N potassium bromate/potassium bromide solution to a 50 mL conical vial.

2) Transfer of sample to conical vial filling to the 50 mL mark.

3) Allow samples to stand for at least 30 minutes before analysis.

4) Add 50 μL hydroxylamine hydrochloride solution to each conical vial.

5) Turn on the automated instrument/detector and allow to stabilize.

6) The sample enters gas/liquid separator with $SnCl_2$ to form mercury vapor.

7) The vapor is analyzed by cold vapor atomic fluorescence spectrometry.

DISCUSSION

The determination of total mercury by automated cold vapor atomic fluorescence spectrometry has a linear range approximately 2 ng-Hg/L to 25 μg-Hg/L. The MDLs as calculated are as follows:

METHOD DETECTION LIMITS FOR MERCURY (ng Hg/L)			
MATRIX	EPA\EMSL-Cin. Glove Box MDL	EPA\Region 4 Clean Room MDL	S.E. Environ. Research, FIU MDL
Reagent Water	1.8	0.31 to 1.0	0.27 to 0.59
Florida Marsh Water	3.3		
Synthetic Sea Water	2.6		
Sea Water			1.4
Lake Water			0.33
Waste Water			0.40

The MDL's may then be used for enforcement of water quality-based effluent limitations (WQBELs) by establishing the interim minimum level (Interim ML) for mercury. The Interim ML is calculated when a method-specific ML does not exist. It is calculated by multiplying the MDL by 3.18. The factor of 3.18 is derived from the ACS definition of level of quantitation (LOQ) that is 10 standard deviation above the average blank signal and is divided by the 3.14 (student t value) for the MDL, i.e. $3.18=10/3.14_t$ for n=7. The calculated ML is then rounded up to 1, 2, 5, 10, 20, 50, etc. The Interim ML for mercury would then range from 5 to 20 ppt depending on the water matrix and the laboratories skill. The interim ML for mercury concentrations would be 10 to 20 times higher than most ambient concentrations found in natural waters. If the risk assessment is used to establish an ML, it is conceivable that the ML will fall below the ambient level for mercury and below the MDL for this method.

ACKNOWLEDGEMENTS

The following individuals are acknowledged for their contributions to this project: Professor Peter Stockwell, Paul Stockwell and Dr. Warren Corns, (P.S. Analytical Ltd., Kent, UK) and Jim Coates (Questron Corporation, Princeton, NJ) are thanked for their technical support. Dr. Ron Jones (Florida International University, Miami, FL) is gratefully acknowledged for providing the surface water sample from the Everglades National Park, Florida and for providing method detection limits.

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DETERMINATION OF SELECTED METALS BY PORTABLE X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

Victoria Taylor, Region 9 Environmental Services Assistance Team, ICF Kaiser, San Francisco, California, 94105

ABSTRACT

X-ray fluorescence (XRF) spectroscopy provides a means for profiling heavy metals contamination quickly through the rapid screening of environmental samples. A study was conducted to estimate the reliability of analytical results generated by XRF for use in site characterization. The purpose of this study was to evaluate the effectiveness of XRF spectroscopy as a field screening tool for the determination of metal and to present field samplers with a technique to reduce the number of fixed laboratory sample analyses and to shorten the time required to obtain usable results. A portable XRF, X-MET 920 (Outokumpu Electronics, Inc.), was used to analyze soil samples collected from two Superfund sites for mercury, lead and zinc. The effects of sample preparation and instrument standardization techniques on data reliability were tested by comparing XRF results to fixed laboratory results generated for the same soil samples. The variable parameters evaluated were the physical sample matrix and the type of materials used to prepare instrument calibration standards. Samples were analyzed directly and after drying and fractionation to a uniform particle size. These studies were designed to test the effects of the sample matrix on method performance. Two types of calibration standards were used to evaluate the effects resulting from the use of different instrument calibration materials: 1) field samples that were previously analyzed by a fixed laboratory to establish contaminant levels, and 2) site background samples into which known quantities of target elements, both as salts and aqueous solutions, were added. The results of this study show that XRF screening may be used to expedite field operations by reducing the number of samples that require fixed laboratory analysis, and to provide reliable concentration profiles for metals contamination in soil.

INTRODUCTION

XRF analysis is based on the interaction of a characteristic X-ray with elements in the sample. The incident or primary X-ray from the probe source has sufficient energy to eject an inner shell electron from the target element. The loss of the inner shell electron creates an opportunity for an outer shell, higher energy, electron to fall into the inner shell vacancy, with loss of energy. This loss of energy is emitted as an X-ray and is detected by the high resolution S(Li) detector in the X-Met 920 Surface Analysis Probe. This process is presented schematically in Figure 1.

For this study, soil samples were obtained from two different site investigations. Twenty four samples, collected as part of a remedial investigation to determine the extent of mercury contamination from mill tailings piles, were analyzed for mercury by XRF and by an EPA Contract Laboratory Program (CLP) laboratory by cold vapor atomic absorption spectroscopy (CVAAS). The samples from the mercury investigation were used to perform initial tests to determine the acceptability of different techniques of standardization. A second set of 37 soil samples was collected as part of a removal project for which the target analytes were lead and zinc. For this project, the XRF was used in the field to analyze samples during the removal activity. All of the samples from the removal project were analyzed by two CLP laboratories using Inductively Coupled Plasma (ICP) Emission Spectroscopy and by the field laboratory using XRF.

EXPERIMENTAL

XRF Sample Preparation: Samples for XRF determination of lead and zinc were prepared by drying and then sieving through a 100 mesh screen. The samples for the mercury investigation were prepared by sieving without drying prior to both CVAAS and XRF analysis. The samples analyzed for lead and zinc were submitted to one CLP laboratory sieved and dried, and to the second CLP laboratory as collected, with the final concentration adjusted for sample percent moisture.

Calibration Sample Preparation: Three techniques were used to obtain calibration standards for mercury XRF analysis. Background samples, which were found to contain no analytes above the XRF limit of detection, were fortified with the elements of interest by the addition of either aqueous solutions or elemental salts. The third type of calibration standard was obtained by selection of field samples which contained an acceptable concentration range of target analytes as determined by fixed laboratory analysis. These samples were treated as calibration standards and the ICP assay was accepted as the true concentration. Calibration samples for the zinc and lead analyses were prepared by fortification of a site background sample with aqueous standards.

Calibration: Individual sample curves were prepared for each metal using the procedures contained in the Outokumpu software. After spectra for each calibration level were collected, a regression equation was selected from the possible combinations from the terms contained in the multivariate regression equation:

$$C_i = b_0 \sum (m_{ij} * f_j)$$

$$\text{where} \quad \begin{aligned} f_j &= I_j \\ f_j &= I_j * I_j \\ f_j &= I_j * I_i \\ f_j &= I_j / Bs \\ f_j &= I_j * I_j / Bs \\ f_j &= 1 / Bs \\ f_j &= 1 / I_j \end{aligned}$$

Several terms may be selected to account for interelement interferences. Acceptable calibration models were selected based on the correlation coefficient and the difference between the standard concentrations determined from the regression line and the true values.

RESULTS AND DISCUSSION

Mercury Determination by XRF: Mercury calibration curves were prepared from a mill tailings pile sample which was below the XRF limit of detection. Nine 3 gram aliquoits of this sample were fortified with mercury from an aqueous atomic absorption standard so that the calibration samples covered the range of 30 to 1600 ppm. A second set of calibration standards were prepared by fortification of aliquoits of the same field sample with arsenic trioxide, resulting in calibration samples with a concentration range of 100 to 15000 ppm of mercury. The third set of calibration standards were obtained from actual field samples, analyzed by CVAAS. The CVAAS results were accepted as the true value and the concentration range of this set of calibration samples was 51 to 1650 ppm. An

unfortified aliquot of the sample was used along with the other fortified samples to construct the calibration curve. The following correlation coefficients were obtained for the calibration models constructed based on the mercury response obtained from each of the calibration sets:

Type of Calibration Sample	Correlation Coefficient
Liquid Fortified	0.998
As_2O_3 Fortified	1.000
Field Samples	0.981

Each standard preparation method appears to produce equivalent linearity. The regression equation used for these calibrations contained one term, with the exception of the As_2O_3 fortified samples. Because of the increased calibration range compared to the ranges obtained with the other calibration techniques, a cross product term was used to account for the nonlinearity encountered at the higher concentrations. The use of a multiterm calibration model did not appear to introduce any bias in the XRF results compared to the fixed laboratory results. Table 1 presents the results of mercury determination using different calibration methods in selected samples:

Table 1: Mercury Results Obtained Under Three XRF Calibration Methods and CVAAS

Sample Number	CVAAS	XRF: Liquid Fortification Calibration	XRF: Solid Fortification Calibration	XRF: Field Sample Calibration	n	Coefficient of Variation
1	1950	1970	550	550	4	49
2	150	210	-----	240	3	7
3	960	1.2	190	28	4	41
4	790	1980	-----	-----	2	21
5	41	110	200	100	4	35
6	0.57	2.6	-----	-----	2	32
7	110	100	100	87	4	6
8	650	2820	1280	1330	4	41
9	260	380	440	-----	3	9
10	0.22	16	45	0	4	106
11	620	450	630	350	4	20
12	310	300	-----	-----	2	0.5
13	77	69	88	70	4	10
14	1230	2560	-----	-----	2	18
15	750	1750	1090	900	4	29
16	1480	830	630	-----	3	15
17	124	334	255	260	4	15
18	110	180	-----	-----	2	12
19	840	640	400	-----	3	18
20	51	72	-----	-----	2	8

Sample Number	CVAAS	XRF: Liquid Fortification Calibration	XRF: Solid Fortification Calibration	XRF: Field Sample Calibration	n	Coefficient of Variation
21	9.8	990	-----	560	3	41
22	800	1600	1080	850	4	25
23	650	1160	-----	-----	2	14
24	17	87	-----	-----	2	16

The results listed above are presented as a bar graph in Figure 2. There are two results which appear questionable. In the case of samples 3 and 21, the CVAAS results and each of the XRF analyses differ by an order of magnitude or more. The source of this difference may be sample nonhomogenaity, or may be the result of an error in sample identification by one or both of the laboratories. Because of this large discrepancy, the results for samples 3 and 21 were not included in the comparison. For each of the calibration methods, the XRF results were plotted against the CVAAS results and the linear regression equation calculated. These plots are presented in Figures 3 through 5. For the regression plots, the log value of concentration was used to maintain a reasonable scale.

Lead and Zinc Determination by XRF: Table 2 presents the results for lead determined by XRF and CLP with the coefficient of variation:

Table 2: Lead Results Obtained by XRF and CLP Analysis

Sample Number	XRF Lead ppm	CLP1 Lead ppm	CLP2 Lead ppm	%CV
1	6830	2450	330	84
2	5260	3410	2460	31
3	2450	1080	900	47
4	1200	1010	260	49
5	430	310	190	32
6	730	550	100	58
7	2090	1600	900	32
8	3920	1720	1170	52
9	1420	570	420	55
10	15000	13000	9140	20
11	3420	2450	6970	45
12	590	1620	1060	38
13	1020	730	500	29
14	1750	1030	530	45
15	6920	3300	4020	33
16	290	120	110	46
17	300	100	80	62
18	3660	3220	4420	13

Sample Number	XRF Lead ppm	CLP1 Lead ppm	CLP2 Lead ppm	%CV
19	1510	620	580	48
20	1100	540	500	38
21	1310	920	1230	15
22	1510	720	350	56
23	1880	700	27	88
24	3360	1750	1080	46
25	5620	3170	2540	35
26	9000	2770	6140	43
27	6300	3560	2370	40
28	7630	3440	4610	34
29	1200	600	370	48
30	5422	4420	3240	20
31	1470	920	490	42
32	6740	1620	1520	74
33	480	300	230	31
34	150	70	40	54
35	1430	830	580	38
36	5850	2440	2310	46
37	5390	2470	640	69

The lead results are presented as a bar plot in Figure 6. The Table 3 presents the nineteen comparable zinc results obtained by XRF analysis and ICP analysis following EPA CLP Statement of Work (SOW) protocols.

Table 3: Zinc Results Obtained by XRF and CLP Analysis

Sample	XRF Zinc ppm	CLP1 Zinc ppm	CLP2 Zinc ppm	%CV
1	160	100	79	32
2	180	200	130	16
3	630	550	480	11
4	79	230	190	39
5	170	170	110	20
6	73	98	110	16
7	120	96	86	16
8	65	190	150	39
9	2310	1060	770	48
10	150	260	180	23

Sample	XRF Zinc ppm	CLP1 Zinc ppm	CLP2 Zinc ppm	%CV
11	71	110	100	18
12	73	92	81	10
13	480	320	570	23
14	110	210	140	25
15	260	410	340	18
16	110	170	57	41
17	410	400	320	10
18	1210	760	861	20
19	1250	820	310	48

The zinc results are presented as a bar graph in Figure 7. The 37 lead and 19 zinc results reported by each of the laboratories were used to prepare linear regression plots to determine the level of correlation. As in the case of the mercury regression plots, a log scale was used for the graphical presentation. Figures 8 and 9 present the results of regression plots for lead and zinc. The extent of correlation between data sets may be estimated by the correlation coefficient, where an r value of 1 represents perfect correlation. For mercury, each of the methods of standard preparation appear to produce data which are correlated with the analysis performed by a CLP laboratory using CVAAS.

The samples analyzed for lead and zinc were analyzed by two different CLP laboratories. In the case of the first CLP laboratory (CLP1), the samples were dried and sieved in a manner identical to the XRF preparation method. In the case of the second CLP laboratory (CLP2), the samples were analyzed on a as received basis and the final result adjusted for sample percent moisture. The effectiveness of drying and sieving samples prior to XRF analysis reduces measurement variations due to random X-ray scattering due to uneven sample particle size distribution. The fractionation of samples does not appear to significantly effect the ICP results, since the CLP1 results are very similar to the CLP2 results, although the correlation with the XRF results is higher for CLP1 than CLP2.

In the case of mercury analysis, no systematic bias was observed between the results obtained from XRF or CVAAS, and no one method of calibration standard preparation appears to produce superior correlation. In the case of lead and zinc analysis, the XRF results are biased high with respect to the ICP results from both laboratories, most significantly with respect to the lead analyses. In the case of both the regression plots for lead and zinc, the slope of the regression line is less than 1, confirming a trend toward high bias on the part of the XRF.

Use of a X-Ray fluorescent spectrometer provides a means for site investigations to obtain high density profiles of site contamination very rapidly. During the removal investigation a total of 125 samples were analyzed over a period of three days and individual sample results were available within a few hours from collection.

Based on the comparison of these data sets, the XRF technique provides information which is in good agreement with fixed laboratory ICP results. Successful calibration samples may be prepared by fortification of site background samples with liquid standards or solid reagents, or by analysis of independently assayed field samples.

Acknowledgements: Special thanks to Beiyi Chen for the experimental work on the XRF.

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Figure 1: Production of X-Rays

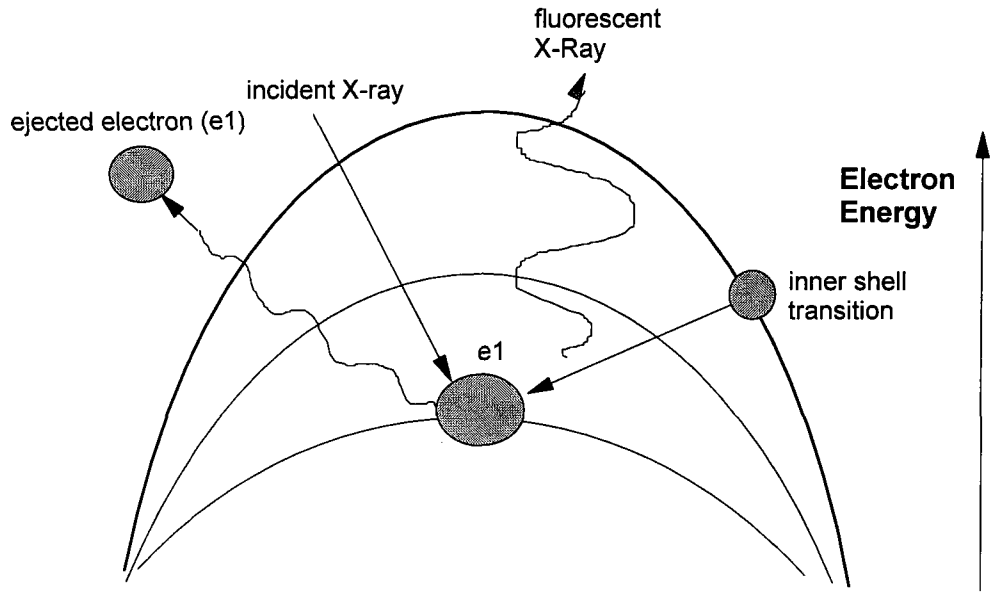


Figure 2: Comparison of Mercury Results From CVAAS and XRF

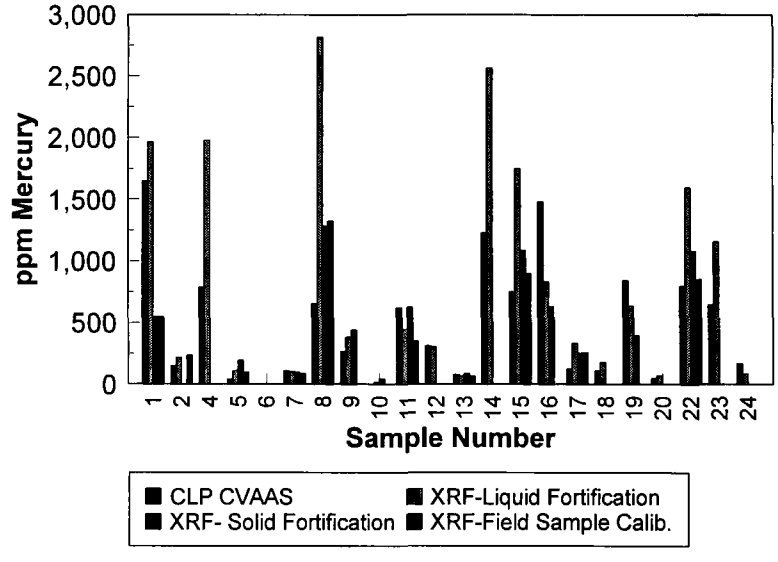


Figure 3: XRF Mercury Results using Liquid Standards vs CVAAS Results

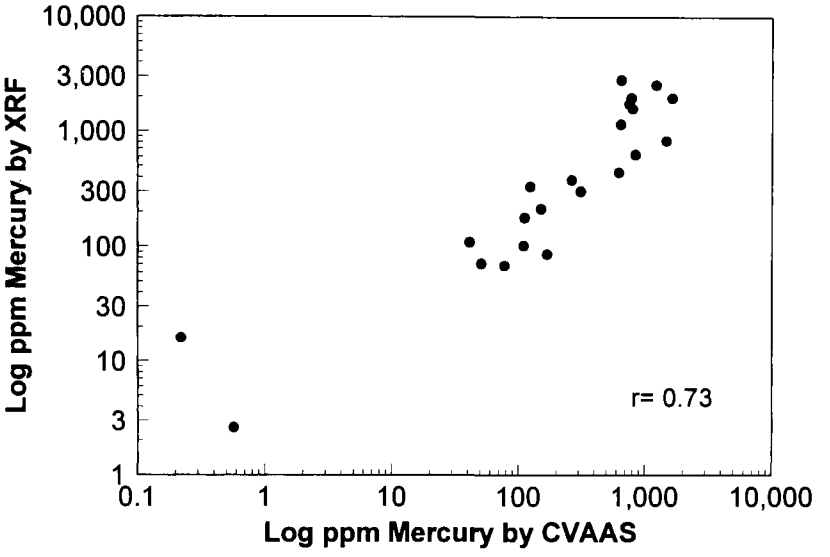


Figure 4: XRF Mercury Results using Salt-Fortified Standards vs CVAAS Results

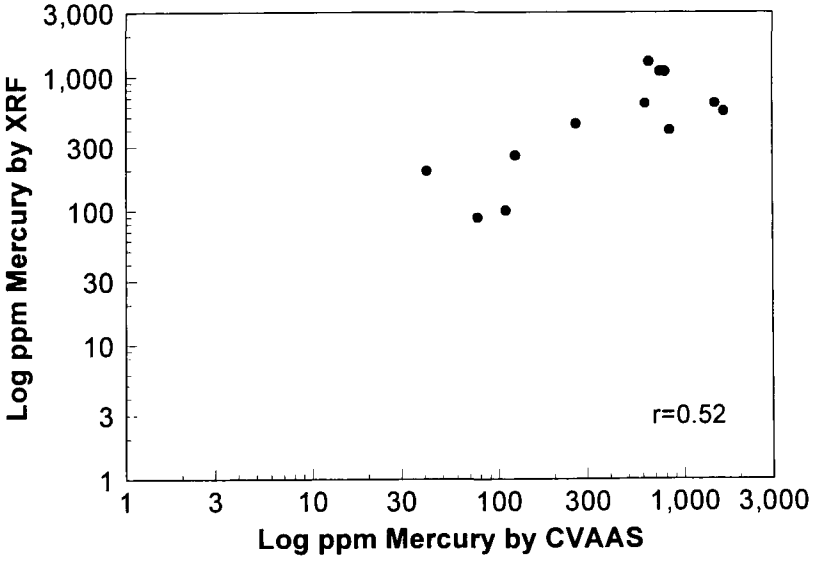


Figure 5: XRF Mercury Results using Field Sample Calibration Standards vs CVAAS Results

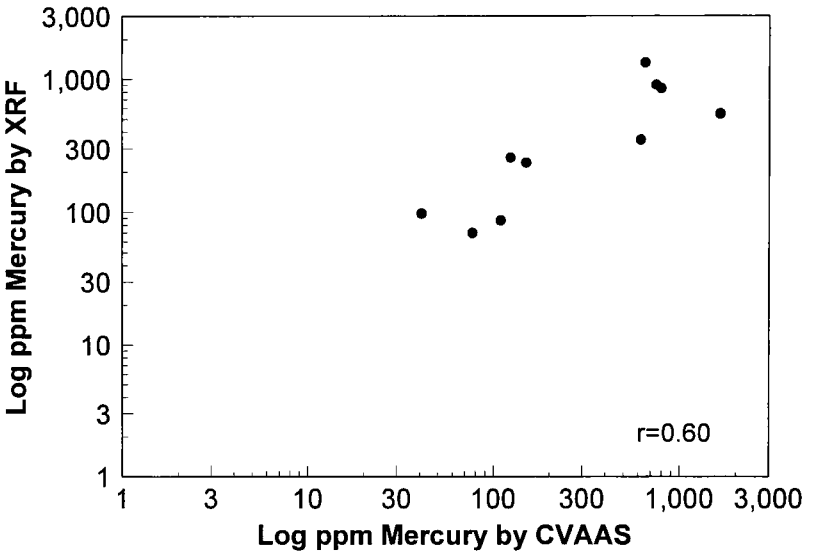


Figure 6: Comparison of Lead Results From Three Determinations

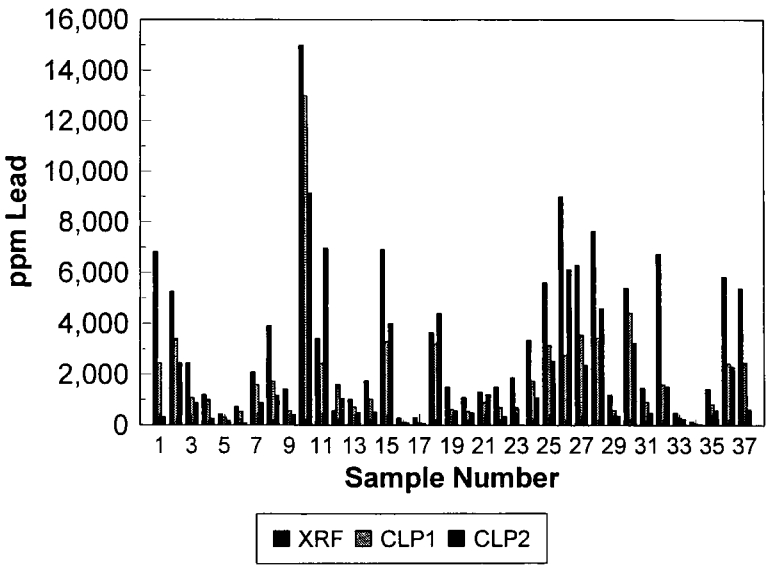


Figure 7: Zinc Results From Three Determinations

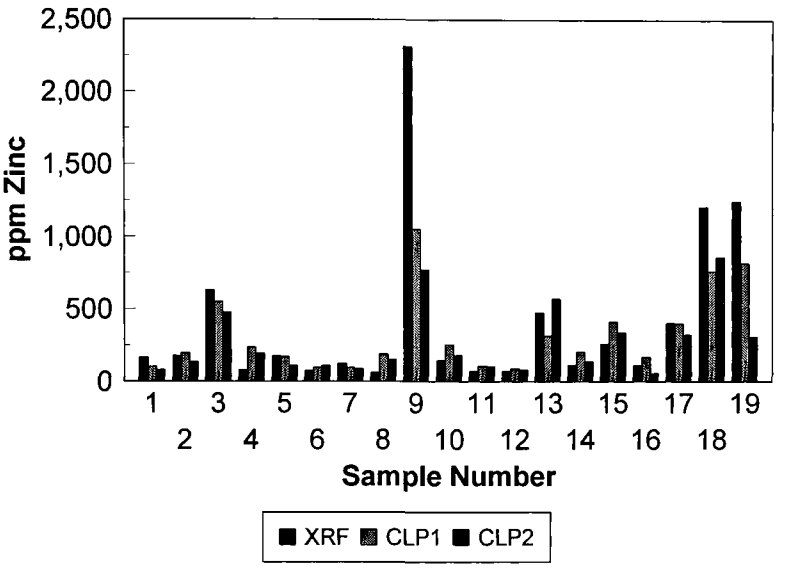


Figure 8: Lead Regression Plot

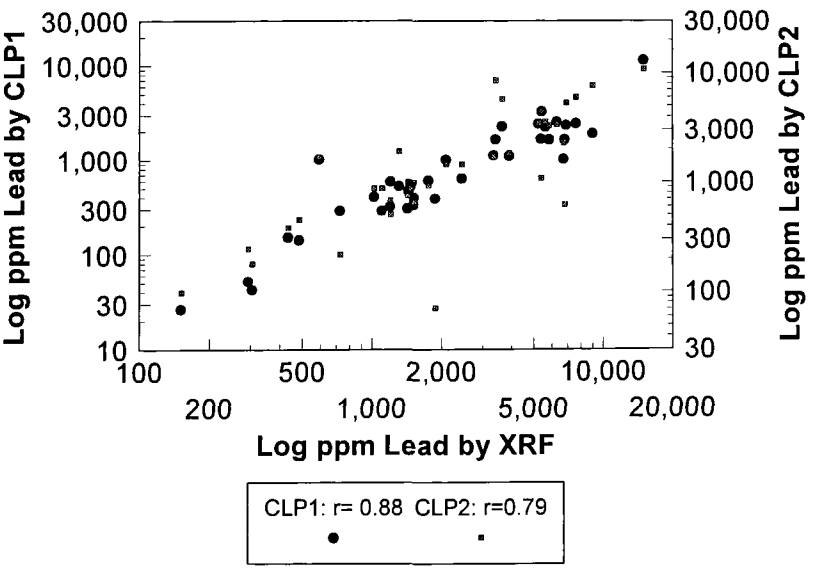
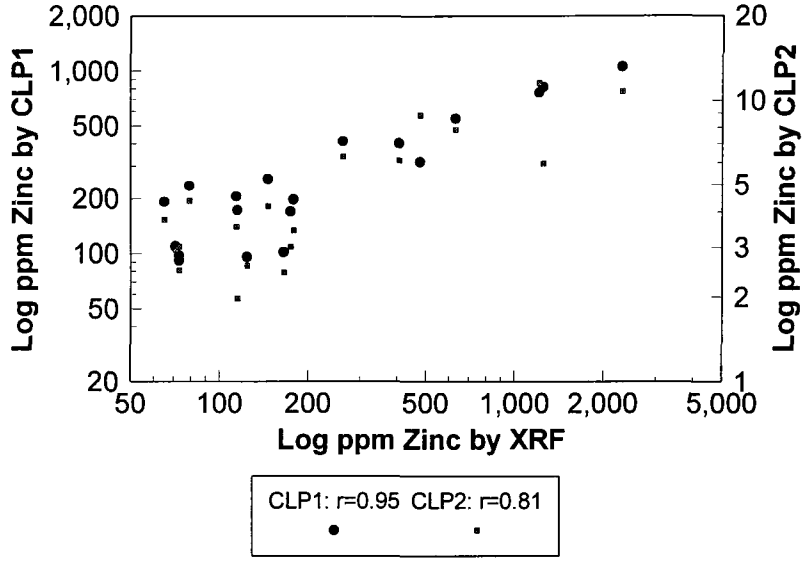


Figure 9: Zinc Regression Plot



Improving Mercury Detection Limits Using a Dedicated Flow Injection System

S. McIntosh, S. Sauerhoff, and Z. Grosser
The Perkin-Elmer Corporation, 50 Danbury Rd, Wilton, CT 06897-0259

Traditionally the determination of mercury in environmental samples has been performed using a cold vapor atomic absorption technique. An atomic absorption instrument equipped with a vapor generation accessory provides mercury detection limits ranging from 50-200 ng/L. This configuration has performed satisfactorily for current EPA requirements. However, as regulatory and environmental pressures force mercury detection limits lower, there is an increasing need for improved instrumentation.

A dedicated mercury system can be optimized for improved detection limits and sample throughput. The Perkin-Elmer Flow Injection Mercury System (FIMS) was characterized and evaluated for the determination of mercury in a variety of water samples.

Experimental

The FIMS optical system consists of a low pressure mercury source, an absorption cell with removable quartz windows and a solar blind detector with maximum sensitivity at 254 nm. The system is automated by using flow injection techniques to add the HCl acid carrier and $SnCl_2$ reductant. The reaction mixture then passes through a gas-liquid separator, which directs the mercury vapor to the absorption cell where the measurement takes place. To minimize moisture transfer to the absorption cell the gas-liquid separator is equipped with a PTFE membrane.

Samples were prepared as specified in EPA Method 245.1. The method has been modified to include flow injection, which has been approved by the EPA under the Alternate Test Procedure (ATP) process. All acids and reagents used for sample preparation and analysis were of "ultrapure" or "mercury-free" grade. To minimize contamination, all glassware and digestion vessels were cleaned and soaked for 24 hours in 1:1 nitric acid solution.

The flow injection (FI) program is shown in Figure 1. The first step, shown as the Prefill step, was used only for the first reading in a series of replicates. This step ensures that the tubing leading from the autosampler to the sample loop is adequately filled with solution. The next step, Step 1, is used for all replicates. In this step the sample loop, located on the flow injection valve, is filled with solution. In the final step, Step 2, the sample is transported from the sample loop by the HCl carrier to the mixing manifold, where the sample is merged with the reductant. At this point the instrument read step is activated and the absorbance signal is measured.

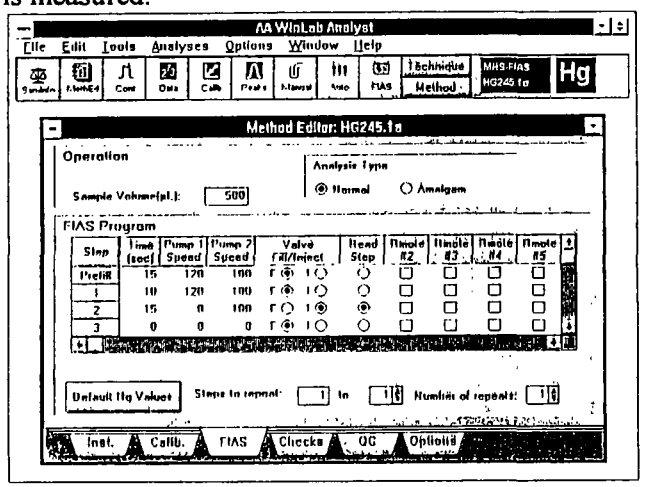


Figure 1. FIMS Flow Injection Program

Data for all determinations were collected using peak height.

Results and Discussion

Figure 2 shows a peak profile of a water sample spiked with 0.1 μg/L Hg, demonstrating the excellent signal to noise ratio of the system.

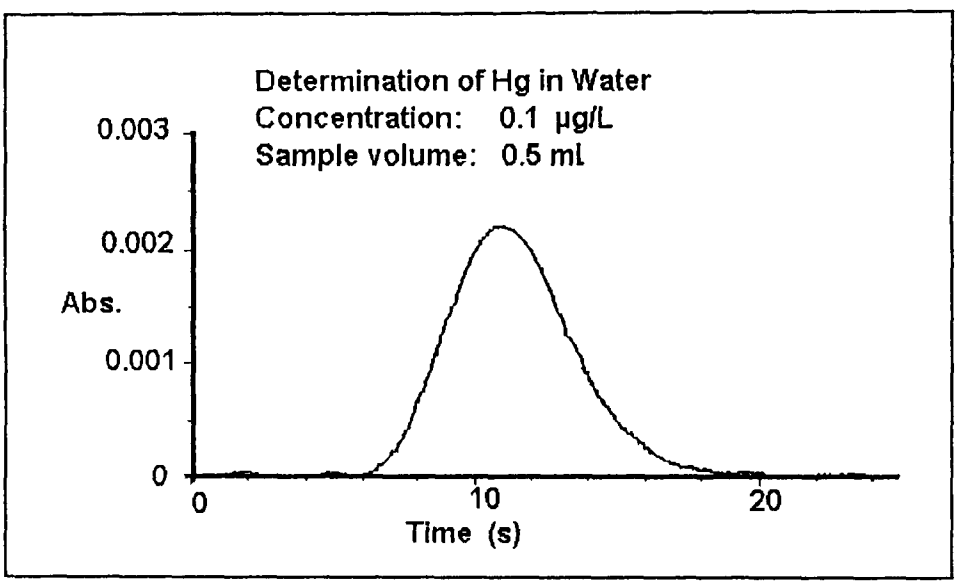


Figure 2. Low Level Water Spike

As part of this study, instrument and method detection limits were measured for typical EPA methods. The instrument detection limit (IDL) for mercury was measured using a procedure outlined in the EPA CERCLA statement of work ILM02. The instrument response for seven replicate analyses of a low-level mercury solution (20 ng/L in this case), conducted on three nonconsecutive days was measured. The standard deviation for each of these analyses was multiplied by the t-distribution value and resulted in a value of 4 ng/L.Hg.

The method detection limit (MDL) for mercury detection limit by EPA method 245.1 was determined following the procedure outlined in the Code of Federal Regulations (40CFR), part 136. Seven individual aqueous standards were carried through the complete sample dissolution procedure described in the method. While the mercury contamination in the original reagents was only at ng/L levels it was the limiting factor in the MDL. The MDL was established at 9 ng/L. Both the IDL and MDL represent a significant improvement in detection limits over the conventional cold vapor system of 10-50 times.

Table I shows the performance of the method in determining mercury in a variety of water matrices. The only certified reference material available is NIST 1641C, which was diluted to 0.2 μg/L, prior to analysis. Also examined were spiked samples of groundwater, drinking water, and SLRS-2 Riverine water, obtained from the National Research Council of Canada. The recoveries demonstrate the FIMS ability to determine trace levels of mercury.

Table I

Analytical Results

Sample	Hg Found (µg/L)
Ground Water spike - 1 µg/L Hg	1.00 (± 0.01)
Drinking Water spike - 1 µg/L Hg	1.00 (± 0.02)
NIST 1641c, diluted to 0.2 µg/L Hg	0.19 (± 0.01)
SLRS-2	0.13 (± 0.01)
SLRS-2 (Duplicate)	0.13 (± 0.01)
SLRS - spiked - 1 µg/L Hg	1.17 (± 0.02)

The system was characterized for a number of variables including the ability to vary detection limits and throughput by varying the size of the sample loop. The sample loop volume can be varied between 40 µL and greater than one mL. Larger sample volumes improve the detection limits and smaller volumes increase the sample throughput. The optimum compromise for this analysis was found to be a sample volume of 500 µL. The detection limits were as noted and the sample throughput was 120 determinations per hour.

The stability of the system was evaluated and found to be approximately 4%RSD over the course of several hours, for a solution containing 0.1 µg/L Hg.

One of the many advantages that flow injection has over the continuous flow technique includes reduced carryover effects. With flow injection, the continuous rinsing action of the carrier stream reduces carry over from samples containing higher concentrations. The analysis of a 100 µg/L Hg standard, followed immediately by the analysis of the blank, shown in Figure 3, demonstrates the effectiveness of the rinsing action.

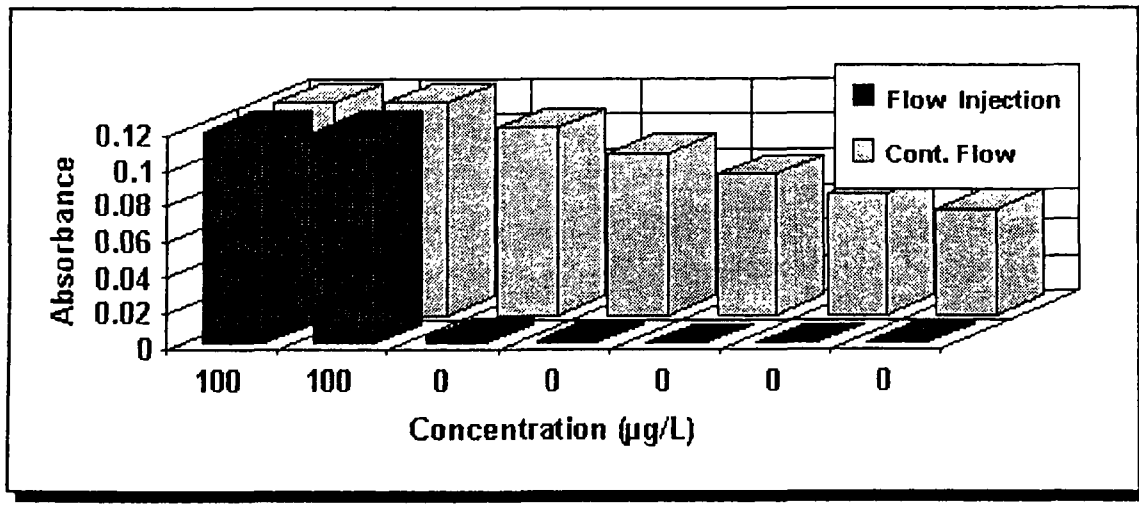


Figure 3. Carry-over Comparison

Conclusion

The advantages of using a flow injection system with improved sensitivity, such as the FIMS, for the determination of environmental mercury are many and include:

- Increased sample throughput for better lab productivity
- Reduced reagent consumption for less initial expense and expense for waste disposal
- Reduced sample consumption, important for critical small samples
- Reduced carry over for better accuracy with a variety of samples
- Improved performance providing ultra-trace Hg detection limits

The determination of mercury in environmental samples can be performed by the FIMS on a routine basis at lower levels than previously possible with this technology. The limiting factor for Hg determinations in environmental samples has become the integrity of the reagents rather than the detectability of the instrumentation.

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RAPID MICRO DISTILLATION OF TOTAL CYANIDE USING LIGAND DISPLACEMENT AND DETERMINATION BY FLOW INJECTON ANALYSIS

William R. Prokopy, Applications Chemist, Lachat Instruments, 6646 W. Mill Rd., Milwaukee, Wisconsin 53218, Maureen Stone, Lachat Instruments, 6645 W. Mill Rd., Milwaukee, Wisconsin 53218

ABSTRACT

In wastewater treatment procedures throughout various industries, cyanide must be monitored as it pollutes the environment and is a significant health hazard. To accurately monitor cyanide, a distillation procedure is required to dissociate metal cyanide complexes and subsequent determination. The classical strong acid macro reflux distillation (EPA Method 335.2) has been in use for many years but does not eliminate interferences such as thiocyanate and sulfide, and is time consuming. Also, the EPA approved cyanide determination step uses dihydrogen phosphate as a buffer that does not have the capacity to effectively control changes in pH.

In this presentation we will introduce a micro steam distillation utilizing the weak acid ligand displacement procedure and determination with Flow Injection Analysis. The distillation is complete in forty minutes. The cyanide in the distillate is buffered with an acetate buffer and reacted with chloramine-T where cyanogen chloride forms a complex with 1,3 - dimethylbarbituric acid. Method support data including interferences, precision, accuracy and method detection limit will be presented.

ADVANCES IN QUALITY ASSURANCE FOR XRF DETERMINATION OF LEAD.

H. A Vincent, U. S. Environmental Protection Agency, EMSL-LV, P.O. Box 93478, Las Vegas, Nevada 89193-3478, and J. E. Kilduff, Lockheed Environmental Sciences and Technologies, 980 Kelly Johnson Drive, Las Vegas, Nevada 89119.

ABSTRACT

The EPA's Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV), has been studying the application of X-ray fluorescence analysis (XRF) to perform lead determinations in a number of different types of sample media. XRF techniques have some unique advantages in applications to solid samples but do present some problems.

XRF lead determinations in paints, soils, and dusts can be made without sample dissolution and often can be done with minimal sample preparation. Prior XRF studies show difficulties in sample-related biases, in false negative or positive reporting, in improper sampling, in lack of traceability to standards, and in calibration for nonhomogeneous samples. For many EPA applications, data from many laboratories must be comparable and must meet both regulatory and technical requirements.

The XRF studies in this project have focused on examining problems for both laboratory-based and portable XRF measurements for lead. XRF experiments were done using external reference materials, but focused primarily on gold. The gold reference material was placed in the optical pathway of the excitation source but anterior to the sample. Both characteristic L-series and K-series lead X-ray lines were studied.

The results reveal some of the difficulties with current data handling systems that correct XRF intensities for various interferences. It was found that an external reference can have value as part of a quality control system. The reporting of false negatives for lead, when the characteristic lead L-series X-rays are used, can be avoided. Similarly, when the lead K-series X-rays are used, false positives can be avoided. Experiments at EMSL-LV show that absorption values for external reference gold X-rays by various sample constituents can be used to adjust lead x-ray intensities affected by the presence of those constituents. This kind of information helps in describing analytical models for the different sample types.

THE STABILITY OF CALIBRATION STANDARDS FOR ICP/AES ANALYSIS: A TWO-YEAR STUDY*

Doris R. Huff, Scientific Associate, and Edmund A. Huff, Chemist, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439-4831

ABSTRACT

The stability of instrument calibration standards for Inductively Coupled Plasma/Atomic Emission Spectrometric analysis was studied over a two-year period. Data were obtained as functions of analyte concentration, acid type, and acidity. The impact of acid concentration on signal-to-background ratios was also assessed. The results show that, with the appropriate choice of inorganic acid preservatives, most analytes maintain their integrity over extended periods; thus frequent standard preparations are not necessary to obtain valid analytical data. This conclusion allows for more efficient use of commercially purchased reference materials, which should reduce procurement costs and minimize chemical waste.

INTRODUCTION

Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) is used extensively in the Analytical Chemistry Laboratory (ACL) to characterize diverse analytical samples. This method simultaneously measures the concentrations of multiple cations in solutions. The working standards used for instrument calibration are generally in the 5-20 µg/mL range. They are prepared from certified single or multi-element stock solutions by serial dilutions and are preserved with inorganic acids. The accuracy and precision of analytical measurements are greatly affected by uncertainties in standard stabilities as functions of preservative type, analyte content, and acid concentration. Consequently, a systematic study was initiated to assess the effect of these parameters on data quality over time. The results have implications regarding standard procurement needs and waste minimization.

EXPERIMENTAL

APPARATUS

The ICP/AES measurements were performed on a spectrometer system that incorporated a 48-channel polychromator and a computer-controlled scanning monochromator (Instruments S. A., Inc., Edison, NJ). Both instruments were focused on a single plasma excitation source. Table 1 lists the instrumentation, and Table 2 details the operating conditions for this two-year study. Typical experimental detection limits (DLs) and their corresponding wavelengths are given in Table 3.

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*Work submitted by the U.S. Department of Energy under Contract W-31-109-Eng.38.

REAGENTS

Instra-Analyzed HCl and HNO_3 (Baker Chemical Co.) were used in blank and standard preparations. Water for dilutions (≥18 Mohm-cm) was obtained from a Sybron/Barnstead ion exchange system. Certified standard stock solutions were purchased from the National Institute of Standards and Technology (NIST), SPEX Industries, and Baker Chemical Co. Test solutions and calibration standards were prepared by making serial dilutions of the concentrates and adjusting to the appropriate acidity. The information on the standard test solutions is summarized in Table 4.

PROCEDURES

The plasma system was optimized with respect to maximum signal-to-background (S/B) ratio as a function of the vertical viewing aperture. The instrument was calibrated at this position by using the two-point calibration procedure with standards and blanks prepared in a 2% acid (HCl or HNO_3) medium. Working standards were prepared on the day of the analytical run and verified against previously used calibration solutions. An agreement of ±3% for this comparative analysis was considered to provide a valid calibration curve for the subsequent analytical run.

Since instrument calibration standards were prepared at a single acid concentration (2%), information on the effect of acidity on signal intensity was needed for data assessment of the diverse analytical matrices. Therefore, S/B ratios were determined as a function of HCl concentration, using a 1-µg/mL multielement standard and a corresponding blank.

The stability of standards is also affected by the possible loss of analyte by diffusion and/or evaporation through plastic containers. Since stock and working standards are stored in polyethylene bottles, diffusion was studied by weight-loss measurements from high density polyethylene (HDPE) and Teflon containers. Bottles were filled with acid solutions, and the change in weight as a function of time was established gravimetrically.

RESULTS AND DISCUSSION

SIGNAL-TO-BACKGROUND RATIOS

One objective of this investigation was to determine the stability of standards as a function of acidity. The analyte response as a function of this parameter is of interest because instrument calibration in our laboratory is generally performed at a 2% acid concentration. Table 5 summarizes S/B ratios for 18 elements in HCl solutions. The data indicate that the presence of mineral acids decreases the emission intensities of atomic and ionic lines for most elements, which is consistent with published results. (1) It has been postulated (cited publication) that these findings are related to the physical state of the plasma at lower acidities (<1M) and to the reduced rate of sample uptake at higher acid concentrations (>1M). A few, very sensitive elements (i.e., Be, Ca, Mg, and Sr) exhibit an increase in S/B ratios, an observation inconsistent with the above mechanism. The results show that for best accuracy, calibration standards,

blanks, and samples should be matched with respect to acid concentration. Furthermore, for the purpose of this study, only relative analyte changes should be considered in stability assessments, since instrument calibration was performed at a single acid concentration.

DIFFUSION

Diffusion data for a nine-month period were presented in an earlier report of this study. (2) Continued measurements (>two years) showed these losses to be a function of container type and acid preservative. Solutions in 2% HNO_3 showed the lowest weight loss in HDPE containers (0.5%). Decreases in weight of 0.7% (5% HCl-1% HNO_3) and 0.9% (2% HCl) are considered to be acceptable for the prolonged storage of ICP/AES standards. Solutions prepared in Teflon bottles maintained their weights best in 5% HCl-1% HNO_3 (0.2% loss). Both 2% HCl and 2% HNO_3 showed a diffusion-related decrease of 0.6% and 1.1%, respectively. This controlled study did not address variables pertaining to repeated sampling of bottles and diffusion effects from partially filled containers. The data do, however, suggest that within the accuracy range of ICP/AES (3-10%), changes via these mechanisms would still provide valid analytical data.

STABILITY DATA

Tables 6 and 7 summarize representative stability results in 2% nitric acid.[a] The data were obtained from 25 independent measurements over a two-year period. None of the listed analytes, except Sn, show excessive fluctuations at any concentration in this preservative. Similar data sets were obtained with all the other preservatives studied.

As expected, deviations from the mean decrease with increasing analyte content, consistent with more favorable statistics at higher signal intensities. Representative data are shown graphically in Figures 1 and 2. A slight, positive trend in the Cu concentration as a function of time (Figure 1) is apparent; this is probably caused by diffusion losses from progressively smaller sample volumes. Similar behavior was observed for other analytes. The Pb values (Figure 2) remained constant, irrespective of analyte concentration, within the 3-10% stipulated range.

Standards of Nb and W were studied only in HCl and HCl-HF acids, since HNO_3 is known to cause precipitation. Figure 3 shows the behavior of W as a function of time and acid composition. A similar trend was noted for Nb. These results verify that HF is required to stabilize these elements in calibration standards and ensure longer shelf lives.

At a low analyte concentration (0.2 µg/mL), elements with relatively high DLs (Figure 4) have relative standard deviations (RSDs) exceeding 10%, a result that can be correlated with greater signal fluctuations. For comparison, an analyte with a low DL (more favorable statistics) is shown in Figure 5.

The unexpected, reasonably good stability of Sn in HNO_3 can be explained by the presence of HCl in the stock standard used to prepare the test mixtures. Separate Sn standards prepared in HNO_3 alone deteriorated severely within one week, presumably through the precipitation of

stannic acid. The stability of Ag standards was studied only in HNO_3 and HCl-HNO_3 preservatives, with satisfactory results. The deterioration of Ag solutions can usually be attributed to the introduction of chloride ions during washout procedures.

During the study, it was noted that the Sb and Si results were increasing with time. Closer examination of the stock solutions(2% HCl) used to prepare working standards revealed that precipitates were forming, causing the Si and Sb concentrations in solution to be lower. This resulted in apparently higher values for Si and Sb in the test standards. New stock solutions were used for the working standards in subsequent measurements, and the Sb and Si values for the test matrices returned to an acceptable range. In retrospect, the stability of Si standards should have been examined in the presence of HF, a medium known to promote complexation reactions and thus avoid precipitation due to hydrolysis.

CONCLUSION

The results on the stability of calibration standards for ICP/AES analysis show that a suitable acid preservative enables analyte solutions (5-20 µg/mL) to maintain their integrity over a two-year period. For the wide range of elements studied, a mixture of 5% HCl-1% HNO_3, suggested by the U.S. EPA Contract Laboratory Program (3), appears to provide the best compromise for acceptable shelf lives for most cations. However, for those situations where the relatively high acidities are impractical or undesirable, 2% HCl or 2% HNO_3 stabilizes analytes satisfactorily, provided any chemical incompatibilities (i.e., precipitation, hydrolysis) are resolved.

The variations in S/B ratios as a function of acidity mandate that for best accuracy and precision, calibration standards, blanks, and samples should be matrix-matched (i.e., same acid type and concentration, same major constituents). However, for analytical data normally reported in the accuracy range of 3-10%, approximate acid concentrations are sufficient for satisfactory results.

Changes in analyte concentrations due to evaporation and diffusion through plastic containers did not, over a reasonable time (one year), appear to make a significant contribution to inaccuracies, compared to the more pronounced effects introduced by the excitation and sample transport system. A trend toward increasing concentration was noted over the second year, although the variation was within the expected accuracy range. Partially filled bottles, frequent sampling, and storage conditions could have a considerably larger impact on standard stabilities than those observed here.

This study clearly shows that the frequency of calibration standard preparations could be reduced significantly for ICP/AES analyses at moderate accuracies (3-10%). A complementary investigation at this laboratory on the stability of standards used for graphite furnace atomic absorption (GFAA) analyses concluded that even lower analyte concentrations (≤0.25 µg/mL) are stable for at least a nine-month period. (4) Thus, mandated standard preparation requirements for environmental sample analyses could be relaxed, which would result in lower standard procurement costs, waste minimization, and better allocation of analytical effort.

Table 1. Instrumentation

Spectrometers

Polychromator	Instruments S. A. Inc., Model J-Y48P 1-m Paschen-Runge with 2550 grooves/mm holographic concave grating, 20-μm entrance and 50-μm exit slits; Hamamatsu R300 and R306 photomultiplier tubes, 48 channels.
Monochromator	Instruments S. A. Inc., Model J-Y38 1-m Czerny-Turner with Spectra-Link controller, 2400 grooves/mm holographic plane grating, variable entrance and exit slits; Hamamatsu R955 photomultiplier tube.

Power and Nebulizer System

Generator	Plasma-Therm Model HFP-2500, 27.12 MHz with 3-turn copper load coil.
Nebulizer	Instruments S. A., Inc. concentric with a Pt-Ir capillary tube.
Torch	Instruments S. A., Inc. demountable in a Mermet-Trassey configuration.
Spray Chamber	Instruments S. A., Inc. double-barrel, constructed from Ryton.

Computer System

Computer	Digital Equipment Corp. PDP-11/73 with 768K byte of memory, three RL-02 disks.
Terminals	Digital Equipment Corp. DEC Writer III hard copy and DEC VT340 video with graphics.
Software	1. Instruments S. A., Inc.-supplied analytical program run by the DEC RSX-11M operating system. 2. ANL-developed report generation and quality assurance programs.

Table 2. Operating Conditions

Forward R.F. Power	1.10 kW	Argon Flow Rates	
Reflected Power	<5 W	Outer Gas	14 L/min
Observation Height	16mm above load coil	Intermediate Gas	0.4 L/min
		Sheath Gas	0.5 L/min
		Nebulizer Gas	0.6 L/min
Integration Times			
Polychromator	10 sec	Sample Uptake Rate	2.8 mL/min
Monochromator	1 sec		

Table 3. Detection Limits

Element	Wavelength, nm	DL[a], µg/L
Ag	328.068	1.9
Al	308.215	38.0
As	193.695	52.0
B	208.959	11.0
Ba	233.527	1.3
Be	313.042	0.4
Ca	393.366	1.3
Cd	226.502	3.4
Co	228.616	36.0
Cr	267.716	4.6
Cu	324.754	2.1
Fe	238.204	2.1
Mg	279.553	1.1
Mn	257.610	1.5
Mo	202.030	14.0
Ni	231.604	9.3
Pb	220.353	90.0
Sb	206.833	54.0
Se	196.026	58.0
Si	251.611	14.0
Sn	189.926	30.0
Sr	407.771	0.5
Ti	334.941	2.2
Tl	190.801	24.0
V	292.402	2.9
Zn	213.856	0.5
Zr	343.823	2.7
Monochromator		
Nb	309.418	8.9
W	224.875	7.9

[a] Detection Limit (DL) = 3 x the standard deviation of the baseline noise.

Table 4. Summary of Standard Solutions

File Name	Concentration, µg/mL	Elements	Acidity
QF01	0.2	Spex A [a]	1% HNO3 + 0.002% HCl
QF02	0.2	Spex A	2% HNO3 + 0.002% HCl
QF03	0.2	Spex A	5% HNO3 + 0.002% HCl
QF04	0.2	Spex A	1% HCl
QF05	0.2	Spex A	2% HCl
QF06	0.2	Spex A	5% HCl
QF07	0.2	Spex A	5% HCl + 1% HNO3
QF08	1.0	Spex A	1% HNO3 + 0.01% HCl
QF09	1.0	Spex A	2% HNO3 + 0.01% HCl
QF10	1.0	Spex A	5% HNO3 + 0.01% HCl
QF11	1.0	Spex A	1% HCl
QF12	1.0	Spex A	2% HCl
QF13	1.0	Spex A	5% HCl
QF14	1.0	Spex A	5% HCl + 1% HNO3
QF15	4.0	Spex A	1% HNO3 + 0.04% HCl
QF16	4.0	Spex A	2% HNO3 + 0.04% HCl
QF17	4.0	Spex A	5% HNO3 + 0.04% HCl
QF18	4.0	Spex A	1% HCl
QF19	4.0	Spex A	2% HCl
QF20	4.0	Spex A	5% HCl
QF21	4.0	Spex A	5% HCl + 1% HNO3
QF22	10.0	Spex A	2% HNO3 + 0.1% HCl
QF23	10.0	Spex A	2% HCl
QF24	10.0	Spex A	5% HCl + 1% HNO3
QI01	1:10 dil.	ICV-1 [b]	2% HNO3
QI02	1:10 dil.	ICV-1	5% HCl + 1% HNO3
QIC1	1:10 dil.	ICV-1	2% HNO3
QIC2	1:10 dil.	ICV-1	5% HCl + 1% HNO3
QA01	0.2	Ag	1% HNO3
QA02	0.2	Ag	2% HNO3
QA03	0.2	Ag	5% HNO3
QA04	1.0	Ag	1% HNO3
QA05	1.0	Ag	2% HNO3
QA06	1.0	Ag	5% HNO3
QA07	4.0	Ag	1% HNO3
QA08	4.0	Ag	2% HNO3
QA09	4.0	Ag	5% HNO3
QA10	10.0	Ag	2% HNO3

[a] Spex A: Al,Ba,Be,Ca,Cd,Co,Cr,Cu,Fe,Mg,Mn,Ni,Pb,Sn,Sr,V,Zn,Zr

[b] ICV-1: Ag,Al,Ba,Be,Ca,Cd,Co,Cr,Cu,Fe,Mg,Mn,Ni,Pb,V,Zn

Table 4. Summary of Standard Solutions (cont'd)

File Name	Concentration, µg/mL	Elements	Acidity
QSi1	0.5; 1.0	B, Mo, Ti; Si	2% HNO3
QSi2	0.5; 1.0	B, Mo, Ti; Si	2% HCl
QSi3	0.5; 1.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QSi4	2.5; 5.0	B, Mo, Ti; Si	2% HNO3
QSi5	2.5; 5.0	B, Mo, Ti; Si	2% HCl
QSi6	2.5; 5.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QSi7	10.0; 20.0	B, Mo, Ti; Si	2% HNO3
QSi8	10.0; 20.0	B, Mo, Ti; Si	2% HCl
QSi9	10.0; 20.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QAs1	5.0	As, Sb, Se	2% HNO3
QAs2	5.0	As, Sb, Se	2% HCl
QAs3	5.0	As, Sb, Se	5% HCl + 1% HNO3
QAs4	20.0	As, Sb, Se	2% HNO3
QAs5	20.0	As, Sb, Se	2% HCl
QAs6	20.0	As, Sb, Se	5% HCl + 1% HNO3
QSn1	5.0	Sn	2% HNO3
QSn2	5.0	Sn	2% HCl
QSn3	5.0	Sn	5% HCl + 1% HNO3
QSn4	20.0	Sn	2% HNO3
QSn5	20.0	Sn	2% HCl
QSn6	20.0	Sn	5% HCl + 1% HNO3
QW01	1.0	W	2% HCl
QW02	1.0	W	2% HCl + 0.5% HF
QW03	5.0	W	2% HCl
QW04	5.0	W	2% HCl + 0.5% HF
QW05	20.0	W	2% HCl
QW06	20.0	W	2% HCl + 0.5% HF
QNb1	1.0	Nb	2% HCl
QNb2	1.0	Nb	2% HCl + 0.5% HF
QNb3	5.0	Nb	2% HCl
QNb4	5.0	Nb	2% HCl + 0.5% HF
QNb5	20.0	Nb	2% HCl
QNb6	20.0	Nb	2% HCl + 0.5% HF

Table 5. Signal-to-Background Ratio vs. Acidity

	Signal-to-Background Ratio					% Change	
Element	**1%HCl**	**2% HCl**	**5% HCl**	**10% HCl**	**20%HCl**	**1-5% HCl**	**1-20% HCl**
Al	1.63	1.64	1.70	1.60	1.60	+4.3	-1.8
Ba	6.50	6.44	6.35	6.20	6.04	-2.3	-7.1
Be	83.4	84.5	88.4	90.7	91.2	+6.0	+9.3
Ca	14.58	15.47	19.13	18.86	18.08	+31.2	+24.0
Cd	7.75	7.65	7.60	7.43	7.26	-1.9	-6.3
Co	2.99	2.98	2.96	2.94	2.84	-1.0	-3.4
Cr	4.36	4.30	4.28	4.25	4.14	-1.8	-5.0
Cu	5.38	5.29	5.31	5.23	5.22	-1.3	-3.0
Fe	5.02	4.86	4.80	4.69	4.62	-4.4	-8.0
Mg	30.1	29.9	38.7	41.2	38.4	+28.6	+27.6
Mn	17.75	17.57	17.45	17.05	16.64	-1.7	-6.3
Ni	2.69	2.71	2.70	2.65	2.59	-0.4	-3.7
Pb	1.57	1.54	1.56	1.53	1.51	-0.6	-3.8
Sn	1.68	1.65	1.61	1.67	1.60	-4.2	-4.8
Sr	63.8	64.8	68.9	70.3	71.2	+8.0	+11.6
V	4.23	4.21	4.19	4.12	4.03	-0.9	-4.7
Zn	18.97	18.90	19.17	18.33	17.43	+1.0	-8.1
Zr	4.21	4.21	4.26	4.19	4.14	+1.1	-1.7

Table 6. Stability of Spex A Standard in 2% Nitric Acid over a Two-Year Period

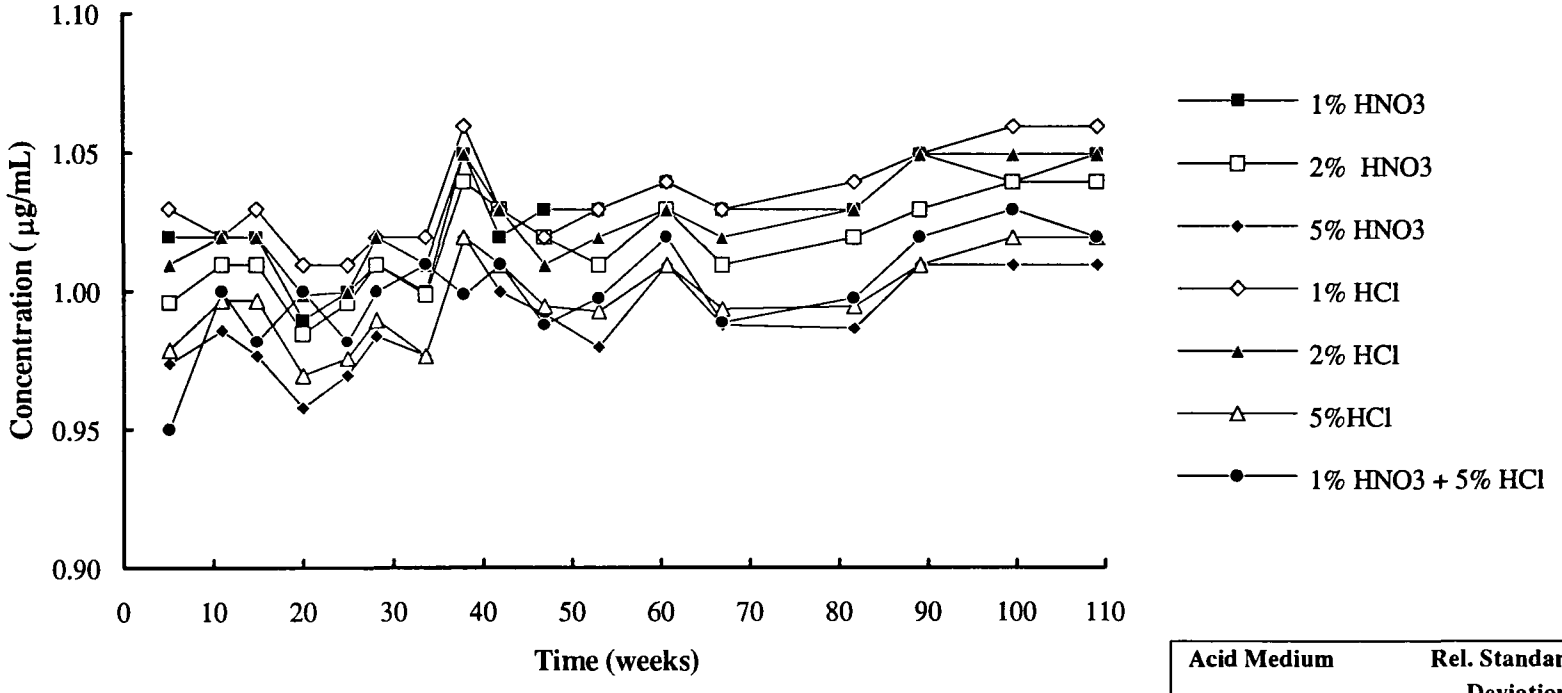
Concentration	0.200 µg/mL		1.00 µg/mL		4.00 µg/mL		10.00 µg/mL	
Element	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Ag	0.200	0.010	1.026	0.017	4.018	0.051	9.800	0.346
Al	0.206	0.020	1.007	0.042	4.051	0.073	10.24	0.236
Ba	0.203	0.004	0.998	0.024	4.018	0.066	10.06	0.274
Be	0.200	0.003	0.973	0.021	3.970	0.065	9.990	0.231
Ca	0.180	0.028	1.000	0.035	4.064	0.092	10.39	0.274
Cd	0.204	0.003	0.999	0.021	3.989	0.073	10.11	0.234
Co	0.207	0.006	1.013	0.027	4.016	0.072	10.26	0.240
Cr	0.212	0.009	1.033	0.042	4.134	0.135	10.39	0.439
Cu	0.206	0.004	1.009	0.023	4.010	0.066	10.25	0.201
Fe	0.203	0.010	1.006	0.026	4.059	0.074	10.17	0.274
Mg	0.201	0.004	1.005	0.019	4.045	0.068	10.22	0.214
Mn	0.206	0.003	1.005	0.020	4.022	0.074	10.20	0.230
Ni	0.203	0.008	0.999	0.026	4.012	0.072	9.946	0.236
Pb	0.196	0.030	0.992	0.049	4.014	0.075	9.949	0.232
Sn	0.223	0.097	0.994	0.255	3.623	0.777	8.432	0.649
Sr	0.204	0.004	0.992	0.024	4.046	0.082	10.25	0.294
V	0.210	0.005	1.016	0.021	4.018	0.064	10.26	0.217
Zn	0.204	0.005	0.990	0.029	4.026	0.102	10.14	0.303
Zr	0.200	0.005	0.996	0.017	3.948	0.088	10.14	0.160

Table 7. Stability of Selected Elements in 2% Nitric Acid over a Two-Year Period

Concentration	0.500 µg/mL		2.50 µg/mL		10.0 µg/mL	
Element	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
B	0.496	0.018	2.418	0.070	9.855	0.207
Mo	0.496	0.024	2.439	0.071	10.06	0.20
Ti	0.511	0.010	2.517	0.070	10.25	0.26

Concentration	1.00 µg/mL		5.00 µg/mL		20.0 µg/mL	
Si	1.023	0.058	5.057	0.217	20.95	0.66
As			5.201	0.148	20.75	0.48
Sb			5.344	0.360	21.26	1.43
Se			4.906	0.141	20.21	0.37

Figure 1. Copper Concentration as a Function of Time



Acid Medium	Rel. Standard Deviation
1% HNO3	1.80
2% HNO3	2.28
5% HNO3	1.75
1% HCl	1.85
2% HCl	1.96
5% HCl	1.90
1% HNO3 + 5% HCl	1.73

Figure 2. Concentration of Lead in 2% HCl as a Function of Time

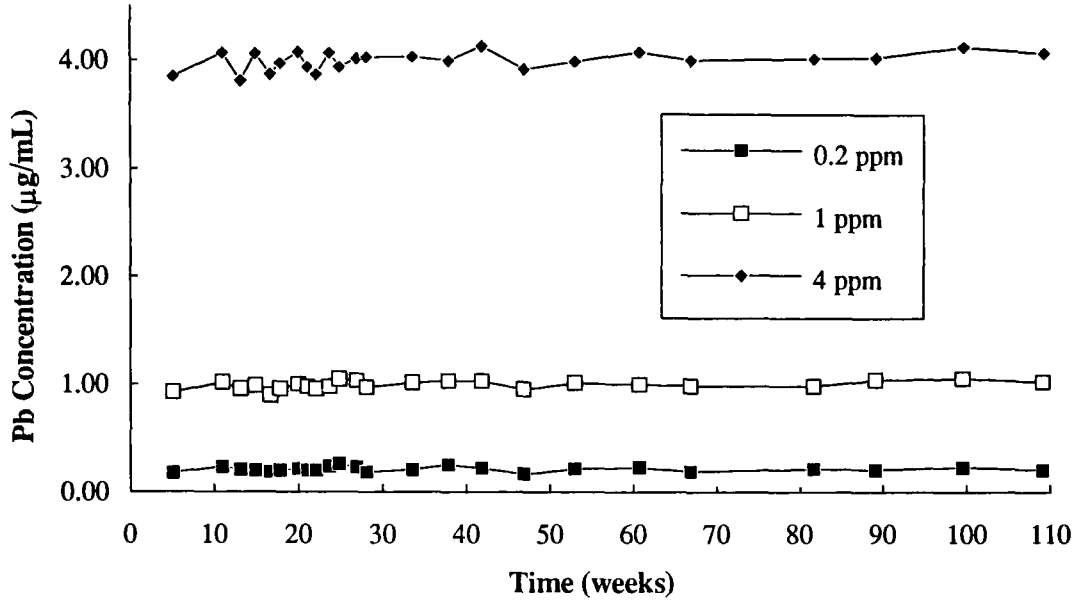


Figure 3. Tungsten Concentration as a Function of Time

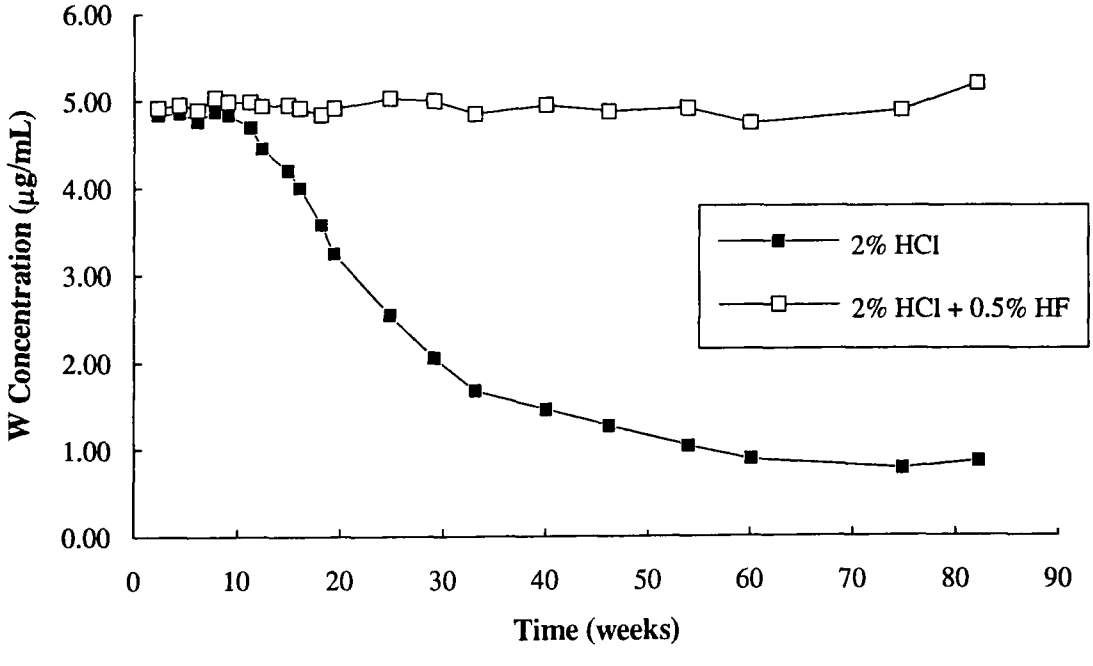


Figure 4. Relative Standard Deviation for Aluminum as a Function of Concentration

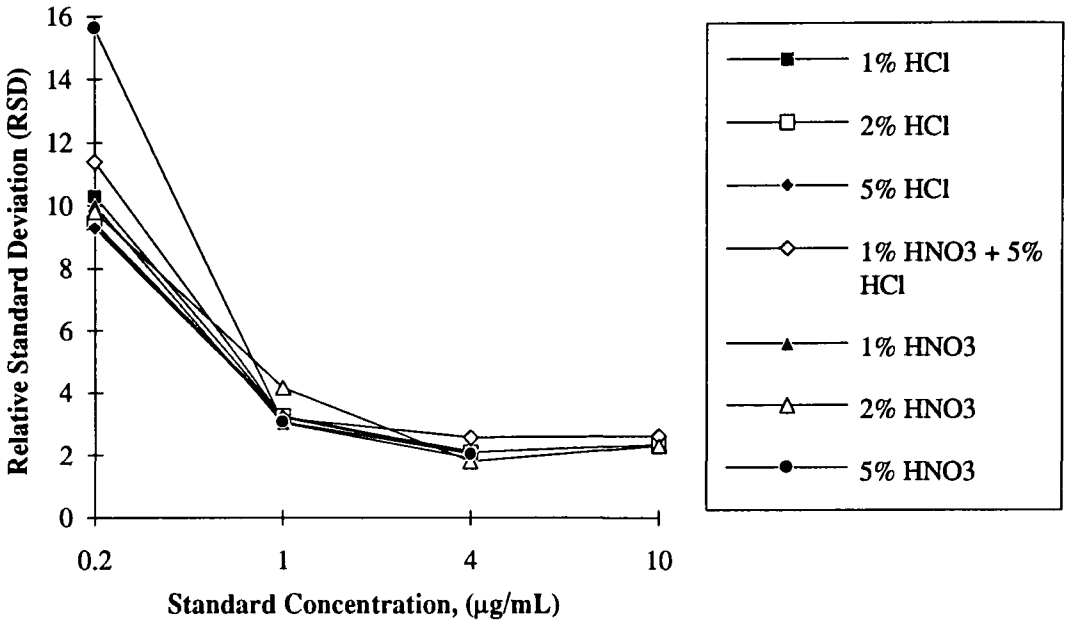
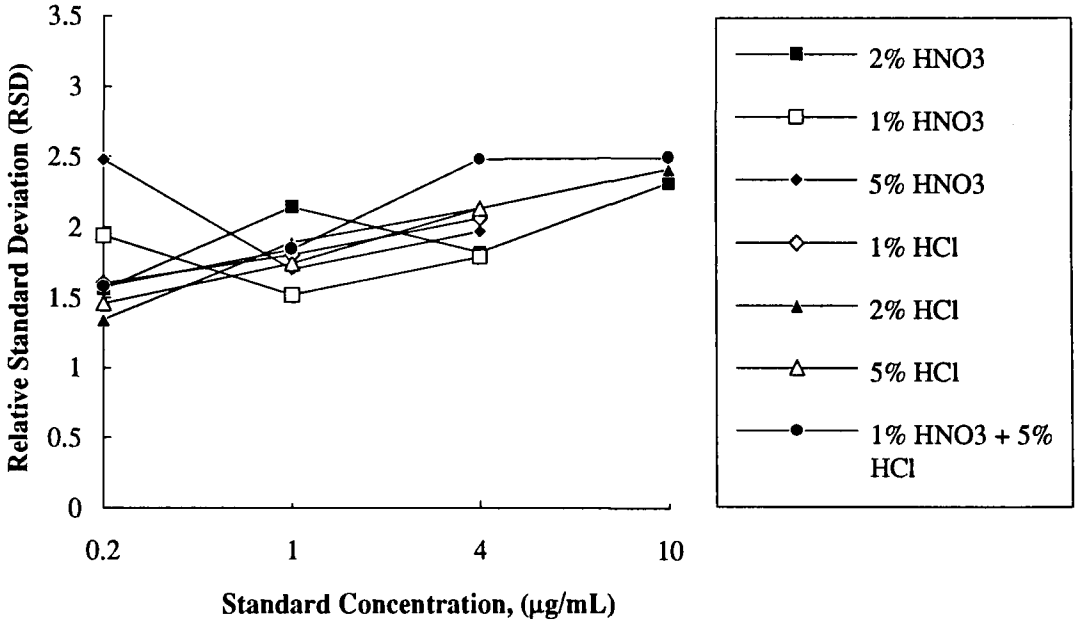


Figure 5. Relative Standard Deviation for Cadmium as a Function of Concentration



[a]The entire data base could not be included in this presentation due to space limitations. This information is available from the authors upon request.

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CLP-Type Analyses Using an Axial Plasma ICP-OES

Marc Paustian, Karen Barnes, and Zoe Grosser
The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0080

Introduction

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1981, updated by the Superfund Amendments and Reauthorization Act (SARA) of 1986 gave the EPA responsibility for the cleanup of hazardous waste disposal sites that have been abandoned. In order to assess the contamination of these sites and monitor the cleanup efforts the EPA has created the Contract Laboratory Program (CLP) to control the collection and disbursement of analytical data. Routine samples are contracted out to commercial analytical laboratories to analyze using a fixed set of protocols specified in the Statement of Work (SOW). The quality assurance and control measures specified in the SOW are quite stringent to ensure that the data can stand alone in a Court of Law in the event that potentially responsible parties are sued for cleanup costs.

Over the years this program has been in effect, the profitability of this kind of sample for the typical environmental laboratory has declined. However, the quality control used by this program has become a standard synonymous with high quality and many customers specify "CLP-like" analyses. Therefore the pressure on the environmental laboratory has been to produce more data, with more QC, at a reasonable cost to maintain a reasonable profit level.

One way to increase productivity, resulting in a lower sample cost, is to streamline testing by performing the analyses required on fewer techniques. Advances in ICP-OES technology have allowed improvements in detection limits of approximately an order of magnitude which permits the elements typically determined by graphite furnace atomic absorption (GFAA), specifically arsenic, selenium, lead, and thallium, to be determined by ICP-OES. Of the conventional inorganic analytes, only mercury must still be determined using a separate technique. This provides substantial savings in time because a separate sample preparation, required for graphite furnace, is eliminated. In addition, the time to do the analysis is reduced because the ICP technique is faster and the number of QC checks required are fewer than specified for graphite furnace.

This paper describes the performance of the ICP method 200.7 modified for the CLP program SOW ILM03. The initial performance of the instrument is demonstrated through the documentation of the linear ranges of each wavelength chosen and instrument detection limits. The conditions used to achieve the best performance on a variety of samples are specified.

Experimental

The Perkin-Elmer Optima 3000 XL ICP-OES was used for the analysis of a variety of CLP samples. The Optima 3000 XL 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 conditions used for the instrument detection limits (IDLs), linear range analysis, and analytical results are shown in Table I.

Table I
Instrumental Conditions

RF Power	1300 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	0.5 L/min
Nebulizer Gas Flow	0.85 L/min
Solution Pump Rate	1.5 mL/min
Nebulizer	GemTip Cross Flow
Equilibration Time	15 seconds

Calibration standards were prepared from PE Pure CLP standards. One standard and a calibration blank were used for calibration. The standards were prepared in a HNO_3/HCl as specified by Method 200.7-CLP-M, to approximate the digested sample matrix.

Method 200.7-CLP-M, as published in the SOW ILM03, was followed for the initial demonstration of the instrument performance and the analytical determination of the samples. The QC checks specified in the method were automated through the use of QC Expert Software. QC Expert will monitor the analysis and make real-time decisions about recalibration, rerunning the samples, or halting the analysis, at the Analyst's direction. This removes the tedious manual calculation of the QC results from the Analyst and makes automated QC charting possible.

Results and Discussion

The instrument detection limits and linear ranges were evaluated to characterize the instrument capabilities. A selection of detection limits are shown in Table II, determined using area processing with simultaneous background correction or using Multicomponent Spectral Fitting (MSF) a mathematical algorithm combining Interfering Element Correction (IEC) capabilities with simultaneous background correction. They are compared with the contract required detection limits (CRDLs) specified in the SOW and, in each case, at least one wavelength is available which meets the criteria.

Table II
Optima 3000 XL Detection Limits (µg/L)

Element	Wavelength	EPA CRDL (µg/L)	AREA - BGC	MSF
As	188.979	10	4.9	3.1
As	193.696	10	4.4	4.3
Cd	214.438	5	0.12	0.11
Cd	226.502	5	0.11	0.09
Pb	216.999	3	6.6	8.6
Pb	220.353	3	2.0	1.8
Se	196.026	5	3.4	2.2
Se	203.985	5	9.2	4.7
Tl	190.800	10	6.3	5.8
Tl	276.787	10	8.8	3.8

The linear ranges are shown for a selection of elements in Table III. The linear dynamic range of the ICP-OES is generally more than five orders of magnitude, allowing the analysis of samples of widely varying concentrations and the compensation of interferences at various concentrations through interfering element corrections (IECs). The linear range was preserved in many cases, in addition to lowering the detection limits.

Table III
Linear Range for Selected Elements (ppm)

Element	Linear Range
As	50
Cd	>200
Pb	>200
Se	>200
Sb	50
Tl	>200
Fe	475
Mg	20
Al	475

Stability is important for long runs without time-consuming recalibrations. Furthermore, IECs rely on a stable system to perform within the required criteria without frequent remodeling. Figure 1 shows the excellent recovery of the continuing calibration verification (CCV) standard over a long-term run. The limits for the CCV are 90-110% and the elements tested (only a subset shown here) all fell within the required range.

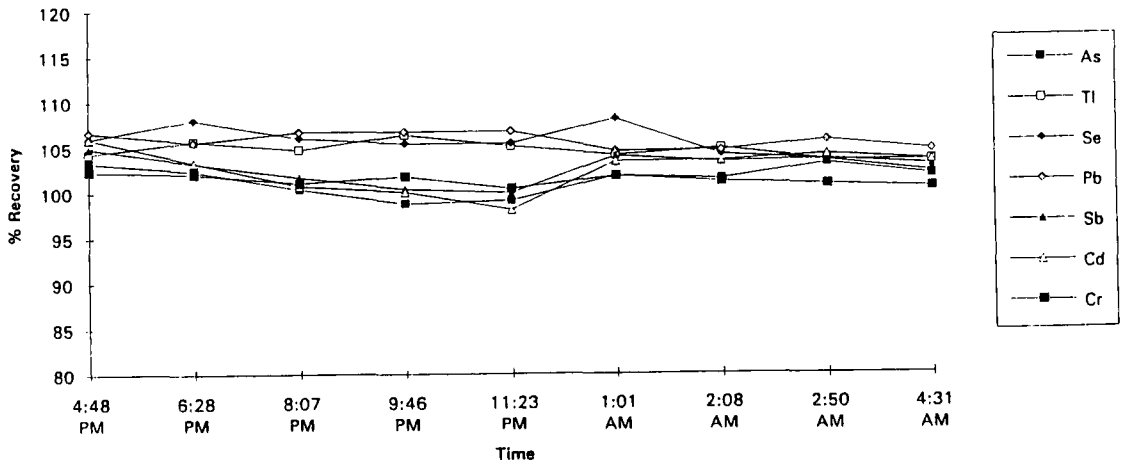

Figure 1. Long Term Stability of the CCV

The results for a variety of CLP-type samples will be discussed. Implementation of the QC and the resulting performance will be examined.

DETERMINATION OF MERCURY BY ICP-MS

David. E. Dobb, J. T. Rowan, and D. Cardenas, Lockheed Environmental Systems & Technologies Company, Las Vegas, NV 89119, and L.C. Butler, U.S. Environmental Protection Agency, Las Vegas, NV 89119

ABSTRACT

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a desirable alternative to cold vapor atomic absorption (CVAA) because of its multielement capability and it serves as a new independent method for the analysis of mercury. CVAA is dependant on the successful reduction of mercury to the metal to accomplish volatilization prior to detection. Since ICP-MS is not dependent on the electrochemical state of species in solution, it is not prone to the same interferences as CVAA. All oxidation states of mercury are measurable by ICP-MS.

The determination of mercury by ICP-MS has been limited by a lack of suitable sample digestion techniques. The high levels of permanganate and persulfate in the CVAA (SW 846 Method 7471) digest are prohibitive for ICP-MS and open-beaker acid digestions have proven inadequate because of mercury losses through volatilization. An aqua-regia digestion in a closed vessel does not experience such losses and recoveries average 10 to 15% greater than those achieved with the CVAA digestion using permanganate and persulfate. In addition to good recoveries in a matrix that is suitable for ICP-MS, the closed-vessel procedure is relatively simple and is as reproducible as CVAA.

Mercury analysis by ICP-MS has traditionally been plagued with long rinse-out times. Low levels of mercury present less of a "memory" problem and longer integration times can be used to compensate for low concentrations and yield the required sensitivity. A rinse solution consisting of 2.5 mg/L Au in 6% v/v HNO_3 has been shown to be effective in dealing with mercury retention in the sample introduction system, particularly if the analytical range is maintained in a region from 0.15 - 25 μg/L. The analytical range can be increased to 50 μg/L if the acid concentration of the rinse solution is increased, but erosion of the nickel sampling cones may result.

The closed-vessel aqua-regia digest has been shown to be appropriate for the rest of the EPA target metals as well. Holding times for mercury, however, are currently much shorter than those for the other CLP metals. The use of gold in solution has been shown to stabilize mercury for as long as the holding times of the other metals. With the stabilization of mercury in solution, all of the EPA target metals can be determined with one digestion and one instrument. This could allow significant savings and improved analytical efficiency over the current practice of using three digestions and three analytical techniques.

NOTICE

Although the research described in this article has been funded wholly by the U.S. Environmental Protection Agency through Contract 68-C0-0049 to Lockheed Environmental Systems & Technologies Company, it has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

The determination of mercury has traditionally been accomplished by cold vapor atomic absorption (CVAA). The analysis relies on a series of electrochemical transitions, all of which are subject to interferences. Mercury is detected as a metal vapor and so it is necessary to reduce the mercury in the sample to the metallic form. The success of this step depends largely on the digestion process and is in turn dependant on the nature of the samples themselves. The reduction step is only effective for free mercury ions. Organo-mercury compounds must be decomposed in order to liberate the mercury ions prior to the reduction step. This requires the use of strong oxidizing agents and heating. The amounts of reagents used depends on the nature of the sample and will vary accordingly. In addition, the presence of oxidizing or reducing agents in the sample may cause premature reduction or prevent final electrochemical reduction to the metal.

Mercury determinations by alternative methods are becoming increasingly feasible. Mercury determinations employing relatively new technologies such as He MIP-AES[1], photoacoustic spectroscopy[2], and ICP-MS with isotope dilution[3,4] and flow injection analysis have been reported. ICP-MS is a most promising alternative to CVAA for the determination of mercury. Sensitivities are comparable, however, ICP-MS has the advantage that all forms of mercury are measurable as long as they can be introduced to the instrument. In addition, ICP-MS can also be used to determine all of the other EPA target metals at the same time as mercury is being analyzed. ICP-MS would also serve as a truly independent method because it is not dependent on the electrochemical states of species in solution and will not be prone to the same interferences as CVAA.

The use of ICP-MS for routine mercury determinations has been limited by the lack of suitable sample digestion techniques. The high levels of permanganate and persulfate in the CVAA (SW 846 Method 7471) digest are prohibitive for ICP-MS and open-beaker acid digestions have proven inadequate because of mercury losses through volatilization[5]. Another problem that is particularly difficult to overcome in the case of mercury is the memory effect[6-9]. In fact, slow rinse-out is traditionally the main reason for not using ICP-MS for mercury analysis. Both sample preparation compatibility and memory problems will need to be overcome in order to successfully apply ICP-MS to the routine determination of mercury.

This paper describes an investigation into the resolution of both of these problems. A closed-vessel nitric/hydrochloric acid digestion was investigated as an alternative to the CVAA digestion, and the use of a gold additive to the instrument rinse solution was examined as a possible solution to the memory problem. An alternative sample introduction system was also evaluated. The resolution of these issues will clear the way to using a single technique for the digestion and analysis of all of the EPA target metals.

EXPERIMENTAL

A digestion method for mercury was developed to be compatible with ICP-MS instrumentation, provide complete extraction of mercury from water or soil samples, and retain mercury without volatilization or adsorption losses. The method described below uses a nitric acid/hydrochloric acid mixture heated in a microwave vessel to satisfy these requirements. Application of the method to a number of heavily contaminated soil samples was performed.

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Digestion Procedure for Total Mercury Analysis by ICP-MS

Prepare a solution of 1 part hydrochloric acid to 6 parts of nitric acid to 17 parts of water in a cleaned container (1:6:17 acid mixture). In standard teflon-lined microwave digestion vessels (equivalent to CEM model MDS-81D, Matthews, NC) add 1 gram of sample weighed to the nearest milligram. Add 24 mL of 1:6:17 acid mixture and, in the event of apparent gaseous reactions, allow to de-gas for at least five minutes. Assemble the microwave vessel. Weigh each container to the nearest hundredth of a gram. Using manufacturer's instructions, attach a pressure controller sensor to a microwave vessel that contains an actual soil sample (not a blank). Adjust pressure sensor to 150 psi, power setting to 100%, and timer to 30 minutes. After microwave timer has cycled and samples have cooled, reweigh samples to check for leakage. Samples that have lost more than 1 gram should be rejected and redigested. Once the weight loss check is completed, pour and rinse contents of the teflon liner into a 100 mL volumetric. Add 0.25 mL of 1000 mg/L $AuCl_3$ (as Au^{3+}) as a preservative. Bring to volume with ASTM Type II water. Allow particulates to settle or centrifuge before ICP-MS analysis. If heavily contaminated samples are encountered, dilute the samples in 6% HNO_3 solution until the Hg is in a 1 to 50 ppb range. The method is also suitable for digestion of other metals of interest in environmental samples.

****

Following digestion, extracts were analyzed on a VG PlasmaQuad ICP-MS using the parameters listed in Table 1.

Table 1. ICP-MS Analysis Parameters.

Parameter (VG PlasmaQuad PQ2+)	Setting
RF Power	1.2 KW
Nebulizer Gas	0.69 LPM
Auxiliary Gas	0.20 LPM
Coolant Gas	13 LPM
Nebulizer; Spray Chamber; Torch	Hildebrand Grid; Chilled Scott Spray Chamber @ 4°C made of glass; ICP (Fassel type) quartz torch
Solution Uptake Rate; Rinse Soln.	1.2 mL/min; 2.5 ppm Au in 6% HNO_3
Sampler, Skimmer Cones	Nickel (1 mm orifice sampler, 0.7 mm orifice skimmer)
Masses (peak jump dwell - μs)	^{159}Tb (2560), ^{200}Hg (40960), ^{202}Hg (40960), ^{209}Bi (2560)
Integration Method	Constant Area - 0.9 amu
Data Collection Parameters	Pulse Collector, 10 sweeps, 5 pts/peak, 5 dac-steps/pt

For comparison, the same samples were digested and analyzed by CVAA using EPA SW-846 Method 7471.

Memory effects were studied by exposing the ICP-MS instrument to a solution of 10 μg/L Hg in 6% v/v HNO_3 for a normal sample analysis time of 3 minutes. Multiple integrations of 15 seconds each were begun, followed by introduction of a rinse solution of 6% HNO_3. Signal counts per second for the rinse solution were measured versus washout times for about 20

minutes or until the mercury signal reached baseline. The experiment was repeated on a rinse solution containing 2.5 mg/L $AuCL_3$ and 6% HNO_3. The washout experiments were also performed on a Perkin Elmer Elan 5000 ICP-MS equipped with a demountable ICP torch with a ceramic injector tip and a plastic spray chamber using conditions similar to those used on the VG instrument. Data was reduced by summing counts per second for mercury isotopes (200 and 202) then dividing by bismuth internal standard counts per second at mass 209. The ratio was blank subtracted to give a net intensity ratio. The net intensity ratio was then divided by the net intensity ratios obtained for the 10 μg/L Hg standard that caused the memory, then multiplied by 100 to give a percent relative intensity for each of the 15 second integrations. Relative intensities were then plotted versus washout time in minutes.

RESULTS AND DISCUSSION

Overcoming Washout Problems

The principal analytical problem in the determination of mercury by ICP-MS is the long washout time that is often found for mercury. Two approaches were followed to limit the washout time. The first approach was to modify the sample introduction hardware where the problem is thought to originate. The second approach was to modify the rinse solution to either prevent mercury from being retained or to free any retained mercury in the sample introduction system. Both approaches were successful, as illustrated in Figure 1.

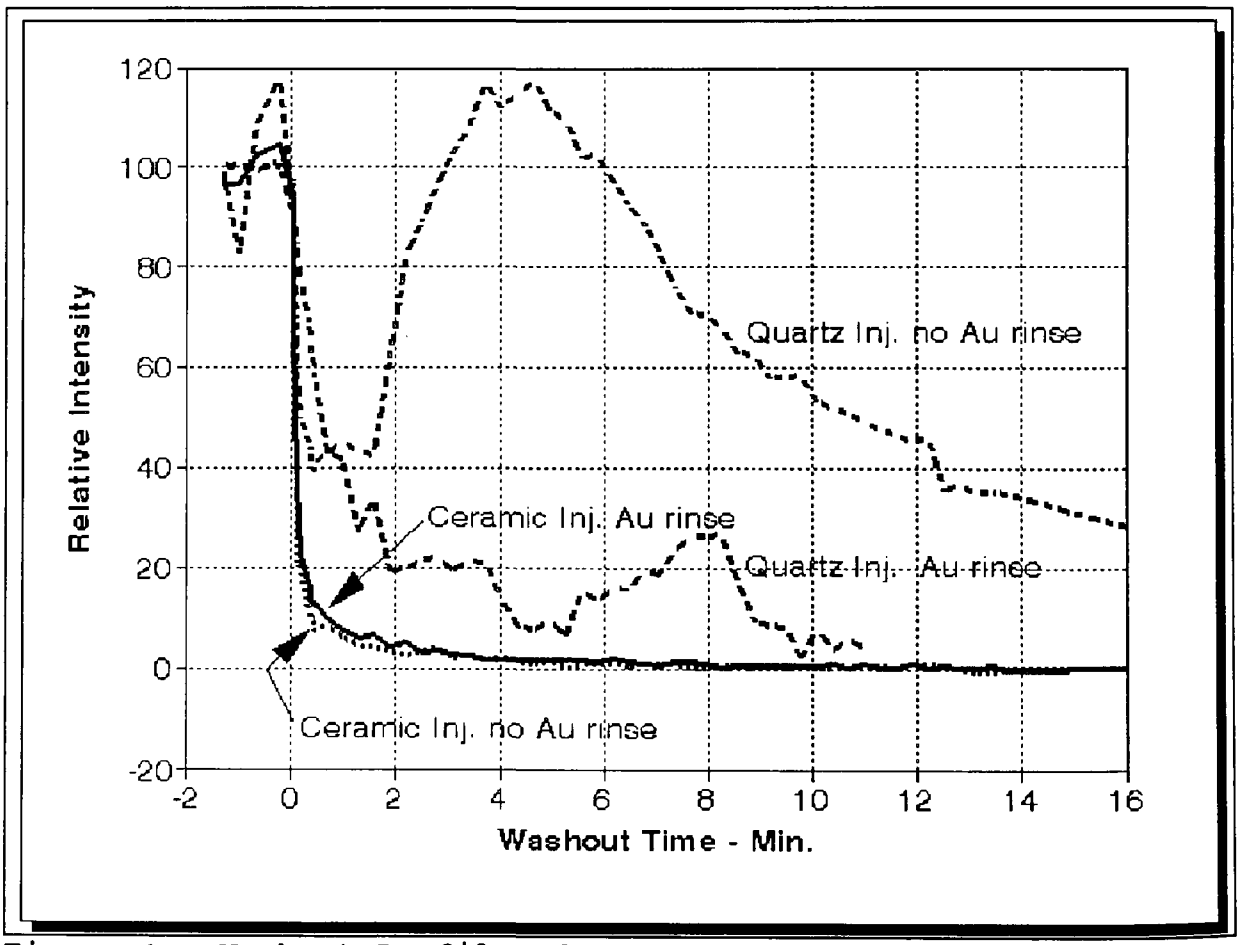

Figure 1. Washout Profiles for Mercury

If nothing is done to restrict memory problems for mercury, washout curves like that shown for the Quartz Injector - no Au rinse, may be seen. In fact, the memory signal can be as high as the previous sample that caused the memory. Clearly, no useful analytical information can be obtained in this situation and it is not feasible to wait for signals to return to their background levels. By modifying the composition of the ICP torch injector tube, where significant memory behavior can originate, instrument manufacturers have found that memory can be greatly restricted. In experiments performed with a Perkin-Elmer SCIEX ELAN 5000, modified with a plastic spray chamber and a ceramic injector tube, no discernable difference was seen in the washout curves whether or not gold was used in the rinse solution. Overall, the modified sample introduction system showed very little memory compared to the traditional quartz components. Unfortunately, the ceramic modifications are not common among ICP-MS installations, but they could obviate the need for rinse solution modifiers. The main component of memory that is left when a ceramic injector tube is used is characteristic of dissipation of the fog in the spray chamber from the previous sample.[6]

In contrast, there is a significant increase in carryover of mercury when a quartz injector tube is used. It has been speculated that there is a chromatographic effect causing the retention in which the hot silica injector tip acts much like a chromatography column.[6,10] The phenomenon has been observed for other metals as well, however, it is much less significant for the other metals than it is for mercury. Unfortunately, most ICP-MS systems use quartz torch injector tips. Therefore, additional methods of limiting memory effects had to be studied. This led to modification of the rinse solution.

Modification of the rinse solution to rapidly strip retained mercury required a reagent that would rapidly desorb mercury and keep it in solution. If compatible, the same reagent could be added to the samples to prevent the mercury from being retained. Studies with gold held the most promise. For the past 20 years, numerous studies[11] have shown that mercury in solution (as Hg(I)) is unstable in aqueous environmental samples, and in contact with materials such as glass or plastic. If Hg(I) is not properly preserved, it can volatilize, adsorb to the container walls, or diffuse through plastic. Adding gold ions to solution mitigates these effects. This led to a separate study by the authors to simulate the equilibrium speciation of Hg(I) preservation with saturated $Au(III)Cl_3$ solution in 0.317M HNO_3 (2%v/v). At 25°C and 0.6 to 1.6 pH, the dominant oxidation-reduction reactions to form the more stable Hg(II) species are:

$$AuCl_4^- + Hg_2^{2+} \rightleftharpoons AuCl_2 + 2Cl^- + 2Hg^{2+}$$

and

$$Au(OH)_3Cl + Hg_2^{2+} \rightleftharpoons Au(OH)_2 + OH^- + Cl + 2Hg^{2+}$$

The maximum Hg(I) concentration that may be preserved in an acidified sample (pH = 0.6) is controlled by the solubility of $Au(OH)_{3(c)}$, and is 785 ± 30 μg/L of Au(III) at 25°C.

Experiments conducted at NIST laboratories[12] showed that spiking with 1 μg/mL of $AuCl_3$ solution could restore adsorbed mercury to its original concentration in glass containers over

a period of weeks. The NIST work also showed that 1.0 μg/L mercury solutions stabilized with 10 μg/mL Au^{3+} (in 0.5N HNO_3) do not lose mercury to containers made of teflon, glass, or polyethylene. In fact, solutions stabilized in this manner are stable for many years. With this evidence it was decided that Au in acidic solution may be useful as a rinsing agent to help avoid memory problems with mercury.

As shown in Figure 1, a rinse solution consisting of 2.5 mg/L Au^{3+} in 6% v/v HNO_3 is very effective in dealing with mercury retention in a glass spray chamber/quartz torch sample introduction system. The improvement is seen upon mercury exposures of up to 25 μg/L mercury. The analytical range can be increased to 50 μg/L if the acid concentration of the rinse solution is increased, but erosion of the nickel sampling cones may result. (The reader should note that the quartz injector data was obtained on a VG Plasmaquad instrument that was operated at maximum sensitivity, hence, more noise was observed). Using this rinse solution with washout times of 3 minutes gives analytical results that are free of memory.

Au can also be added directly to the sample to prevent mercury from being retained in the first place. This, in conjunction with Au in the rinse, will provide no opportunity for mercury to be retained and cause memory. A side benefit is the fact that Au preserves mercury much more effectively than nitric acid alone.[13] Holding times for mercury are currently much shorter than those for the other CLP metals. The use of gold in solution has been shown to stabilize mercury in solution for as long as the holding times of the other metals (at least six months). With the stabilization of mercury in solution and matching holding times with the other metals, all of the EPA target metals can be determined with one digestion and one instrument. This could allow significant savings and improved analytical efficiency over current practices which require three digestions and three analytical techniques.

Performance of the Closed Vessel Digestion Method

Since the CVAA digestion technique yields a sample matrix that is untenable for ICP-MS, an alternative digestion technique would be required before ICP-MS could be applied to the routine determination of mercury. Open vessel procedures such as are typically used for ICP and GFAA digestions have proven unsuitable for mercury because of losses through volatilization and during the digestion. Digestion in closed vessels in a mixture of nitric and hydrochloric acid does not suffer the losses experienced by open beaker techniques. Mercury recoveries are comparable to those achieved by CVAA with Method 7471 on most samples. On samples that are heavily contaminated with mercury (> 1000 ppm), the closed-vessel method actually performs better, averaging 10 to 15% greater extraction than that which can be achieved by Method 7471. If adopted, the closed-vessel digestion would have a number of advantages over current digestion methodology for mercury. The sample matrix is suitable for ICP-MS, the procedure is relatively simple, it is quick, reproducibility is comparable to CVAA, and the closed-vessel mixed-acid digest has been shown to be appropriate for the rest of the EPA target metals as well.

A number of soil samples were obtained from a site heavily contaminated with a variety of mercury compounds. The samples were digested using the microwave assisted mixed acid method, then analyzed by ICP-MS using the aforementioned rinse solution. Results are shown in Table 2. Comparison with CVAA analyses (by EPA Method 7471) of the same samples indicated both methods agree up to 1000 μg/g, but the ICP-MS determinations get slightly larger totals on higher samples. This may be a limitation of the ability of the 7471 digestion method to extract large quantities of mercury from a soil.

Table 2. Comparison of total mercury results in heavily contaminated soils.

Soil Sample	Mercury in μg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	56.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1,670	1,360
10	73.5	64.8
11	2,090	1,830
12	96.4	85.6
13	1,060	1,190
14	294	258
15	3,300	2,850
16	301	281
17	2,130	2,020
18	247	226
19	2,630	2,060

There are few available solid reference materials with certified values for mercury, probably due to it's poor stability. However, accuracy can be evaluated by analyzing soils that are accurately spiked with mercury compounds. Table 3 shows a typical spike recovery as well as an indication of overall method precision.

Table 3. Results of ICP-MS analysis of the Laboratory Control Sample (LCS) for total Hg

ASTM Standard Soil		
Mercury Spike (mg/kg)	Mercury Found (mg/kg)	Mercury Found (%)
939	901	96
939	1001	107
939	848	90

CONCLUSIONS

ICP-MS has been successfully used for analysis of heavily contaminated soil samples. This was possible after development of a closed-vessel mixed-acid digestion method for mercury that is compatible with ICP-MS. Washout problems with mercury were also successfully overcome. Mercury retention in the sample introduction system can be mitigated by application of a rinse solution of 2.5 mg/L Au^{3+} in 6% v/v HNO_3, or by application of a ceramic ICP torch injector tube\plastic spray chamber design. The combination of the digestion method and the multielement capabilities of ICP-MS will allow analysis of all EPA target metals on a single instrument at the same time. This could represent significant analytical cost savings for the Agency.

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Errors Eliminations and Quality Assurance Procedures for the Determination of Germanium, Arsenic and Selenium in Biological Sample by Inductively Coupled Plasma Mass Spectrometry

Fu-Hsiang Ko, Institute of Nuclear Science, National Tsing Hua University, Hsinchu, 30043, Taiwan; and Ti Yeh, Center for Measurement Standard, Industry Technology Research Institute, Hsinchu, 30042, Taiwan

ABSTRACT

The matrix components in biological tissues are rather complicated, thereby making the determination of trace elements in biological tissues quite difficult. In the past, the sensitivity of instrumentation has been limited. Recently, inductively coupled plasma mass spectrometry (ICP-MS) has shown highly promising potential for direct trace element determinations. Recognizing those errors which arise from matrix effects is essential. Those errors can then be hopefully understood, with the ultimate intentions of controlling and eliminating them.

The types of errors in ICP-MS can be divided into three basic categories, i.e., gross error, statistical error and systematic error. The systematic errors which arise in the determination of germanium, arsenic and selenium in a biological sample by ICP-MS occur due to additive or multiplicative interferences, i.e. the formation of polyatomic ions, refractory oxide ions and doubly charged ions. In addition, isobar overlap, salt build-up on the cone of interface, the process of sample introduction and transport, the pathway of ion extraction in ion optics, and sample matrix induced ion suppression or enhancement are also feasible origins of systematic errors. The optimal approach of eliminating the systematic errors in ICP-MS measurement involves overcoming the interferences due to spectroscopy or non-spectroscopy.

The origins of errors in ICP-MS measurement are clearly understood. The quality assurance program is developed to ensure that the analytical result is reliable. Experimental results have indicated in this study that although principles of quality control and assurance are fairly specific, their interpretation and utilization are treated considerably different in distinctive programs. This difference shown is obvious since each organization tends to adjust its program towards its own operations and requirements. What may be suitable for a large complex laboratory involved with several disciplines or examines a variety of products may not be appropriate for a small laboratory whose activities are limited to a few tests or a few products. However, regardless of differences in laboratory complexity, conventional practices and procedures require being incorporated into the quality assurance program.

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique employed for the measurement of trace elements; however, it is not always readily applicable for all elements in every conceivable sample. The direct determination of As, Se and Ge by ICP-MS in complex matrix is relatively difficult. Generally, Cl and Na are either removed by chemical separation procedures (1-4) or treated with a high-

resolution mass spectrometer (5).

Up to now, the standard method is limited (6) for using ICP-MS as a multi-element detector. Vanhoe and co-workers (7-8) have published a method for the determination of 11 ultra-trace elements in human serum by ICP-MS. Alves *et. al.* (4) added a small dose (2%) of H_2 to the aerosol gas flow that enhanced analyte signals by a factor of 2-3 for V, Ni and As in seawater and urine reference materials by ICP-MS.

The primary aim of this work involves establishing the hyphenated system and, then, applying it towards the determination of As, Se and Ge in urine samples. The matrix in urine sample was separated by the system, and the interference was removed. A series of analytical datas were listed and the suspected data was tested. The nomality and randomness were also tested. Finally, the quality assurance program is designed to ensure the analytical result is reliable.

EXPERIMENTAL

COLUMN PREPARATION AND REAGENTS: Anion, AG1-X8 (100-200 mesh, Cl^-form), exchange resin was purchased from BIO-RAD (USA) and the resin was slurry packed into a 4.6 mm i.d. x 25 cm PEEK column (Alltech Associates, USA) with a packing machine obtained from Alltech Associates. The self-prepared column was successively rinsed with 100 ml of 10% HNO_3 and 100 ml of water.

Unless specified otherwise, all reagents were of analytical or higher grade (E. Merck, Darmstadt). Stock standard solutions (1000 ppm) of Se(VI) were prepared from sodium arsenate (Aldrich, USA), and the other standard solutions of Ge(IV) and As(V) were purchased from Aldrich and E. Merck, respectively. All buffers and eluents were prepared in Millipore (MA, USA) Milli-RO 10 PLUS water system which was used throughout the study. High purity nitric acid was obtained by sub-boiling distillation of reagent grade acid from a quartz apparatus. The pH values of the solutions in the range 1-4 were adjusted with dilute nitric acid. In the pH range 4-7, the buffer contained ammonium acetate and acetic acid, or ammonium hydroxide and ammonium acetate for the range 7-12. The pH value of solutions in the range 12-13 was adjusted with sodium hydroxide. All buffers were purified by passing through the column. After the uptake (purification) step, the retained analytes were eluted with 10% of HNO_3 solution

APPARATUS: The liquid chromatographic system consisted of a solvent delivery pump (DIONEX, MODEL DQP-1, USA) equipped with a self-constructed 5-port valve and the ELAN 5000 ICP-MS system (PERKIN-ELMER SCIEX, THORNHILL, ONTARIO, CANADA), The operating parameters of the mass spectrometer are summarized in Table 1. The schematic diagram of the hyphenated system is provided in Figure 1.

SAMPLE PREPARATION: A freeze-dried human urine reference material [National

Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2670 Low Level Toxic Metals in Human Urine] was reconstituted by an addition of 20 mL of pure water. The solutions were transferred into a 120 mL of moderate-pressure closed Teflon PFA vessel and 10 mL H_2O_2 and 1 mL HNO_3 were added. These vessels were processed through microwave digestion (CEM, MDS-81D, USA), which was monitored with pressure monitoring equipment. The pressure limit was set at 90 psig and the digestion program is gived in Table 2.

RESULTS AND DISCUSSION

MATRIX SEPARATION: In order to optimize the chromatographic conditions for retention of the arsenate (AsO_4^{3-}), selenate (SeO_4^{2-}) and germanate (GeO_3^{2-}) in the strong anion-exchange column, the recovery was monitored spectrophotometrically while changing the pH value of the loading eluent. The results (9) show that the efficiency of arsenate was retained quantitatively in the pH range 3.2-12.6. The selenate was recovered at the 100% level in the wide pH range 1.6-12.6, however the pH range is critical for germanate between 10.7-12.2. The typical performance of the proposed hyphenated technique for matrix separation is shown in Figure 2(a). Figure 2(a) clearly indicated that the sodium cation was not retained by the anion-exchange resin and eluted out first. During the loading step, the column effluent was directed to waste in Figure 2(b) indicated that the sample pH was around 11.5 and all of the three analytes were retained by this column. Next, in the cleaning step, water was pumped through the column for 2 min in order to remove matrix completely. Next the 6-port valve was switched to direct the column effluent into the nebulizer of ICP-MS. Finally, in the washing step, the 5-port valve was switched to elute the germanate and arsenate. Next the 5-port valve was switched again to elute selenate and chloride, respectively. It should be expected that the polyatomic interference occurring from the chloride was alleviated to minimum by chloride separation with $^{72}Ge^+$, $^{73}Ge^+$ and $^{75}As^+$, respectively. Experimental results indicated that the selective isotope of selenium avoids spectroscopic interference as discussed later. A detailed evaluation of the accuracy and precision about the proposed method has been provided in reference 9.

THE TYPES OF INTERFERENCES IN ICP-MS: Tschopel and Tolg (10) have mentioned the reasons which produce a systematic error and described the available methods to detect this error. The systematic error includes the spectroscopic and non-spectroscopic interferences in ICP-MS. The interferences originated from ICP-MS may lead to analytical errors as shown in Figure 3, which involve the additive or multiplicative interferences, i.e. the formation of polyatomic ions, refractory oxide ions and doubly charged ions. In addition, isobar overlap, salt build-up on the cone of interface, the process of sample introduction and transport, the pathway of ion extraction in ion optics, and sample matrix induced ion-suppression or enhancement are also the feasible sources of errors. Notably, the most interferences were placed under best control after sample digestion and instrumentation optimization. Experimental results revealed that errors were strongly dependent on salt induced

effects, salt clog the interface, isobar and polyatomic interferences for the arsenate, germanate and selenate in urine samples. As mentioned above, the matrix was separated and bypassed to the waste. Table 3 lists the polyatomic interference for Ge, As and Se. The selenium mass 78 was selected to prevent the chloide interference. The responses for the influence of various sodium chloride concentration are tabulated in Table 4, The analyte concentration equivalents arising from various acid are displayed in Table 5. The effect of ion induced suppression occurred where the concentration of sodium chloride reached 1000 ppm, indicating that a small amount of sodium chloride would have slightly promoted the signal.

OUTLIER, GOODNESS OF FIT AND RUN TEST: The proposed hyphenated technique has been successfully applied towards urine sample analysis. The replicate determinations of arsenic in urine (normal) NIST SRM 2670 are 58.1, 60.0, 57.8, 55.2, 54.7, 60.3, 58.0, 62.9, 63.2, 59.8, 57.0, 65.7, 63.2, 57.5, 56.2, 59.8, 61.2, 58.8, 64.3, 64.0, 67.2, 70.9, 66.2, 57.6, 58.4 and 50.6 ppb, respectively. One approach of assessing a suspect measurement involves making a comparison of the difference in the analysis results. Table 6 indicates that the critical value 50.6 and 70.9 were accepted under a 95% confidence level for various tests. Table 7 shows that the result of chi-square test, Clearly reveal that the data series were normality under a 95% confidence limit. Table 8 indicates that the data series were random under a 95% confidence level.

QUALITY ASSURANCE PROCEDURES: The origins of interference in ICP-MS measurement have been clearly understood, Therefore, the quality assurance program is developed in this study to ensure that the analytical result is reliable. The quality control diagram shown in Figure 4 should be applied towards the determination of trace elements in a biological sample. Garfield (11) has already mentioned that although principles of quality control and assurance are fairly specific, their interpretation and utilization are treated considerably different in distinctive programs. Each organization tends to adjust its own program toward its specific operations and requirements. For example, a large complex laboratory involved with several disciplines or determines various samples may not be appropriate for a small laboratory whose activities are limited to only a few samples. However, regardless of differences in laboratory complexity, conventional practices and procedures require being incorporated into the quality assurance program.

SUMMARY

The concentration of trace elements in the human body is extremely low; that is, analysis of these elements would be rather difficult. The analytical results for a biological tissue is beneficial for all human beings. Obtaining no analytical result is generally more acceptable than obtaining the wrong one in the sense that the wrong conclusion would be drawn on the basis of inaccurate results. The reliable data obtained from ICP-MS correlates sufficiently with a good quality assurance program (12) in any laboratory.

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Table 1 LC-ICP-MS operating conditions

Plasma conditions		
	R. f. power/W	1050
	Plasma gas flow rate/l min^{-1}	15
	Auxiliary gas flow rate/l min^{-1}	0.9
	Nebulizer gas flow rate/l min^{-1}	0.9
Mass spectrometer settings		
	Bessel box lens/V	10.95
	Bessel box plate lens/V	-73.8
	Photon stop lens/V	-10.05
	Einzel lenses 1 and 3/V	1.57
LC conditions		
	Column	Strong anion exchange
	Eluent flow rate/ml min^{-1}	1.72

Table 2 Microwave digestion parameters for urine samples

Step	Time (min)	Power (%)	Pressure (psig)
1	10	30	4
2	10	50	21
3	10	50	81
4	10	30	78
5	10	30	84
6	30	20	88
7	30	16	85
8	30	16	86

Table 3 Polyatomic interferences for As, Se and Ge, respectively

Element	Natural abundance(%)	Possible polyatomic interference
Ge-70	20.5	^{70}Zn, $^{35}Cl^{35}Cl$, $^{36}Ar^{34}S$, $^{38}Ar^{32}S$, $^{54}Cr^{16}O$
Ge-72	27.4	$^{35}Cl^{37}Cl$, $^{40}Ar^{32}S$
Ge-73	7.8	$^{40}Ar^{33}S$, $^{36}Ar^{37}Cl$, $^{38}Ar^{35}Cl$
Ge-74	36.5	^{74}Se, $^{37}Cl^{37}Cl$, $^{40}Ar^{34}S$
Ge-76	7.8	^{76}Se, $^{36}Ar^{40}Ar$, $^{40}Ar^{36}S$
As-75	100	$^{40}Ar^{35}Cl$, $^{38}Ar^{37}Cl$
Se-74	0.9	^{74}Ge, $^{37}Cl^{37}Cl$, $^{40}Ar^{34}S$
Se-76	9.0	^{76}Ge, $^{36}Ar^{40}Ar$, $^{40}Ar^{36}S$, $^{31}P^{31}P^{14}N$
Se-77	7.6	$^{40}Ar^{37}Cl$, $^{40}Ar^{36}Ar^{1}H$
Se-78	23.5	^{78}Kr, $^{38}Ar^{40}Ar$, $^{31}P^{31}P^{16}O$
Se-80	49.6	^{80}Kr, $^{40}Ar^{40}Ar$, $^{31}P^{31}P^{18}O$
Se-82	9.4	^{82}Kr, $^{12}C^{35}Cl^{35}Cl$

Table 4 The effect of various NaCl concentrations on the signal of As, Se and Ge

[NaCl]ppm	0	15	20	60	100	500	1000	2500	7500	10000
Ge72	100	109	115	109	112	98	89	80	70	69
Ge73	100	108	116	109	113	98	89	80	71	70
Se78	100	113	114	114	109	90	77	63	48	46
Se82	100	111	116	114	110	89	76	63	50	44
As75	100	112	113	113	111	98	90	78	64	62

n=20.

Table 5 Analyte concentration equivalents (ppb) arising from interference at various concentration

mass	various nitrogen concentration (ppm)						
	90.4	110	170	226	440	1760	7040
70	0	0	0	0	0	0	0
72	0	0	0	0	0	0	0
73	0	0	0	0	0	0	0
74	0	0	0	0	0	0	0
75	0	0	0	0	0	0	0
76	0	0	0	0	1	1	1
77	0	0	0	0	2	3	12
78	0	0	0	0	0	0	0
82	0	0	0	0	0	0	0

mass	various sulfur concentration								
	33.3	56.7	133	250	333	395	1579	6314	25256
70	0	0	0	0	0	0	0	0	0
72	0	0	0	0	0	0	1	2	7
73	0	0	0	0	0	0	0	0	0
74	0	0	0	0	0	0	0	0	0
75	0	0	0	0	0	0	0	1	5
76	0	0	0	0	0	0	0	0	0
77	0	0	0	0	0	0	0	0	0
78	0	0	0	0	0	0	1	2	4
82	-	-	-	-	2	2	6	23	100

mass	various chlorine concentration								
	76	100	400	750	760	1000	3040	6080	12160
70	-	1	0	0	0	0	5	15	44
72	0	0	0	0	0	0	2	7	20
73	0	0	0	0	0	0	1	2	6
74	0	0	0	0	0	0	0	1	2
75	-	1	4	5	11	-	70	150	274
76	0	0	0	0	-	0	4	5	6
77	3	6	17	23	55	-	348	762	1390
78	0	0	0	0	0	0	3	11	16
82	0	0	0	0	0	0	3	9	19

mass	various phosphorus concentration							
	14	29	115	230	575	1150	2300	4598
70	0	0	0	1	1	2	2	2
72	0	0	0	1	1	1	1	1
73	0	0	0	2	3	1	4	4
74	0	0	0	1	1	1	1	1
75	0	0	0	1	1	1	2	3
76	0	0	0	1	2	2	7	8
77	0	3	2	11	11	13	16	20
78	0	0	0	4	5	5	9	10
82	0	0	3	9	11	13	23	37

mass	various carbon concentration					
	11	88	446	892	1785	3569
70	1	0	1	1	1	1
72	0	0	1	1	1	0
73	0	0	1	1	1	1
74	0	0	0	0	0	0
75	0	0	1	1	0	0
76	0	0	0	1	0	0
77	1	0	-	-	-	-
78	1	1	1	0	0	0
82	1	1	1	0	0	0

* The background counts at mass 80 is too high due to $^{40}Ar^{40}Ar^{+}$

Table 6 Various outlier tests for verifying suspected data

Data series: 50.6< 54.7< 55.2< 56.2< 57.0< 57.5< 57.6< 57.8< 58.0< 58.1< 58.4< 58.8< 59.8= 59.8< 60.0< 60.3< 61.2< 62.9< 63.2 = 63.2 < 64.0< 64.3< 65.7< 66.2< 67.2< 70.9

$X \pm S = 60.3 \pm 4.5$

(a) The huge error test (M= | suspect-mean |/s, M>4 then M is outlier)

$M(70.9) = (70.9-60.3)/4.5 = 2.4 < 4$

$M(50.6) = (60.3-50.6)/4.5 = 2.2 < 4$

All data are accepted.

(b) The Dixon test (Under 95% confidence limit)

$r_{min} = r_{50.6} = (X_4-X_1)/(X_{L-2}-X_1) = (56.2-50.6)/(66.2-50.6) = 0.359<0.4$

$r_{max} = r_{70.9} = (X_L-X_{L-3})/(X_L-X_3) = (70.9-65.7)/70.9-55.2) = 0.331<0.4$

All data are accepted.

(c) The Grubbs test (Under 95% confidence limit)

$T_{min} = T_{50.6} = (X-X_1)/S = (60.3-50.6)/4.5 = 2.156<2.663$

$T_{max} = T_{70.9} = (X_n-X)/S = (70.9-60.3)/4.5 = 2.356<2.663$

All data are accepted.

Table 7 Normal distribution test for data series

Measurement ppb	Observed O_i	Theoretical probability P	Theoretical e_i	$(O_i-e_i)^2/e_i$
< 56.38	4	0.192	5	0.2
56.38-58.97	8	0.192	5	1.8
58.97-61.63	5	0.231	6	0.2
61.63-64.22	4	0.192	5	0.2
> 64.22	5	0.192	5	0
Sum	26	1.0	26	2.4

$\chi^2(0.95,2) = 5.99 > 2.4$, The data series is normal distribution.

Table 8 Randomness test for data series

Data sequence:		58.1	60.0	57.8	55.2	54.7	60.3	58.0	62.9	63.2
		-	+	-		-	+	-	+	+
59.8	57.0	65.7	63.2	57.5	56.2	59.8	61.2	58.8	64.3	64.0
-		+	+			-	+	-	+	+
67.2	70.9	66.2	57.6	58.4	50.6					
+	+	+	-	-						

The median is (59.8+59.8)/2 = 59.8
$n_1 = 12$, $n_2 = 14$, $r = 13$ (Under 95% confidence limit), $r_U = 20$, $r_L = 8$,
then $r_U=20 > r = 13 > r_L = 8$, the data sequence is randomness.

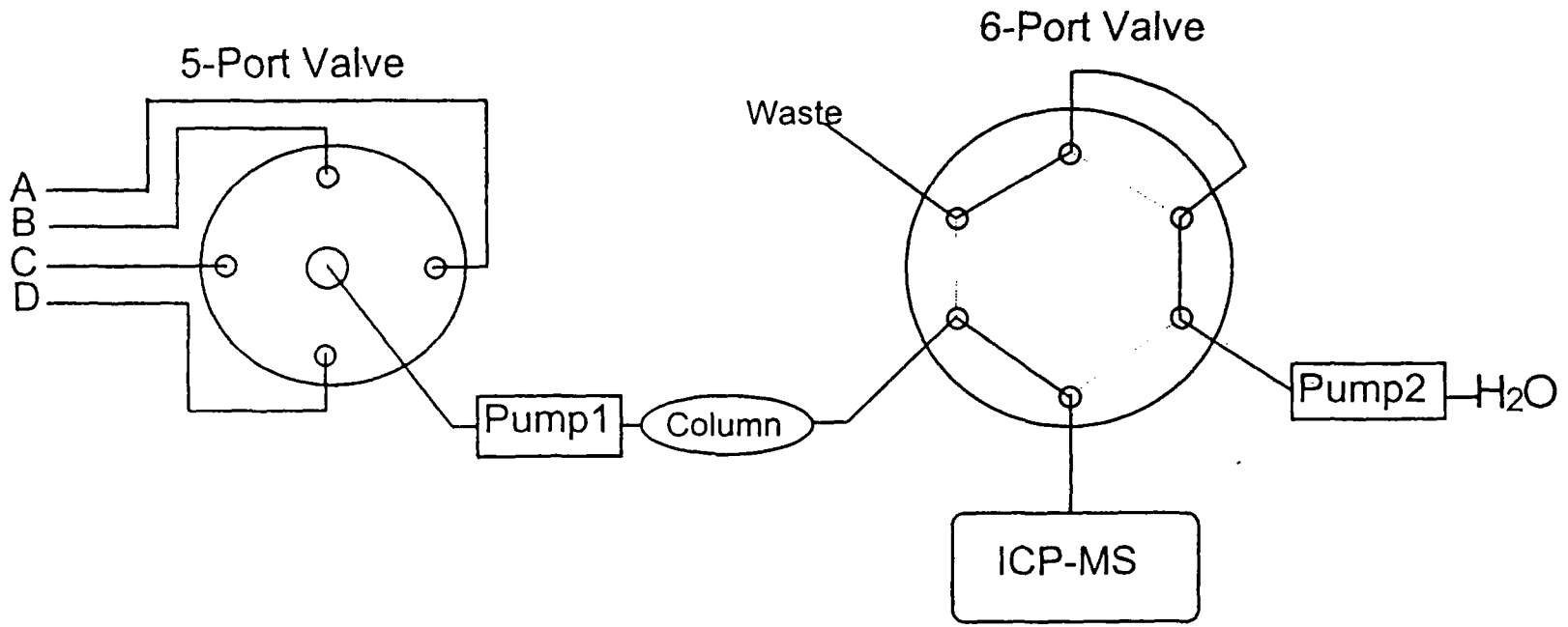
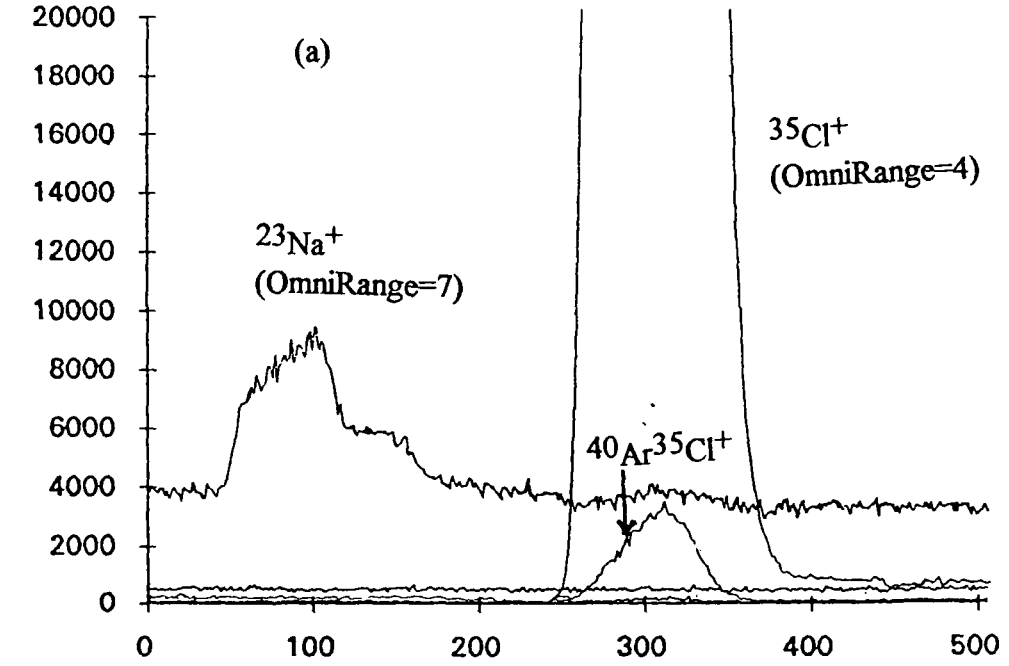


Figure 1 Schematic diagram of the hyphenated system



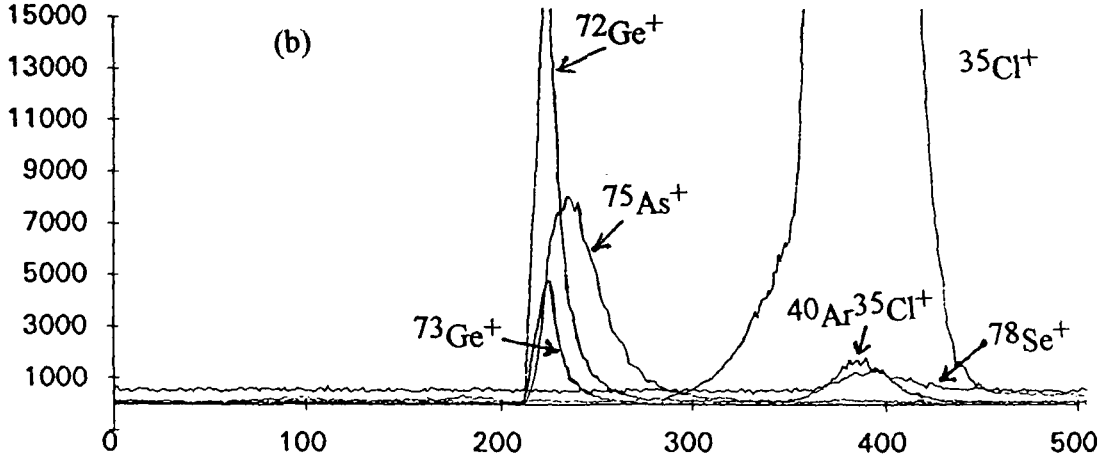


Figure 2.(a) Elution performance of 10 mg NaCl; 1-200 sec is pretreatment step at pH 11, 201-500 sec is eluted with 4% HNO_3. (b) Chromatogram of 24 ng As, Se and Ge in 10 mg NaCl matrix; 1-160 sec is pretreatment step at pH11, 161-320 sec is eluted with pH1.25 HNO_3 solution and 321-500 sec is eluted with 4% HNO_3 solution.

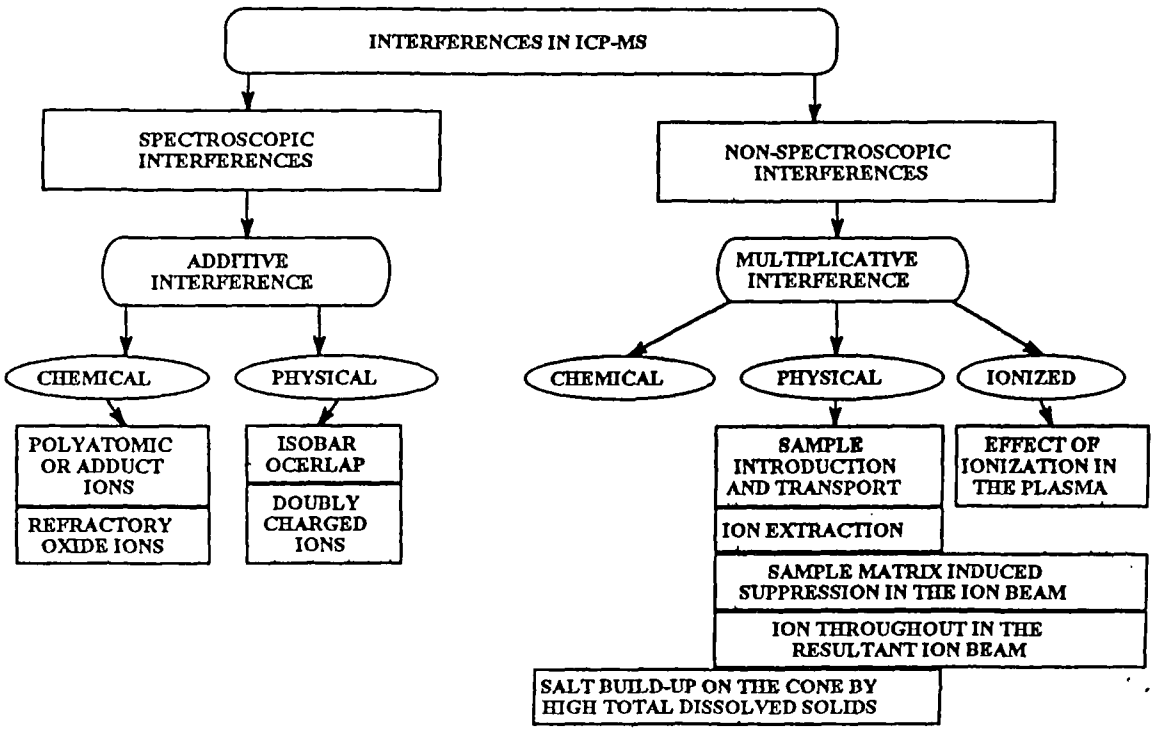
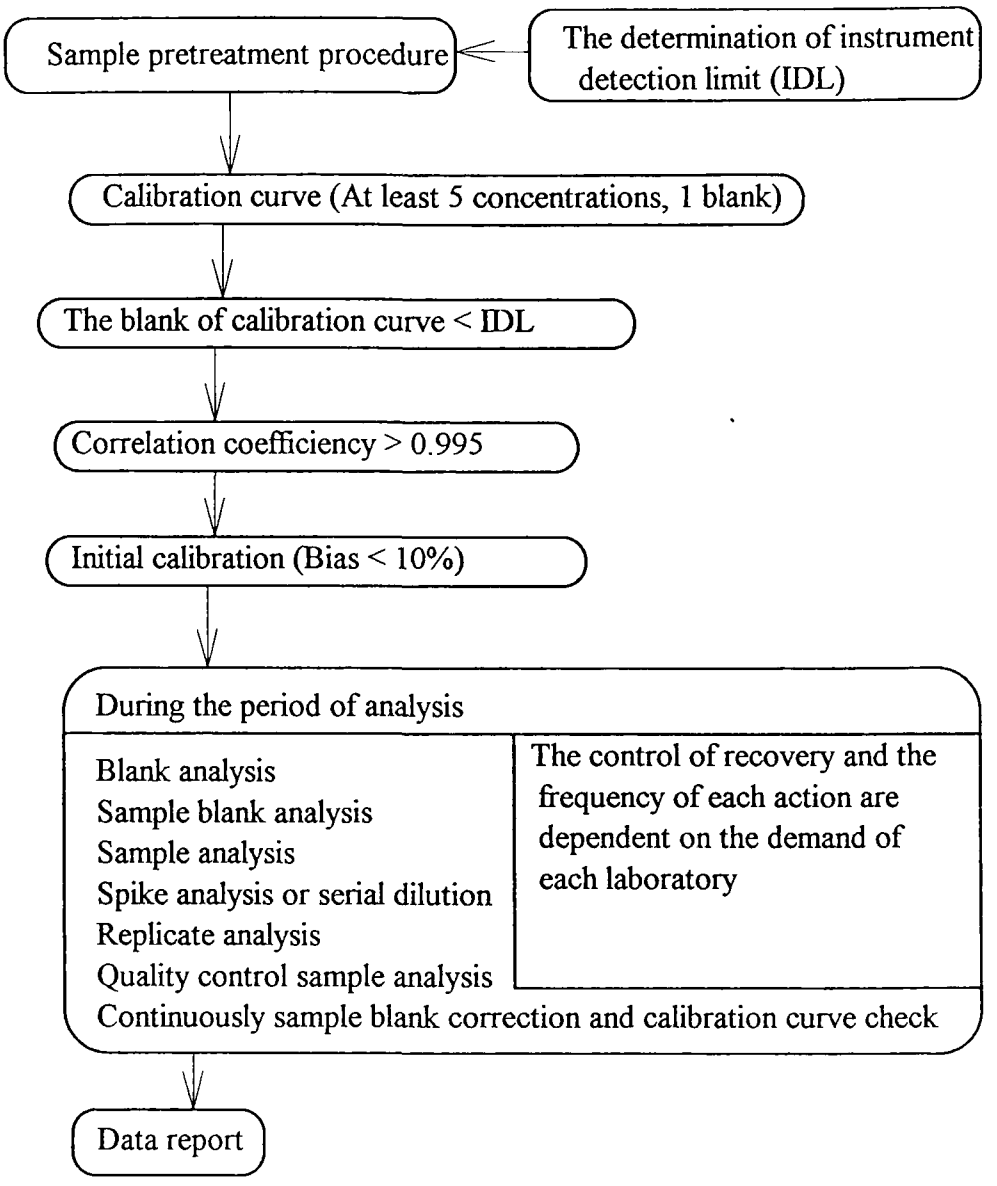


Figure 3 Various types of interferences in ICP-MS

Figure 4 The diagram of quality control procedure in ICP-MS measurement



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IMMUNOASSAY METHODS: DEVELOPMENT AND IMPLEMENTATION PROGRAM AT THE USEPA

by Barry Lesnik, USEPA, Office of Solid Waste, Methods Section (5304), 401 M St., SW, Washington, DC 20460

Introduction and Background

Immunoassay technology has several attributes which make it a useful tool for environmental monitoring, e.g. selectivity, sensitivity, portability, and rapid turnaround time. Immunoassay kits can be tailored to target specific analytes or classes of analytes, thus eliminating the need for cleanup methods in most cases to remove interferences. They also have the capability of detecting target analytes at very low levels, which are needed in many environmental applications. The portability of immunoassay test kits and speed of analysis allows for rapid analyses to be run on a site in the field. This capability can be especially useful in lowering the costs of cleanup projects because equipment does not have to lay idle while awaiting the results of laboratory analyses.

The USEPA has been looking at the potential use of immunoassay technology for environmental monitoring for several years. The early methods development efforts were unsuccessful because the immunoassay chemistry utilized in the methods was not sufficiently rugged for use on real world environmental matrices. The methods performed well on clean water matrices and spiked samples, but did not perform effectively on natural environmental samples. Because of this poor initial performance on real samples, EPA Program Office interest in the technology declined.

In January, 1992, EnSys, Inc. demonstrated a viable immunoassay test kit for pentachlorophenol in both soil and water matrices to EPA's Office of Solid Waste (OSW). Since that time, OSW has been working with several manufacturers to develop and validate a whole battery of immunoassay test kits both for individual analytes and for classes of analytes. Currently, OSW has issued four immunoassay methods which can be used for analyses performed under the Resource Conservation and Recovery Act (RCRA). Two others are in the final stages of validation and several more are in various stages of validation.

General Guidelines for Development of Screening Methods

The primary applicability that we, in the RCRA Program, see for immunoassay methods is for quantitative screening purposes. By quantitative screening, we mean setting a quantitative action level (usually the regulatory action level), where a positive response

means that the analyte is present at or above the action level, and a negative response tells us that the analyte is either absent or present below the level of regulatory concern. Analyses can be run at multiple action levels giving a useful range of concentrations for specific target analytes. For example, if we are mapping a site contaminated with polychlorinated biphenyls (PCB) to determine the extent to which it needs to be cleaned up, knowing where PCB levels are <10 ppm, between 10 and 100 ppm, and >100 ppm can be useful in planning and expediting the cleanup.

The OSW Methods Section distributes a letter, on request, to potential developers of screening methods providing guidance on what general validation criteria should be applied to a screening method that will potentially be included in SW-846. While screening procedures need not be fully quantitative, they should measure the presence or absence of target analytes at or below regulatory action levels. Therefore, initial demonstration of method performance involves measuring the percentage of false negatives and false positives generated using the procedure for a single sample matrix. Data should be submitted for split samples analyzed using the developer's technique and an appropriate SW-846 quantitative method. A candidate procedure should ideally produce no false negatives and no more than 10% false positives. Definition of a false negative is a negative response for a sample that contains up to two times the stated detection level of the target analyte(s). Definition of a false positive is a positive response for a sample that contains analytes at one half the detection level. Specific details on initial submission criteria are included in the guidance letters, and I will not include them in this article.

Other factors to be considered are interferences and matrix effects. The effects of interferences, both positive and negative, resulting from both target and non-target analytes should be evaluated. Method performance and matrix effects in a variety of RCRA matrices (e.g., soils, concentrated waste, ash, groundwater, leachate, or wastewaters) should be demonstrated. It may not be necessary or appropriate to spike all of the target analytes listed within a chemical class for these initial method evaluations. If field data is available, it would be valuable to be able to compare the results obtained using the screening procedure with sample concentrations determined in a laboratory using SW-846 methods.

To summarize, the Methods Section does not require an unreasonable body of data for the initial evaluation of new techniques. Data will need to be submitted on the percentage of false negatives, percentage of false positives, sensitivity to method interferences, and matrix-specific performance data. In addition to these data, the developer should also provide a description of the procedure and a copy of any instructions provided with the test kits.

Validation Criteria for Immunoassay Methods

In addition to the guidelines for developing screening methods in general, OSW, based on its own experience, has generated some validation criteria specifically applicable to immunoassay methods. These validation criteria are required to be submitted to OSW for review for all immunoassay test kits, whether the kits are to be the basis for a new method or as an alternative kit being added to existing methods. The data needed for validation of immunoassay methods that will be included directly in the method is as follows:

1) Cross Reactivity with similar analytes,

2) Cross Reactivity with dissimilar analytes which may be reasonably expected to be found at waste sites,

3) False Negative/False Positive Rates,

4) Extraction efficiency (for soil test kits),

5) Performance data on spiked samples in environmental matrices validated against standard SW-846 analytical methods, and

6) Performance data on actual environmental field samples validated against standard SW-846 analytical methods.

Since interferences can be a major problem in environmental analyses, it is important to demonstrate that the analytes of concern can be identified in the presence of similar analytes or dissimilar analytes which may be present in environmental samples. In many instances, substantial cross reactivity with other analytes is a desirable situation. Examples of desirable cross reactivity include sensitivity to esters of 2,4-dichlorophenoxyacetic acid (2,4-D) as well as the 2,4-D, and for other 3-, 4-, and 5-membered polynuclear aromatic hydrocarbons (PAH) when testing for phenanthrene in a PAH screening method.

The false negative/false positive rate for a particular immunoassay kit is very important. OSW screening methods are designed to generate 0% false negatives and up to 10% false positives at the regulatory action level. Slightly higher false positive rates are tolerable, e.g. up to 25%. High false positive rates, i.e. >25%, negate the cost effectiveness of the technique because of the excessive numbers of confirmatory tests that would need to be performed. High false negative rates, i.e. >5% at the regulatory action level eliminate the potential use of the method for regulatory purposes.

The extraction efficiency data is important for setting the appropriate action level for a soil analysis. Recoveries are the primary determining factor for making sure that the analyte of

concern can be detected at the regulatory action level and for minimizing false negative/false positive rates.

The performance data generated from environmental samples spiked with the target analytes gives a good indication as to whether or not an immunoassay method will work. However, the performance generated in the field on real environmental samples is the key determining factor on whether or not the immunoassay method is sufficiently rugged to be included in SW-846 as an analytical method.

Additional data that OSW requests, but does not include in the method and treats as confidential business information (CBI), includes dosage curves and the manufacturer's internal validation and quality control criteria. The slope of the dosage curve can be a good indication of whether or not an immunoassay method will exhibit a high rate of false positives. Manufacturing quality control and validation information gives a good indication as to continued test kit availability.

Up to this time, all of the immunoassay test kits (10-15) that the OSW has evaluated have been extensively tested and validated by the manufacturers. EPA validation has primarily consisted of confirmation of the manufacturers' results and performing some additional testing on well-characterized environmental samples, which are more easily available to EPA Regional laboratories.

Overview of the Regulatory Approval Process

As I have mentioned in other articles, RCRA methods are published through an official regulatory notice printed in the *Federal Register* incorporating them by reference into SW-846. These methods must be issued as regulations, because any method in the manual could be required for potential use under the few sections of the RCRA regulations where the use of SW-846 methods is mandatory. For the majority of RCRA applications, "any reliable analytical method" may be used, i.e., a method which will determine the analytes of concern in the matrix of concern at the regulatory level of concern at the necessary confidence level.

I will now very briefly explain the regulatory process by which methods are incorporated into SW-846, and the status and applicable uses of methods at the various stages of the process. The regulatory process for analytical methods briefly consists of the following phases:

1) Technical Workgroup Review,

2) Proposed Regulation for Public Comment through a *Federal Register* Notice,

3) Response to Public Comment, and

4) Promulgated Final Regulation through a *Federal Register* Notice.

The first phase in the method approval process is the only EPA technical review during the approval process. All subsequent reviews by EPA are administrative in nature. Public comments may be either technical or administrative, and all must be addressed.

The most critical phase of the review process for methods is the Technical Workgroup Review. The SW-846 Technical Workgroups are made up of EPA chemists from across the Agency representing Program Offices, ORD, Regional Laboratories, and Enforcement. The methods are carefully reviewed to determine whether they demonstrate appropriate performance and applicability to address RCRA requirements. After Workgroup approval, the Methods Section addresses any Workgroup comments on a method, both technical and editorial, and prepares a "Draft" method. "Draft" methods are available from the Methods Section on request, and can be used for any RCRA application for which they are appropriate, and for which the use of SW-846 methods is not mandatory.

The individual "Draft" methods are then assembled as a package and a *Federal Register* Notice is prepared for public comment proposing that the methods be added to SW-846. The methods are now considered "Proposed" methods, but still have the same regulatory status as "Draft" methods, i.e., they can only be used for RCRA analyses where the use of SW-846 methods is not mandatory.

The public comment period is normally 45-60 days. Comments are compiled and addressed. Any appropriate technical and editorial changes are made to the "Proposed" methods in response to public comment. The final edited methods are again assembled as a package and the methods are added to SW-846 through a second *Federal Register* Notice. The methods are now "Promulgated" or "Approved" methods and can be used for any appropriate RCRA application including those where the use of SW-846 methods is mandatory.

Status of the EPA Immunoassay Methods Development Program

Several EPA Program Offices are investigating the potential applicability of immunoassay methods to their programs. However, the OSW is the first EPA Program Office to formally incorporate these methods into its methods program. OSW began evaluation of its first immunoassay method (for pentachlorophenol) in January of 1992, followed by two others in rapid succession. As of September, 1993, OSW has completed validation of four immunoassay methods utilizing five kits, and is in the final stages of validating two

additional methods and several additional kits for existing methods. For an EPA regulatory Program Office, this is very rapid progress. The four validated methods are

Method 4010: Pentachlorophenol (PCP) in Water and Soils by Immunoassay,

Method 4020: Polychlorinated Biphenyls (PCBs) in Soil by Immunoassay,

Method 4030: Total Petroleum Hydrocarbons (TPH) in Soil by Immunoassay, and

Method 4035: Soil Screening for Polynuclear Aromatic Hydrocarbons (PAHs) by Immunoassay.

The two methods in the final stages of validation, i.e., field testing are

Method 4015: 2,4-D in Water and Soils by Immunoassay and

Method 4031: Soil Screening for BTEX By Immunoassay.

Currently, Methods 4020, 4030, and 4035, are "Draft" methods. Method 4010 was promulgated on January 4, 1994 as Update IIA to the Third Edition of SW-846 (59 **FR** 458-69) and is an "approved" method. Methods 4020, 4030, and 4035 are available on request from the Methods Section Office, and can be used for RCRA analyses for which the use of SW-846 methods is not mandatory. Method 4010 is also available from the Methods Section Office, and can be used for any RCRA application for which it is appropriate. The final validation studies for Methods 4015 and 4031 are expected to be completed with Workgroup approval in 1994.

OSW is working with several of the manufacturers to initiate validation studies on kits for many additional analytes, primarily pesticides, which are coming on the market. Some of the target analytes scheduled for evaluation include Alachlor, Aldicarb, Carbofuran, Cyclodienes, DDT, Lindane, and mercury as mercuric ion. OSW is also working with the manufacturers to develop new test kits by delineating groups of target analytes that would be useful and appropriate to determine by immunoassay methods. These analytes include dioxins and furans, halogenated volatile solvents, phenols, benzidines, and other amines.

Some of the other EPA Program Offices are also looking at immunoassay methods to address some of their analytical requirements. OPPTS is considering using immunoassay methods in its Pesticide Registration Program. OW is beginning to look at using the technology in both the Drinking Water and Wastewater Programs. However, they may have to revise some of their regulations to allow for the use of "less than" values in reporting

Minimum Contaminant Levels (MCL) or look toward developing quantitative immunoassays.

Potential Environmental Applications for Immunoassay Methods

OSW decided to take a cautious approach to the introduction of a new technology to the environmental field, with which most analytical practitioners were unfamiliar, and limit the initial applications of immunoassay methods to quantitative screening. We were aware that the technique had been used in Clinical Laboratories for many years in both screening and determinative applications. Since Regulatory Agencies tend to be slow to accept new and different approaches to analysis, anyway, we decided to take a "walk before you run" approach to introducing the new methodology to the people actually doing site assessments and cleanups.

The two primary applications of immunoassay methods in the RCRA Program are mapping of contamination at well-characterized sites slated for cleanup and monitoring the effectiveness of cleanup activities. Immunoassay lends itself very well to these two particular applications. It is not particularly applicable to the identification and characterization of unknown contaminants at waste sites when compared to much more comprehensive techniques such as gas chromatography/mass spectrometry (GC/MS). However, for monitoring applications of known contaminants, its specificity, sensitivity, and cost effectiveness are excellent.

Over the past year, the general acceptability and willingness to use immunoassay methods within the EPA Regions for RCRA and Superfund applications has increased exponentially. A significant factor in this change of attitude, in addition to OSW's attempts to educate users in the applicability of the technique, is the specter of shrinking budgets. Field people who are charged with actually doing cleanups are looking for more cost effective ways to do their jobs with less available money. A technique, such as immunoassay methodology, which can generate high-quality results in real-time, and can keep the bulldozers rolling can contribute significantly to reducing the costs of cleanups, and is being looked upon more favorably.

The initial application of immunoassay technology in the RCRA Program was for determining compliance at wood surface treating facilities with PCP regulatory limits. The selectivity and sensitivity of the immunoassay method easily met the regulatory action limit of 0.1 ppm. Use of the PCP immunoassay method (Method 4010) for compliance monitoring was encouraged by OSW and the method was proposed for inclusion in SW-846 as a part of the Wood Surface Treatment Rule.

The major applications for which immunoassay methods are

currently used in the RCRA Program are site mapping and monitoring cleanups at sites contaminated with PCBs. Use of the PCB method (Method 4020) has resulted in cost savings at many sites in several Regions. The speed and low cost of the test allows for more extensive mapping of contamination at a site, because many more samples can be analyzed on site, thus generating a more detailed map of the site. This results in lower cleanup costs, since the cleanup efforts can be directed only at the places that need to be cleaned up, instead of to a broader area. The design of the method allows for rapid determination of whether or not the site cleanup level has been met, thus reducing costs of cleanup in both time and equipment. With the recent availability of the PAH method (Method 4035), the technique is now beginning to be used on sites contaminated with PAHs.

Another major application within OSWER is for mapping and cleanup of sites contaminated with petroleum hydrocarbons from leaking storage tanks for the Office of Underground Storage Tanks (OUST). The TPH method (Method 4030) is effective for determining gasoline, diesel, kerosene, and jet fuel at required cleanup levels.

Additional analytes will be targeted as new methods are developed and validated. Eventually, OSW intends to perform quantitative analysis either using immunoassay methods for direct quantitation or as concentration techniques using affinity chromatography, with quantitation by existing techniques, e.g. HPLC or GC/MS. The latter approach will be particularly effective for doing analyses where multiple analytes within a class need to be individually identified.

Barriers to Use of Immunoassay Methods

There have been some initial barriers to getting immunoassay methods accepted for routine use in the environmental community. These barriers have been both technical and cultural in nature. The technical barriers include lack of knowledge about analytical options; use of expensive time-consuming methodology when more efficient methodology is available; poor planning of the initial analytical scheme; failure to identify proper questions to be answered resulting in generation of data inappropriate to address the problem at hand. Cultural barriers include inappropriate or excessive regulatory restrictions on use of new methods, e.g. requiring the use of only promulgated methods for program applications that do not have these requirements, and requiring the use of expensive broad-scope methods, e.g., GC/MS, for limited monitoring applications for only a few known and well-characterized analytes.

An additional issue of concern was whether the Regulatory Program Offices could live with analytical values that were not a

specified number, i.e., a less than value (usually the regulatory action level) vs. a definite number (0.1 ppm) or a range of values (>5 and <50). We, in the RCRA Program, decided that we could indeed use these values to answer the basic questions for which these analyses were performed, i.e., Have we attained our cleanup criteria? Where do we have to focus our cleanup efforts? We decided that our normal operating procedures for confirming quantitative screening results would be to use the standard reference method to confirm positives and to spot check a certain percentage (usually 10%) of negative results.

Other Program Offices in EPA, such as the OW may have some restrictions in their current regulations which require them to generate a definite analytical value. If this is indeed the case, their focus would be on quantitative immunoassay methods rather than screening methods.

OSW has initiated a major effort to train EPA permit writers, enforcement people, and others who deal with analytical methods in their jobs in the regulatory aspects of using RCRA methods. Historically there have been problems where only promulgated methods were allowed to be used in many applications under the RCRA regulations where this was not a requirement. The Methods Section is in the process of developing a formal training program for RCRA personnel in the Regions and at Headquarters to make them aware as to which methods are allowable and appropriate to use under the RCRA regulations in both mandatory and non-mandatory applications, and how to prepare efficient, cost effective sampling and analysis plans.

State programs are a little more difficult. Since RCRA is a Federal Program which has been passed down to most States to administer, the State regulations can be more restrictive and tend to vary greatly. Some States mandate the use of SW-846 methods for all RCRA analytical applications within the State. Flexibility within State Programs varies from allowing only the use of promulgated methods to using any method that may be appropriate for an application. Through dialogue with the EPA Regions and Headquarters, some of the States are beginning to take an interest in utilizing immunoassay methods. TPH analysis is the major focus right now in State Programs, since it is not regulated at the Federal level. Several States are beginning to adopt Method 4030 for use in their Underground Storage Tank (UST) Programs, e.g. Georgia and California.

Summary and Conclusions

The OSW immunoassay methods program was initiated in January, 1992, with the evaluation of the screening method for PCP. Methods for PCBs and TPH followed soon after. These three screening methods were recommended for inclusion in SW-846 by the Technical

Workgroup. A fourth method for PAHs, also received Workgroup approval last summer. Two other methods are in the final stages of validation, with several more beginning the validation process. For a Regulatory Program, immunoassay methodology has advanced very rapidly.

There was initially a general reluctance among the regulatory and regulated community to use immunoassay methods, even for applications for which they were appropriate. This was due to a lack of knowledge about the technology and a belief among both the regulators and regulated community that only promulgated SW-846 methods could be used for all RCRA applications.

The climate has changed considerably during the past year regarding the use of screening methods in general, and immunoassay methods in particular in the environmental community. We have noticed a much greater willingness for EPA Regional and some State regulators to allow for the use of immunoassay methods in their RCRA Programs. Apparently, the dissemination of information about the effective performance of immunoassay methods and a budget crunch which drives both regulatory and remediation personnel to look for more cost effective means to do their jobs have begun to have an impact in the environmental community.

The future looks bright for the environmental application of immunoassay methodology. Many other Federal Agencies with massive cleanup problems, e.g. The Department of Energy (DOE) and The Department of Defense (DOD), have become interested in the technology for its overall utility in significantly cutting the costs of cleanup operations. Within the next two years, we expect to focus more on quantitative immunoassay methods. When the environmental community has reached an appropriate comfort level with using immunoassay screening methods, we will introduce the quantitative methods. The EPA will continue its cooperative effort with the immunoassay manufacturers and other methods developers to develop the methods that are needed for its environmental programs.

QUANTITATIVE ENVIRONMENTAL IMMUNOASSAY, THE NEXT STEP?

Dr. P.J. Marsden and S.F. Tsang, Environmental Health and Safety Group, Science Applications International Corporation (SAIC), 4161 Campus Pt. Ct., San Diego, California 92121

ABSTRACT

Immunoassay or enzyme-linked immunosorbant assay (ELISA) is a powerful tool for providing analytical support during environmental monitoring and cleanup projects. Immunoassays can produce accurate, cost-effective and sensitive measurements of specific contaminants. Immunoassay methods currently promulgated for the RCRA program or being considered for SW-846 are suitable only for sample screening. Analysts must demonstrate the suitability of quantitative immunoassay techniques before they can be used to support environmental decisions. Demonstration of the suitability of quantitative immunoassay will require rigorous comparisons between those techniques and promulgated chromatographic methods. Refinements in immunoassay methods will be required to ensure that measurements are quantitative including improvements in extraction, measurement and QA procedures.

Data are presented in this paper from two studies that provide a side-by-side comparison of immunoassay with GC/ECD analysis (Method 8081) for multicomponent analytes. The first study involved the analysis of Toxaphene; the second study involved the analysis of PCBs. In both studies, results are provided for laboratory spiked and *in situ* contaminated soils. Soil was contaminated with Toxaphene through pest control activities in New Mexico (i.e., sheep dips for scabies). Comparison of the Toxaphene concentrations measured using immunoassay and using Method 8081 provided an excellent correlation over a concentration range of 0.5 to 400 ppm. Soil and waste contaminated with PCBs were provided as reference materials by the Research Technology Corporation of Laramie, WY.

The results of these studies illustrate the suitability of quantitative immunoassay. The paper also presents a discussion of some of the current barriers to the adoption of quantitative immunoassay as an environmental tool, including the variety of RCRA matrices, the need to train staff to perform and interpret immunoassays as well as some requirements for validating these procedures. Measurement scientists must overcome these barriers before quantitative immunoassay can be adopted for environmental monitoring.

INTRODUCTION

Immunoassay (enzyme-linked immunosorbent assay [ELISA]) is gaining acceptance as a screening technique for measuring specific compounds in environmental samples. Immunochemical analyses are suitable only for the

analysis of specific target analytes for which specific antibodies have been prepared. Therefore, immunoassay is not appropriate for initial site characterization. However, once the nature of contamination at a site has been established using conventional chemical analysis, immunoassay field screening may be used to (1) reduce the number of expensive chromatographic analyses required for site monitoring, (2) focus resources on the worst portion of the site, (3) analyze more samples or (4) obtain analytical data more rapidly. While immunoassay is usually considered as a field technique, the use of immunoassay as a laboratory screening procedure could benefit our industry by (1) reducing the need to analyze samples with less than detectable levels of contamination and (2) reducing the need to dilute samples with very high levels of contamination. SW-846 immunoassay methods have been proposed or promulgated for pentachlorophenol (Method 4010), polychlorinated biphenyls (PCBs, Method 4020) and petroleum hydrocarbons (Method 4030). Additional techniques are being considered by the Office of Solid Waste Organic Methods Workgroup for possible inclusion in future updates of SW-846. The Office of Pesticide Programs is testing immunoassay techniques for the analysis of Alachlor, Metalochlor, Atrazine and 2,4-D. The Office of Water is considering the use of immunoassay for several target analytes including cyanazine.

Immunoassay differs from conventional chromatographic techniques in both the measurement technique and the sample preparation procedures. Methanol extraction is specified for immunoassay procedures rather than methylene chloride/acetone extraction because methanol is more compatible with the biochemicals (*e.g.,* antibodies and proteins) required for immunoassay. The use of different extraction solvents for immunoassay and GC analyses results in two major concerns, (1) data obtained using the two techniques may not be fully intercomparable and (2) a requirement for two different extraction procedures may limit the acceptance of immunoassay as a laboratory screening procedure.

In contrast to environmental applications where they are applied only as screening procedures, immunoassays are routinely used for quantitative clinical analyses. This paper provides quantitative environmental data comparing immunoassay with the chromatographic procedure, Method 8081. We will also provide data that demonstrates that immunoassay kits are suitable for screening laboratory extracts (methylene chloride/acetone) after exchange to methanol. Finally, we will provide discussion of some of the barriers to adopting quantitative immunoassay for environmental applications.

EXPERIMENTAL DESIGN

SAIC conducted a side-by-side comparison of analyses of chlorinated multicomponent pollutants using immunoassay techniques and GC/ECD. These studies were funded separately under contract to the Millipore Corporation and EnSys, Inc. Samples included both soil spiked in our laboratory and contaminated soils collected in the field. Toxaphene

immunoassays were performed by Immunosystems in Maine using the Millipore EnviroGard kit. PCB immunoassays were conducted by SAIC using the EnSys PCB RIS$^{\underline{c}TM}$ kit in our San Diego laboratory according to Method 4020. All of the GC/ECD analysis were conducted in the SAIC Methods Laboratory at San Diego according to Method 8081. Soil samples were extracted by Soxhlet extraction using methylene chloride/acetone (Method 3540) or by methanol swirled in a polyethylene bottle with five stainless steel ball bearings using the extraction procedure described in Method 4020.

Toxaphene

Initial studies were conducted using San Diego (low-organic) soil spiked with Toxaphene at 0.25, 0.5, 1.0, 2.5, and 5 ppm. The Toxaphene standard was obtained from Supelco (cat# 4-8700M, 2000 µg/mL in methanol). Aliquots of the spiked soils were extracted using Method 3540 (Soxhlet extraction) with a solvent mixture of methylene chloride/acetone (1:1 v/v). Three replicate extractions were performed on each level of fortification and each extract was analyzed by Method 8081. Individual aliquots of each spiked soil were also analyzed using the Millipore EnviroGard Toxaphene kit.

Millipore provided 31 real-world samples contaminated with Toxaphene from New Mexico. The site had been used for sheep dips where Toxaphene had been used to remove fleas, ticks and other exoparasites from the animals. The soil samples analyzed by GC/ECD were extracted in a Soxhlet apparatus using methylene chloride/acetone (Method 3540). Each extract was concentrated to a volume between 1 and 10 mL using a Kudurna-Danish apparatus. Extracts were exchanged to hexane under a stream of dry nitrogen and analyzed by Method 8081. Two matrix spike/matrix spike duplicate pairs and blanks were analyzed with the set of 31 samples.

SAIC also demonstrated the suitability of a back extraction technique for preparing methanol extracts for GC/ECD analysis. This was accomplished by preparing a Toxaphene standard in methanol and partitioning the target analyte into hexane, a solvent more suitable for GC/ECD analysis. The solvent partition was accomplished by adding 1 mL of the methanol sample to 5 mL of distilled water, extracting the aqueous methanol two times with 5 mL hexane. The resulting hexane extract was concentrated to 1.0 mL for GC/ECD analysis.

PCBs

Initial experiments were performed using laboratory spiked soils. San Diego (low-organic) soil was spiked with Aroclor 1242 at 4 µg/g and 50 µg/g and with Aroclor 1260 at 0.8 µg/g, 10 µg/g, 50 µg/g using standards purchased from Ultra Scientific. Spiking solutions were prepared in methanol, added to soil in a clean jar and stirred. Homogeneity of the spiked soil was ensured by mixing each spiked sample on a rock-tumbler roller for at least one hour.

Five portions of each spiked soil were extracted using Method 3540 (Soxhlet) with methylene chloride/acetone (1:1 v/v). The extracts were then split. One aliquot from each extraction was blown to dryness, redissolved in methanol and analyzed using the immunoassay procedure for PCBs in proposed Method 4020. The other methylene chloride/acetone aliquot was exchanged to hexane and analyzed using GC/ECD (Method 8081). GC/ECD conditions are provided in Appendix 1. Five replicate extracts and one blank were analyzed by each method at each level of fortification in order to compare the accuracy and precision of PCB measurements using immunoassay and GC/ECD.

One to seven days later, three portions of each of the spiked soils were extracted using methanol in a polyethylene jar according the procedure described in Method 4020. One aliquot from each extraction was analyzed using immunoassay procedure. A second 1.0 mL aliquot of each methanol extract was diluted with water and the PCBs were back extracted into hexane. The hexane fractions were analyzed using GC/ECD (Method 8081). These analyses provided a direct comparison of the measurement of PCBs extracted with methanol using immunoassay and GC/ECD.

The performance of immunoassay was also compared with GC/ECD analysis using five real-world samples contaminated with PCBs. Two of these samples were reference materials provided by the Research Technology Corporation (RTC of Laramie, WY); EnSys provided the other three real-world samples as unknowns. The design of the experiments using the real-world samples was similar to that used for spiked soils. Five portions of soil were extracted using Method 3540 (Soxhlet) with methylene chloride acetone (1:1). The extracts were split. One aliquot of each extract was blown to dryness, redissolved in methanol and analyzed using the EnSys PCB RISc™ test kit procedure (proposed Method 4020). The other aliquot from each extraction was exchanged to hexane, subjected to sulfuric acid cleanup (proposed Method 3665) and analyzed using GC/ECD (Method 8081). Previous studies at SAIC have confirmed that the sulfuric acid cleanup does not destroy PCBs and can significantly improve the quantitation of PCBs. Five replicate Soxhlet extractions and one blank were analyzed for each of the RTC samples. However, only one Soxhlet extract was analyzed for each of the EnSys samples because the amount of material was insufficient for replicate analyses.

One to seven days later, three portions of each of the RTC soils and one portion of the EnSys soils were extracted using methanol. Those extracts were split. One aliquot from each methanol extract was analyzed using the immunoassay. The PCBs in a 1.0 mL aliquot of each of the methanol extracts was back extracted into hexane. The hexane extracts were analyzed using Method 8081 in order to compare. the measurement of PCBs in samples using immunoassay and GC/ECD.

It was also demonstrated that immunoassay measurement is not affected by a small amount of methylene chloride (1 %) that might remain after solvent exchange by spiking aliquots of each of the methanol extracts with 1 percent methylene chloride prior to some immunoassays.

RESULTS

Toxaphene Analyses

Soil samples spiked with Toxaphene and real-world samples contaminated with Toxaphene were analyzed using GC/ECD and immunoassay. Three aliquots of spiked samples were extracted using Method 3540 (Soxhlet) and analyzed using Method 8081. An aliquot of each extract was sent to ImmunoSystems at Maine and analyzed using the Millipore Toxaphene EnviroGard Toxaphene kit. This kit has significant cross-reactivity with other cyclodiene insecticides (*e.g.*, Aldrin, Dieldrin, and Heptachlor), none of which were detected in these samples. However, significant amounts of DDE were observed in some samples using GC/MS. Measurement of Toxaphene was accomplished using a GC/ECD calibrated with the Toxaphene standard; a single response factor was calculated using the five major peaks present in that analytical standard. Thirty one real world samples were analyzed by Millipore Inc., and were also extracted and analyzed using Method 8081 in San Diego.

The Toxaphene concentrations measured using Soxhlet extraction (Method 3540) and GC/ECD (Method 8081) were compared with quantitative immunoassay as part of the performance testing of the method. Results for the analysis of spiked soil determined by SAIC San Diego and by ImmunoSystems are provided in Table 1. Results for the analysis of New Mexico soil using both methods are provided in Table 2. The correlation between GC/ECD analyses and immunoassay results are represented graphically using log/log axes in Figure 1

TABLE 1. RESULTS FOR SOIL SPIKED WITH TOXAPHENE

Spike in ppm (µg/g)	Immunoassay (µg/g)	GC/ECD range (µg/g)
0.25	0.27	0.16 - 0.20
0.50	0.66	0.30 0.37
1.0	1.02	0.77 1.0
2.5	2.8	2.5 3.1
5.0	6.7	5.4 - 5.7

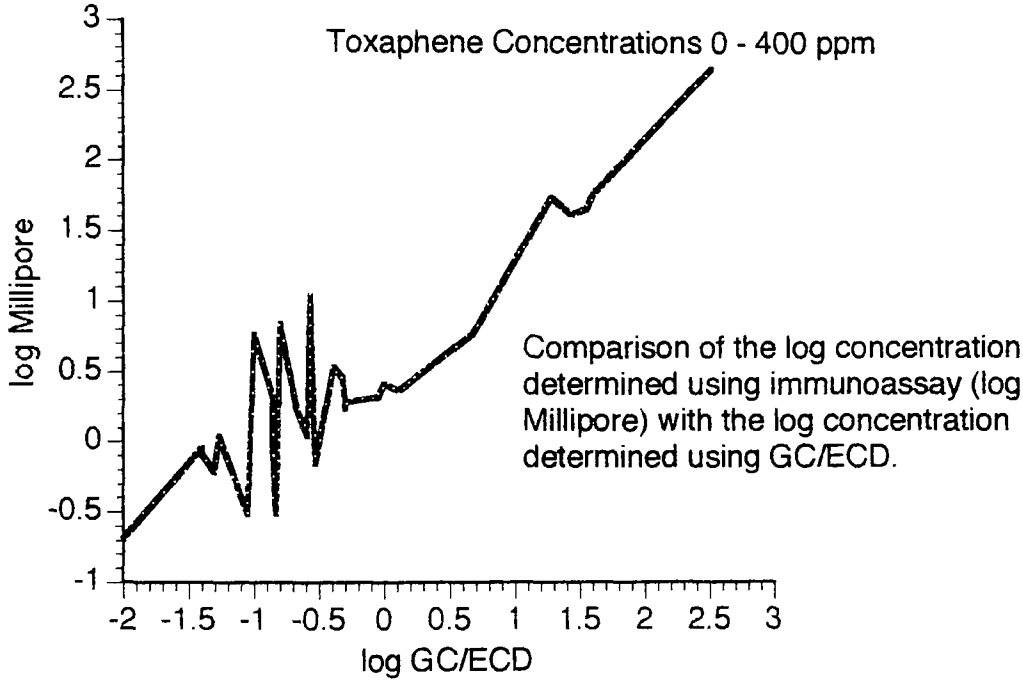
RSDs for triplicate GC/ECD analyses 2.7 12.4%

TABLE 2. RESULTS FOR SOIL CONTAMINATED WITH TOXAPHENE

Sample number	GC/ECD, µg/g	Immunoassay, µg/g
28, 89	0.09 J	0.3
70,104	0.04 J	0.9
54, 89	0.04 J	0.8
103, 50	0.01 J	0.2
10, 30	40	58
45, 33	19.3	54.8
Nazalini soil #12	<0.5	0.2
0, 33	<0.5	1.7
23,104	0.26 J	1.1
78, 33	1.0	2.6
64, 5	0.14 J	2.1
53, 75	0.27 J	11
35, 75	27.2	3.8
17, 75	0.14 J	0.9
65, 33	0.48 J	2.8
82, 75	0.21 J	1.8
19, 50	4.8	6.0
97,104	0.05 J	0.6
48,104	0.05 J	1.1
0, 50	1.3	2.3
102, 75	0,15 J	0.3
84, 50	0.06 J	0.9
25, 33	88.3	130
0, 75	0.5	1.9
12, 40 pit	34.1	45.5
0, 89	0.16 J	6.9
0,104	0.88	2.1
98, 89	0.41	3.4
104, 33	0.30 J	0.7
76, 89	0.10 J	5.8
40, 50	324	460

J = an estimated value. This is used to indicate the result is less than the lowest calibration point but greater than the method detection limit.
Sample numbers were assigned by ImmunoSystems and represent a grid at the site.

FIGURE 1. COMPARISON OF IMMUNOASSAY AND GC/ECD ANALYSES



The quality of the measurements of Toxaphene in soil was confirmed using matrix spike and matrix spike duplicate analyses.

TABLE 3. MATRIX SPIKE RECOVERIES FROM NEW MEXICO SOIL

Sample ID	MS % recovery	MSD % recovery	% RPD
M16 70,104	115.9	115.6	0.33
M24, 0, 75	112.0	106.9	4.7
2M2 (methanol ext.)	40.0	37.0	7.8

The performance of a hexane back extraction of Toxaphene from methanol extracts was established experimentally. A 1 µg/mL Toxaphene standard which was analyzed by GC/ECD. The determinations gave a mean recovery of 87% for five replicate extractions of the Toxaphene standard. The performance of the back extraction is presented below.

TABLE 4. BACK EXTRACTION OF TOXAPHENE FROM METHANOL

	ext -1	ext - 2	ext - 3	ext - 4	ext - 5
conc.	0.83	0.89	0.86	0.84	0.95
% rec	82.5	89.3	86.2	83.7	94.7
				Mean rec.=	87.3
				std =	4.9
				%RSD =	5.6

PCB Analyses

Establishing the suitability of immunoassay as a laboratory screening procedure requires a comparison of the measurement of PCBs using Soxhlet extraction using methylene chloride/acetone (Method 3540) and immunoassay (Method 4020). Direct injection of two different extracts is not an appropriate means of comparison because the use of different injection solvents may significantly affect GC/ECD results. Difficulties arising from differences in injection solvents were minimized by using the hexane back extraction

procedure described in this paper for three 1.0 mL portions of methanol spiked with Aroclor 1242 at 1.0 µg/mL. Those results are provided in Table 5.

TABLE 5. AROCLOR RECOVERY AFTER SOLVENT EXCHANGE

	1 µg/g std Aroclor 1242	extraction 1	extraction 2	extraction 3
area	392988	418996	431546	430156
percent recovery	NA	106.6	109.8	109.5

Extracts of soil spiked with PCBs (Aroclor 1242 and 1260) were analyzed using both the PCB RISc™ kits and GC/ECD in order to compare unambiguously the results of the different extraction and measurement techniques. These data are reported in Table 6 for Aroclor 1242 and in Table 7 for Aroclor 1260. The first column of each table gives the spiking level, column two gives the results for immunoassay and GC/ECD measurements for PCBs in methylene chloride/acetone extracts and column three gives the immunoassay and GC/ECD measurements for PCBs in methanol extracts. These data demonstrate that methanol extracts somewhat less than half of the PCBs than does methylene chloride/acetone. These data also document the slightly positive bias of the immunoassay kits for PCBs (*e.g.*, 5 of 5 kits were greater than 2 µg/g when the GC/ECD results were 3.8 µg/g, 2 of 3 kits were greater than 2 µg/g when the GC/ECD results were 1.5 µg/g). These data demonstrate the suitability of immunoassay as a conservative laboratory screening procedure that is unlikely to produce false negatives.

TABLE 6. ANALYSIS OF AROCLOR 1242 IN SPIKED SOIL

Spike Level µg/g	DCM/acetone, µg/g		MeOH, µg/g	
	Immunoassay	GC/ECD	Immunoassay	GC/ECD
4	>2, <25 n = 5	3.78 ± .36 (recovery 94.4%)	>2, <25 n = 2 <2, <25 n = 1	1.5 ± .3 (recovery 37.2%)
50	>2, >25 n = 5	45.6 ± .7 (recovery 91.1%)	>2, >25 n = 3	22 ± 1.4 (recovery 44%)

TABLE 7. ANALYSIS OF AROCLOR 1260 IN SPIKED SOIL

Spike Level µg/g	DCM/acetone, µg/g		MeOH, µg/g	
	Immunoassay	GC/ECD	Immunoassay	GC/ECD
0.8	>0.4, <5 n = 3 >0.4, >5 n = 2	0.78 ± .12 (recovery 98%)	>0.4, <5 n = 2 <0.4, <5 n = 1	0.35 ± 0.7 (recovery 44%)
10	>0.4, >5, n = 5	10.3 ± 1.3 (recovery 103%)	>0.4, >5 n = 3	4.9 ± .4 (recovery 49%)
50	>5, >25 n = 5	54.5 ± 3.0 (recovery 109%)	>5, >25 n = 3	15.2 ± 2.5 (recovery 30%)

These results demonstrate that immunoassay can be used to produce internally consistent Aroclor data. However, it is recommended that more than one ELISA determination be made when samples are near the reporting limit . The results for the immunoassay of the methylene chloride/acetone extracts indicate that ELISA techniques may be used as laboratory screening or even quantitative procedures for PCBs. Evaluation of these data generated near the detection limits also support the OSW requirement that at least 10% of the non-contaminated samples should be submitted for GC/ECD analyses. Each set of immunochemical measurements included methanol extracts of the samples spiked with 1 percent methylene chloride. This experiment was designed to ensure that any residual methylene chloride remaining after solvent exchange to methanol would not effect ELISA measurements. These data indicate that immunoassay can tolerate low levels of methylene chloride.

SAIC performed replicate analyses of two RTC samples contaminated with PCBs using immunoassay and GC/ECD. These results are presented in Tables 8,9 and 10. The values determined for Aroclors in the RTC samples are 40.5 µg/g Aroclor 1242 in RTC sample #0912 (Table 8)and 1.5 µg/g Aroclor 1254.in RTC sample #4179 (Table 9). RTC sample #4179 also contained high concentrations of PAH. The EnSys samples contained Aroclor 1260 (Table 10). The GC/ECD results are fully consistent with the immunoassay results for each of these samples. The methylene chloride/acetone extraction gave somewhat higher recoveries than methanol extraction. These higher recoveries are best

evidenced by the fact that all of the immunoassays of the methylene chloride/acetone extracts gave >25 µg/g for RTC sample #0912 (40 µg/g) while that concentration was detected in only 1 of 3 methanol extracts. Further evidence is provided by the fact that all 5 of the methylene chloride/acetone extracts of RTC sample 4179 (1.5 µg/g) were assayed at >2 µg/g while 3 methanol extracts were assayed at <2 µg/g. Both methanol and methylene chloride/acetone extracts produced false positives by immunoassay when measuring PCBs in EnSys sample #126. False negatives were not observed during the analysis of any of these soil and waste samples.

These results demonstrate that measurements made using immunoassay and GC/ECD analyses are generally intercomparable. These data also indicate that immunoassay may be used to produce reliable environmental data. They further demonstrate that methylene chloride/acetone extracts can be blown to dryness and reconstituted in methanol as part of a laboratory screening procedure using immunoassay. Use of this technique for screening environmental samples would have reduced our project analytical costs and produced no false negatives. The limited number of false positives would have resulted in some additional GC/ECD analyses which seems quite reasonable given our mission of generating data and methods that are used to monitor pollution which poses a hazard to human and environmental health.

TABLE 8. ANALYSIS OF RTC SAMPLE #0912

Immunoassay results µg/g, Aroclor 1242 kit			GC/ECD results µg/g, n = 5 mean ± s.d. Aroclor 1242
DCM/acetone	methanol	methanol + 1 % DCM	
>2, >25 n = 5	>2, >25, n = 1 >2, <25, n = 2	>2, >25, n = 3	40.5 ± 1.1

TABLE 9. ANALYSIS OF RTC SAMPLE #4179

Immunoassay results µg/g, Aroclor 1260			GC/ECD results µg/g, n = 5 mean ± s.d. Aroclor 1254
DCM/acetone	methanol	methanol + 1 % DCM	
>2, <25 n = 5	<2, <25, n = 3	<2, <25, n = 1 >2, <25, n = 2	1.5 ± .1

TABLE 10. ANALYSIS OF EnSys SAMPLES (SINGLE DETERMINATIONS)

Sample number	Immunoassay results µg/g, 1260 kit			GC/ECD, µg/g
	DCM/acetone	methanol	methanol + 1% DCM	
126	>5, >25	>5, >25	>5, >25	10.5, 1260
254	>5, >25	>5, >25	>5, >25	49.6, 1260
148	>5, >25	>5, >25	>5, >25	37.8, 1254

DISCUSSION

Clinical immunoassay is not an exact model for the requirements of the RCRA program . Unlike tissue, urine or feces, hazardous waste and environmental samples can pose very different, site-specific matrix problems. Adopting quantitative ELISA techniques as part of SW-846 will require proof that immunoassay can be used to measure specific toxicants in a variety of sample matrices. The authors believe that there are four major issues that must be addressed before immunoassay is viewed as a quantitative technique for RCRA matrices.

Intercomparability of data - Analysis of Toxaphene and PCBs using immunoassay and GC/ECD analyses involves two different measurement technologies and two different extraction techniques. The EPA requires comparison of the performance of both methods using a variety of sample matrices. The fact that methanol extraction is less effective than methylene chloride/acetone will require specific method performance data to establish that data obtained using immunoassay kits can be compared with GC/ECD results.

Suitability for waste matrices Immunoassay has not been demonstrated as suitable for the tremendous variety of waste matrices considered under the RCRA program. Data on the suitability of immunoassay should be collected over time as more investigators use immunoassay to measure toxicants in waste and soil samples.

Performing immunoassays a number of the operations required for immunoassay (*e.g.*, use of the repeating pipettor) are not generally used in environmental laboratories. Analysts in environmental laboratories will need to be trained in biochemical techniques in order to use immunochemical techniques for quantitative measurements during site monitoring or for laboratory screening procedures.

Interpretation of data interpretation of immunochemical data is not straightforward. Because the assays work by enzyme-linked visualization techniques after competitive binding with the antibody, the amount of color developed in a tube is inversely related to the amount of analyte in the sample. More color means less analyte. Analysts and data reviewers will need to be trained to interpret these data and to use dual wave length data for immunochemical measurements. The measurement technique used in immunoassay are very different from chromatography methods.

CONCLUSION

These studies demonstrate that immunoassay kits can be used for measurement of multicomponent organochlorine pollutants in soil. Use of immunoassay for the analysis of Toxaphene and PCBs may actually result in less measurement uncertainty and interlaboratory differences in quantitation than conventional GC/ECD analysis (Method 8081) because the GC/ECD method requires significant analyst interpretation of peak patterns in order to identify and quantitate the target analytes.

Immunoassay is biased to produce false positives for samples with contaminants near the detection limit. This bias makes it unlikely that a contaminated sample will test as a non-detect when it is contaminated above the limit of detection. However, analysts should expect to see both positive and negative results when contamination levels are near the method detection limits for samples analyzed by immunoassay.

The studies reported here also demonstrate that methylene chloride/acetone sample extracts can be blown to dryness and reconstituted in methanol prior to an immunoassay laboratory screening procedure. Experiments established that immunoassay is relatively insensitive to small amounts of methylene chloride that might be left from incomplete blow down of sample extracts.

APPENDIX

GC/ECD Conditions, Method 8081 for Toxaphene and PCBs:

Inj.temp.	200°C
Det. temp.(ECD)	320°C
Initial temp:	150°C
initial time:	0.5 min
rate:	5°C/min
final temp.:	275°C
final time:	8 min
carrier (N_2)	5 ml/min
makeup (N_2)	55 ml/min

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TOXAPHENE IN SOIL/TRICHLOROETHYLENE/RAPID DIOXIN SCREENING BY IMMUNOASSY. T.S. Fan, B. Young, D. Crouse, H. Allen, R.O Harrison, H. Shirkhan, R.E. Carlson

This presentation was a combination of T.S. Fan's Organic paper #s 84 and 88, and R.O. Harrison's Organic paper #100.

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TNT AND RDX BY IMMUNOASSAY. G. B. Teaney, J.M. Melby, J.W. Stave, R. T. Hudak

This presentation was a combination of G. B. Teaney's Organic paper #s 90 and 94.

COMMERCIAL LABORATORY POSITION ON THE USE OF SW-846

Jerry L. Parr, Chair, Technical Committee, International Association of Environmental Testing Laboratories (IAETL), 1911 N. Fort Myer Drive, Arlington, Virginia 22209

ABSTRACT

Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846) is stated to provide test procedures and guidance that are recommended for use in conducting the evaluations and measurements needed to comply with the RCRA regulations. While several of the hazardous waste regulations under Subtitle C of RCRA require that specific testing methods described in SW-846 be employed for certain applications, the document states that any reliable analytical method may be used to meet other requirements.

The International Association of Environmental Testing Laboratories (IAETL) has been in existence for six years, has over 170 members in the U.S. and Canada, and represents more than half the revenue generated in the environmental analytical testing industry. IAETL's Technical Committee supports EPA's position on the use of SW-846 as a viable guidance document.

The objective of our presentation is to share our concerns regarding the current confusion on the use of SW-846. The presentation will address prescriptive use versus guidance, varying levels of interpretation by laboratories, regulators, and data users of SW-846, and areas of concern.

We intend to present ideas that will clarify the use of SW-846 as guidance and speed the process for incorporation of new technology for cost-effective monitoring.

SURROGATE-BASED CORRECTIONS OF DATA FOR METHOD 5032

Michael H. Hiatt and Carole Farr,
United States Environmental Protection Agency
EMSL-LV, Nevada 89119

ABSTRACT

As part of the Environmental Monitoring Systems Laboratory-Las Vegas Quality Assurance Research Program, the quality assurance necessary for analytical methods is investigated and optimized. We are reporting on work that was conducted to identify compounds which could be utilized as surrogates for a vacuum distillation procedure (Method 5032). Recovery of analytes using Method 5032 is found to be related to specific physical properties of the analytes. Therefore, surrogate compounds selected to assess losses related to individual physical properties, are used to predicate analyte recoveries. Such predicted recoveries can be expected to exceed 95% of the experimentally measured recoveries. This approach is shown to be applicable to a variety of samples.

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STATIC HEADSPACE ANALYSIS OF SOIL SAMPLES

J. Purcell, A. Tippler, G. McClure and J. Ryan, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859

The analysis of soil samples for volatile organic compounds (VOCs) can be a difficult procedure. Use of SW-846 method 8260 requires that VOCs in samples be introduced to a gas chromatograph either by purge-and-trap or direct injection. These sample introduction techniques can cause significant problems with inter-sample analyte contamination and carry over. In addition, the transfer of samples from collection container to dynamic purge vessel can result in significant losses of VOCs.

A means of alleviating these problems has been developed. Using automated static headspace instruments, it has been shown that soil samples can be analyzed for their volatile constituents without fear of cross contamination and with a minimum of sample preparation. Laboratory productivity is improved.

This static headspace VOC method is performed by adding 3 mL of chilled water directly to a chilled soil sample. The headspace vial is then sealed and the sample sonicated for 15 minutes, following which it was transferred directly to the automated headspace analyzer without further preparation.

While method performance can vary depending on the sample type, data will be presented for the analysis of VOCs from a range of soil types showing that recovery and reproducibility statistics compare favorably with those of method 8260.

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SOLIDS PHASE EXTRACTION OF TCLP LEACHATES

Craig G. Markell, 3M-New Products, St. Paul, Minnesota, *Li Song*, 3M-New Products, St. Paul, Minnesota and *Rich Pieper*, 3M-New Products, St. Paul, Minnesota

ABSTRACT

A method has been developed to use solid phase extraction disks for TCLP leachates. Results will be presented on pesticides, herbicides, acid extractables, and base neutral extractables.

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Dianne A. Bennett, Barry Lesnik* and S. Mark Lee
Chemistry Laboratory Services Branch
California Department of Food and Agriculture
Sacramento, CA 95832

*Organics Method Program
USEPA Office of Solid Waste
Washington, D.C. 20460

SUPERCRITICAL FLUID EXTRACTION OF ORGANOCHLORINE PESTICIDE RESIDUES FROM SOILS

An analytical method has been developed for the supercritical fluid extraction of organochlorine pesticide residues from soils. The method development strategy will be outlined to demonstrate how the optimum extraction conditions were established. Key experimental parameters include fluid density, temperature, fluid composition, flow rate, extraction time, and extraction mode (static/dynamic). The influence of the chemical and physical properties of the analytes on the extraction method were also investigated, as well as the effects and consequences of analyte-matrix interactions.

The results from experiments using fifteen organochlorine pesticides and three soil matrices will be presented. These results include spike recovery, precision, method bias and method detection levels. A comparison with Soxhlet extraction for soils containing "native" organochlorine residues will also be presented.

SUPERCRITICAL FLUID EXTRACTION (SFE) OF ORGANOCHLORINE AND ORGANOPHOSPHATE PESTICIDES FROM SOILS

John L. Snyder, Senior Chemist, Lancaster Laboratories, Inc., 2425 New Holland Pike, Lancaster, PA 17601

ABSTRACT

In this study, 12 pesticides representative of common organochlorine and organophosphate pesticides were extracted from spiked soils and real-world samples using a Suprex SFE-50 instrument. The organochlorine pesticides included two EPA CLP surrogates, Tetrachlorometaxylene (TCMX) and Decachlorobiphenyl (DCB), and also Endrin, Endrin Aldehyde, p,p' DDT, and Mirex. The organophosphate compounds were Dichlorvos, Ronnel, Parathion, Methidathion, Tetrachlorvinphos, and Diazinon.

Both carbon dioxide and carbon dioxide modified with 3% methanol were used to extract the soils. The pesticides were then quantified using either gas chromatography with electron capture detection (GC-ECD) or with gas chromatography mass spectrometry in the selective ion monitoring mode (GC-MS-SIM).

Experiments were also performed to demonstrate the effect of extraction conditions such as density and pressure, temperature, and extraction volumes of supercritical fluid on the recoveries of the pesticides. The effects of other variables such as pH, moisture, and different types of soil matrices on pesticide recovery were also investigated.

It was found that quantitative recovery of the more polar pesticides such as Endrin Aldehyde and most of the organophosphate pesticides could not be achieved in soil matrices using only CO_2. Quantitative recovery of all the pesticides could, however, be achieved in all soils, when 3% methanol was added to the CO_2. Density and pressure were found to have a much greater effect on the pesticide recovery than did temperature.

Lastly, a comparison was made between SFE and the classical sonication and Soxhlet extraction techniques. A large batch of top soil was fortified with each of the pesticides and extracted repetitively using each extraction method. It was found that the overall average recoveries of the 12 pesticides by sonication, soxhlet, and supercritical fluid extraction were 94.7%, 93.1%, and 91.6%, respectively. SFE

demonstrated the best precision of the three extraction methods with the overall average relative standard deviation for all the pesticide compounds being 2.94%. Supercritical Fluid Extraction (SFE) was equivalent to the sonication extraction in recovering organochlorine pesticides from real-world soil samples.

INTRODUCTION

The sonication and Soxhlet extractions are promulgated by the the United States Environmental Protection Agency (USEPA) as an extraction method for removing organic contaminants from soil samples (1,2). However, both the sonication and Soxhlet extractions are undesirable because they require large amounts of expensive solvents, many of which are chlorinated and are hazardous to the environment and humans. Regulations aimed at saving our ozone layer may ban the production and sale of these solvents in the future (3). After the sonication and Soxhlet extractions it is also necessary to concentrate the analytes in the sample extracts by evaporating the solvent in order for the analytes to be detected by instrumental methods. This further increases the likelihood of human exposure and air pollution.

The advent of SFE in recent years offers an alternative to the liquid-solid extraction for removing organic pollutants from soil samples prior to analysis (4). In the environmental area, supercritical fluid extraction (SFE) has been used by numerous investigators to extract organic contaminants from soils and other environmental samples. Often SFE has been compared to the Soxhlet or sonication extraction techniques. Most of the time, SFE has been reported as being superior in extraction efficiency and faster (5-12).

This study investigated the effect of varying SFE conditions and soil matrix variables on the recoveries of the pesticides listed in Table I. The SFE recoveries of these organochlorine and organophosphate pesticides were also compared with the recoveries of these pesticides from spiked soils and contaminated native soils using the classical sonication and Soxhlet extraction methods.

EXPERIMENTAL

Reagents

1. Standards

The pesticide compounds used in this study were obtained from Chemical Services Inc., West Chester, PA, and the Environmental Protection Agency Repository, Research Triangle Park, NC. Stock solutions of each compound at 1 mg/mL were prepared in methanol.

Five levels of working calibration standards were prepared in methyl *tert*-butyl ether (MTBE) by serial dilution of an intermediate standard, which was prepared from the 12 individual stock solutions and also made in MTBE. The concentration ranges were as follows: dichlorvos and diazinon 100 to 2100 ng/mL; TCMX and DCB 6 to 120 ng/mL; ronnel 5 to 100 ng/mL; parathion 15 to 310 ng/mL; methidathion 19 to 400 ng/mL; tetrachlorvinphos 7 to 150 ng/mL; endrin and endrin aldehyde 8 to 180 ng/mL; p,p′ DDT 7 to 160 ng/mL; mirex 15 to 310 ng/mL. Spiking solutions were also prepared in acetone by dilution of the intermediate standard.

2. Solvents

Only pesticide grade methylene chloride ($MeCl_2$), acetone (Ac), and methyl *tert*-butyl ether (MTBE) were used in this study. These were obtained from Fisher Scientific (Atlanta, GA).

3. Supercritical Fluids

SFC grade carbon dioxide and carbon dioxide containing 3% methanol (Scott Specialty Gases, Plumsteadville, PA) were used for all supercritical fluid extractions.

Extraction Methods

1. Supercritical Fluid Extractions

All extractions were performed singly on a Suprex SFE 50 using 2-10 mL stainless steel extraction vessels. After optimization experiments, all extractions were performed at 350 atm pressure and 50°C using CO_2 modified with 3% methanol. When 10 g of soil were

extracted, a 10 minute static soak was performed prior to a 40-50 minute dynamic extraction. Back pressure was maintained and the flow controlled in the 10 mL extraction cell using a 30 to 50 cm length of 50 μm i.d. fused silica tubing restrictor for the outlet.

The analytes were collected by bubbling the vented CO_2 through 5 mL of methyl *tert*-butyl ether (MTBE) contained in a 40 mL vial capped with a Teflon faced septum. The restrictor was inserted through this septum and the end was placed at the bottom of the vial about 15 mm under the surface of the MTBE. The vial was vented to atmosphere using a wide bore stainless steel syringe needle pierced through the septum. No attempt was made to control the temperature of the collection fluid. Because of the cryogenic effect of the expanding CO_2, the vial was well below room temperature during the collection process. Occasionally the vial had to be immersed in warm water to unplug the end of the capillary restrictor which would freeze. Because some of the MTBE evaporated during the extraction all final volumes of extract were adjusted to 5 mL with additional MTBE.

2. Sonication and Soxhlet Extractions were conducted according to the USEPA Methods 3540 and 3550 except 10 g of soil was used and the solvent volume was scaled accordingly (1,2).

Gas Chromatographic Analysis of Extracts

The pesticides in the extracts were determined by gas chromatography and an electron capture detector (GC-ECD). Direct injection of 1 μL of the extracts was performed using an autosampler. The injection port was maintained at 250°C and the ECD was maintained at 300°C. The temperature program was started at 140°C, held for 1 minute, and then ramped at 4°C/min to a final temperature of 290°C, and held for 15 min. Helium was used as the carrier gas at 5 mL/min and nitrogen was used as a make up gas to the ECD at 25 mL/min. Quantification was performed using a 5-point calibration curve plotting peak area versus concentration.

RESULTS AND DISCUSSION

Figure 1 shows plots of recoveries vs. density for the organophosphate and organochlorine pesticides. None of the organophosphate pesticides were recovered at 0.2 g/mL. At a density of 0.4 g/mL significant increases in recoveries were observed for ronnel, parathion, and dichlorvos. Very low recoveries (10-20%) were found for some of the more polar pesticides, namely diazinon, methidathion, and tetrachlorvinphos at this density. Over the remainder of the density range, the recoveries of ronnel, parathion, and dichlorvos appear to remain consistent. Nearly quantitative recoveries were achieved for ronnel and parathion, two of the less polar organophosphate pesticides, at a density of 0.60 g/mL.

Similar trends can be noticed for the organochlorine pesticides which are also shown in Figure 1. With the exception of endrin aldehyde, it appears there is a threshold density of about 0.4 g/mL above which good recoveries can be obtained for the organochlorine pesticides. Endrin aldehyde, which contains a polar oxygen on one end of the molecule, showed poorest recoveries and was only partially recovered (approx. 70%) at the maximum density.

Curves plotting recoveries of the organophosphate and organochlorine pesticides vs. density are shown in Figure 2. The addition of the polar methanol modifier increased the extraction efficiencies for most of the pesticides. Quantitative recoveries were obtained for the polar pesticides which CO_2 alone was unable to remove from the soil. It appears from these figures that above densities of about 0.5 g/mL (or pressures > 100 atm) acceptable recoveries (> 90%) can be obtained for most of the pesticides.

Supercritical fluid extractions performed on fortified soil at temperatures of 40°, 60°, 80°, 100°, and 120°C keeping the density constant at 0.7 g/mL demonstrated that temperature had little influence on the recoveries of the pesticides. Decreases in the recoveries of dichlorvos and endrin were observed at the elevated temperatures (100-120°C).

Five soils (reagent sand, top soil, river sediment, clay, and the top soil after treatment in a muffle furnace) were extracted repetitively with CO_2 modified with 3% methanol and pure CO_2. When CO_2 modified with 3% methanol was used as the extraction fluid, recoveries ranging from 60-110% were obtained for all of the pesticides from all of the soil

matrices. These recoveries are listed in Table II. The overall average recovery of the 12 pesticides from the sand, the furnaced top soil, the river sediment, the clay, and the top soil was 94% (N=3 or 4). The precision for these experiments yielded an overall average RSD of 5% for all the pesticides in all five soils. RSDs for the pesticides in the river sediment were generally higher and ranged from 6-39%, while in the other soils, all pesticide RSDs were less than 9%. The poorer precision observed for dichlorvos (RSD=39%) and low average recovery (63%) for the river sediment (these were included in the overall averages given above) were due to a background peak attributed to the sediment matrix which eluted at the same retention time as dichlorvos. The area of this peak was subtracted from the area of the dichlorvos peak when recoveries were calculated.

The results of the extractions when the soils were extracted with CO_2 alone using identical SFE conditions are shown in Table III. In general, recoveries are lower and the precision is poorer with pure CO_2 than when methanol modified CO_2 was used. The overall average recovery for 12 pesticides in all the soils was 72% and the overall average precision was 23%. Carbon dioxide alone was effective in removing the pesticides from sand only; the overall average recovery was 96% and RSDs ranged from 4.3-17%. The sand matrix does not adsorb the pesticides as tightly because of the large particle size and the relatively inert silica surface. Recoveries were lower with the other soil matrices. The overall average pesticide recoveries for the clay, furnaced top soil, top soil, and river sediment were 65%, 70%, 66%, and 65%, respectively. The precision in extracting these soils with CO_2 yielded overall average RSDs for the 12 pesticides of 21%, 29%, 30%, and 28% for the furnaced top soil, river sediment, top soil, and clay, respectively. The poorest precision (12-118%, RSD), as shown in Table III, was observed for the polar pesticides, diazinon, methidathion, tetrachlorvinphos, dichlorvos, and endrin aldehyde. Diazinon was one the most difficult pesticides to recover using pure CO_2 (0-81%).

Tables IV and V show a comparison of recoveries of the organochlorine and organophosphate pesticides, respectively, from a batch of top soil specially spiked with the pesticides and extracted repetitively using SFE and the classical Soxhlet and sonication extractions. The top soil was spiked in a large batch (400 g) by immersing the soil in methylene chloride, adding the spiking solution, and slowly evaporating the solvent. After the methylene chloride was completely evaporated and the soil was tumbled to ensure homogenuity, 10 g portions of the fortified top soil (FTS) were used for each of the extraction methods.

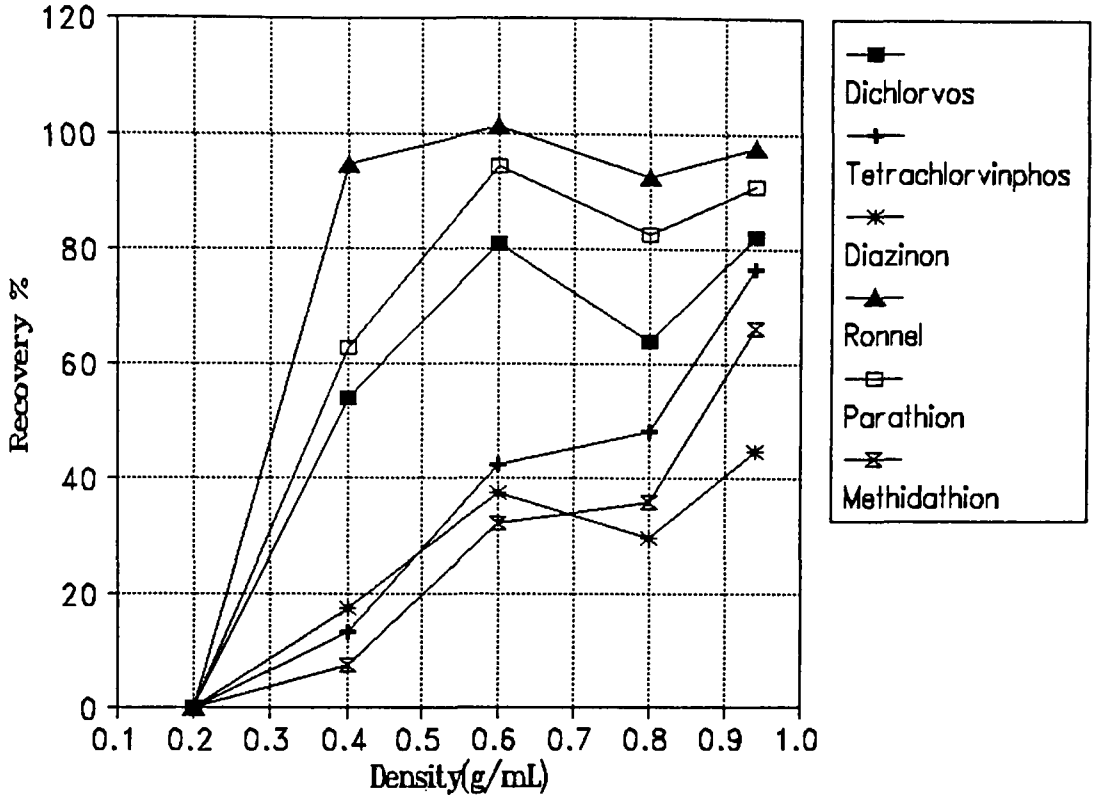
Good extraction efficiencies were observed for the three extraction methods as measured by the overall average of the mean recoveries of the 12 pesticide compounds. Sonication was highest at 94.7% and was followed by Soxhlet at 93.1% and SFE at 91.6%. The low recovery of Parathion obtained by the Soxhlet extractions was deleted from this average. The sonication extraction, however, gave statistically better recoveries from a majority of the individual pesticides when compared to SFE. When comparing the Soxhlet to SFE, the majority of the individual pesticides had no significant difference in recovery at the 95% confidence level.

In this study SFE was found to have the best overall precision as indicated by an overall average RSD for the 12 pesticides of 2.94%. Sonication ranked second with an average RSD of 4.47%. However, for many of the individual pesticides, there was no significance in the difference in the precisions at the 95% confidence level between sonication and SFE. The Soxhlet extraction was found in these experiments to be the least precise and the average RSD for the 11 of the pesticides, excluding parathion which was poorly recovered, was 7.42%.

Three real-world soil samples submitted to our laboratory for pesticide analysis and found to contain significant levels of organochlorine pesticides were repetitively extracted by SFE and sonication. These soils are designated Real-world Soil #1, Soil #2, and Soil #3. Comparisons of the organochlorine pesticide recoveries found by SFE and the sonication extraction from these three soils are presented in Tables VI, VII, and VIII. No significant difference was found between the sonication and SFE recoveries and the precisions of the extraction methods.

CONCLUSION:

SFE has been shown to be a successful analytical technique in extracting organochlorine and organophosphate from a variety of spiked and native soils. In practical terms, the SFE method was faster and easier to perform than either the sonication or Soxhlet extraction. Less solvent was consumed by SFE. Approximately 400 to 500 mL of solvent was consumed per Soxhlet extraction and about 150 to 200 mL per sonication extraction. SFE required only 5 to 10 mL of solvent. Because of the small amount of solvent necessary, SFE required no solvent concentration step using the Kuderna Danish apparatus. During this process the chance for analyte loss because of evaporation, breakdown or reaction of the compound is greatly increased.



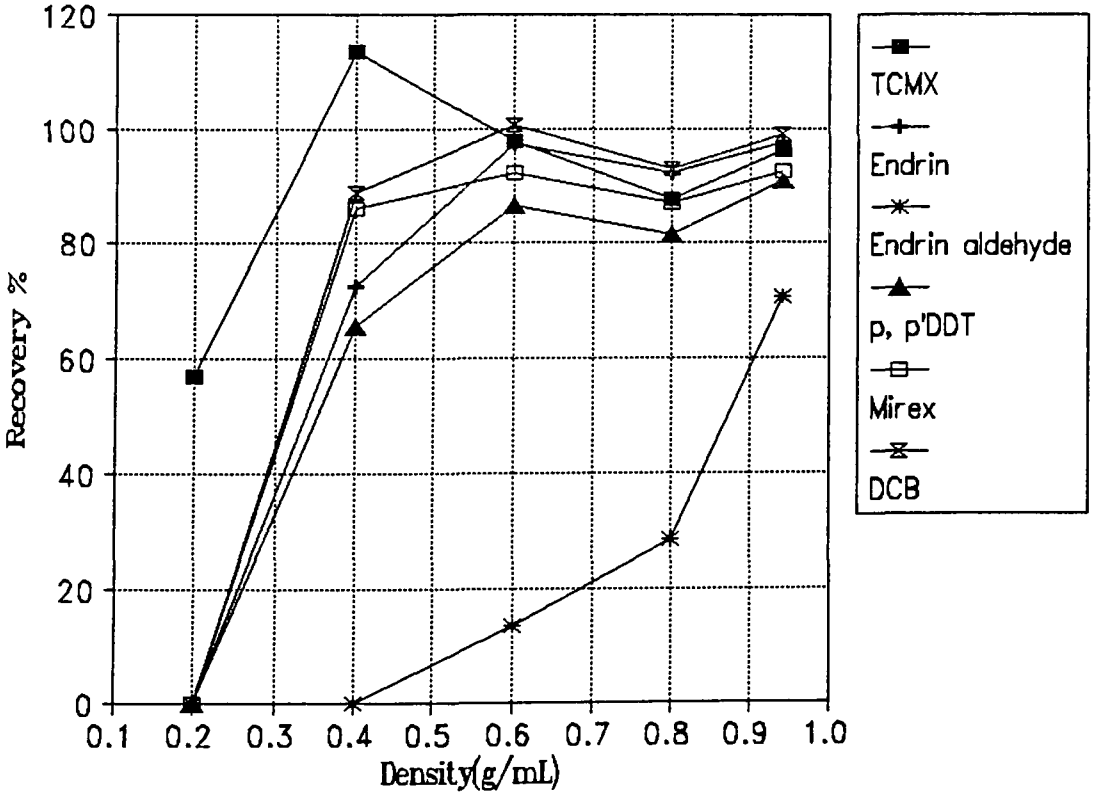
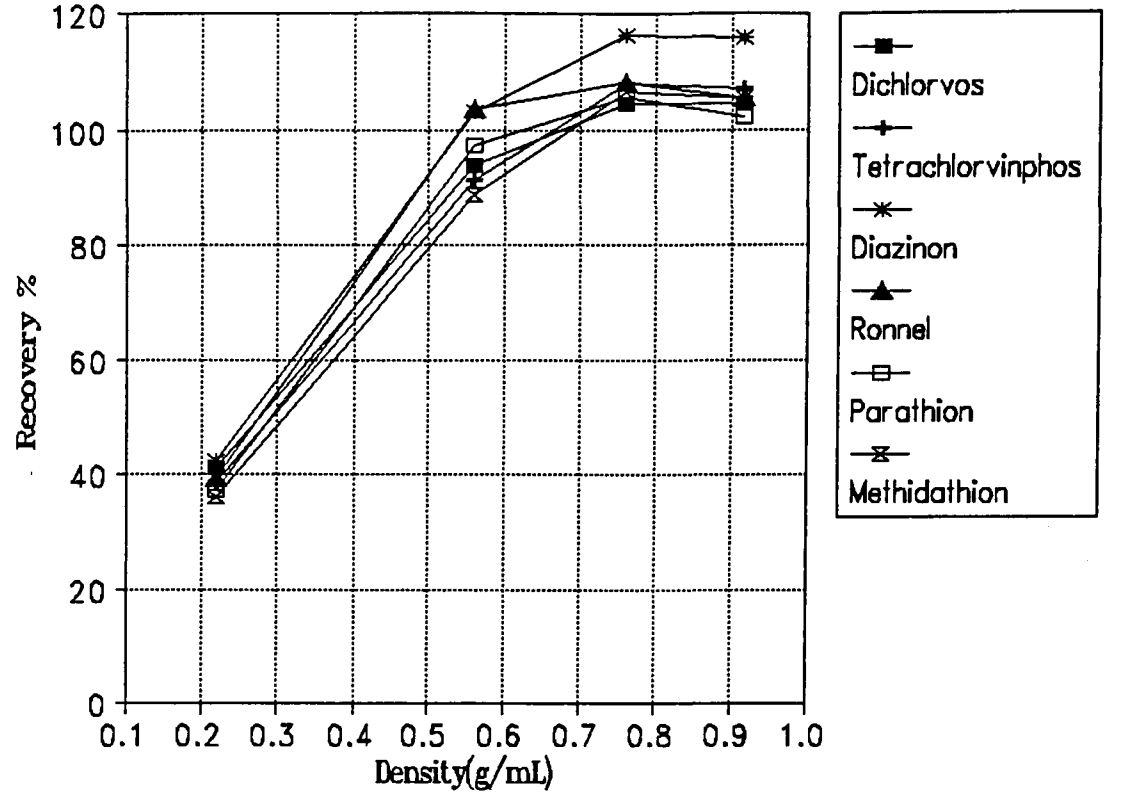


Figure 1. Effect of density on the recoveries of pesticides using pure CO_2. Temperature was kept constant at 50°C; 2 g of spiked top soil; n=2.



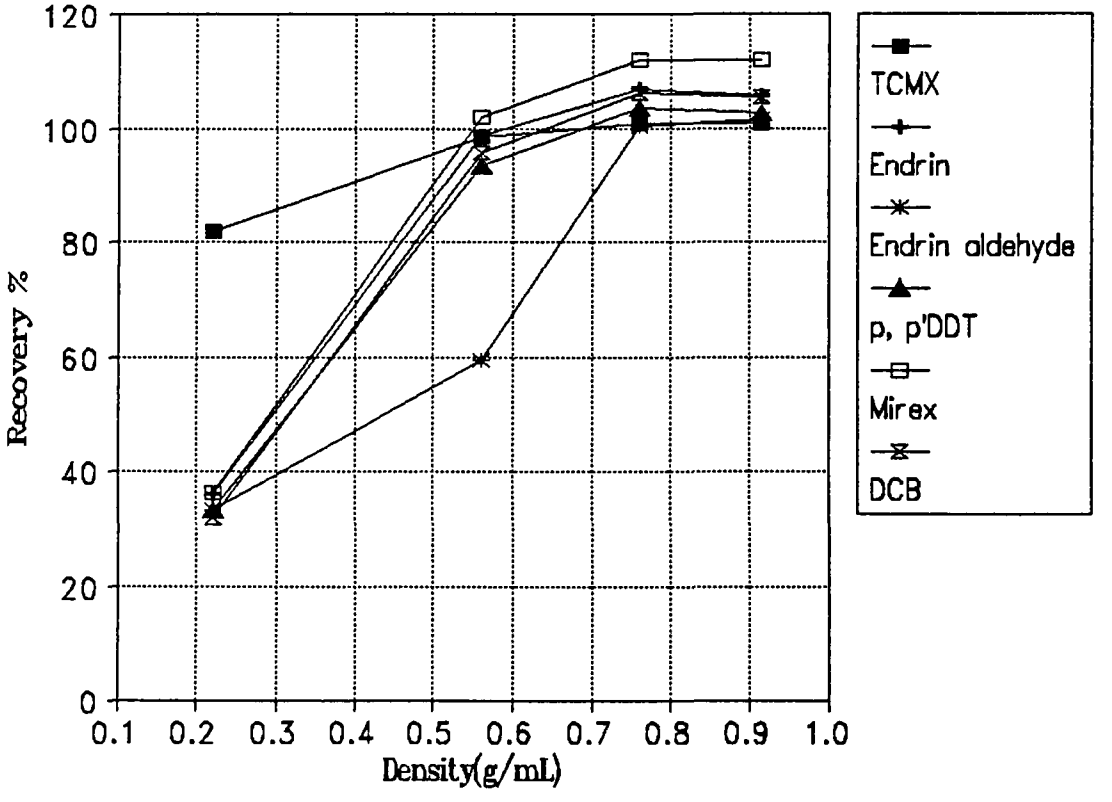


Figure 2. Effect of density on the recoveries of pesticides using CO_2 with 3% methanol. Temperature was kept constant at 50°C; 2 g of spiked top soil; n=2.

Table I. Chemical Names and Formulas of Organochlorine and Organophosphate Pesticides

Compound's Common Name	Chemical Formula	CAS No.	M.W.
tetrachlorometaxylene (TCMX)	$C_8H_6Cl_4$	877-09-8	244
dichlorvos	$C_4H_7Cl_2O_4P$	62-73-7	221
diazinon	$C_{12}H_{21}N_2O_3PS$	333-41-5	304
ronnel	$C_8H_8C_{13}O_3PS$	299-84-3	322
parathion	$C_{10}H_{14}NO_5PS$	56-38-2	291
methidathion	$C_6H_{11}N_2O_4PS_3$	950-37-8	302
tetrachlorvinphos	$C_{10}H_9Cl_4O_4P$	22248-79-9	366
endrin	$C_{12}H_8Cl_6O$	72-20-8	381
endrin aldehyde	$C_{12}H_8Cl_6O$	7421-93-4	381
p,p' DDT	$C_{14}H_9Cl_5$	50-29-3	355
mirex	$C_{10}Cl_{12}$	2385-85-5	545
decachlorobiphenyl (DCB)	$C_{12}H_{10}Cl_{12}$	2051-24-3	499

Table II. Recovery of Organochlorine and Organophosphate Pesticides from Spiked Soils Using Carbon Dioxide with 3% Methanol

	amount added (ng/g)	sand n=4		furnaced top soil n=4		river sediment n=4		clay n=4		top soil n=4	
		% recv	RSD, %	% recv	RSD, %	% recv	RSD, %	% recv	RSD, %	% recv	RSD, %
dichlorvos	1040	81	3.6	93	7.0	63	39	91	3.2	101	2.5
TCMX	60	87	6.0	94	4.1	88	8.9	102	2.9	105	1.3
diazinon	1030	101	3.4	93	8.5	92	18	113	4.1	90	4.7
ronnel	51	90	2.9	99	4.3	86	18	109	2.8	109	0.3
parathion	155	88	5.6	94	6.8	86	10	97	2.1	104	1.5
methidathion	199	81	2.9	95	5.9	90	11	94	2.5	108	3.9
tetrachlorvinphos	72	81	3.6	97	6.1	85	11	89	4.6	111	3.1
endrin	91	86	2.1	102	5.8	91	6.2	100	2.5	111	3.1
endrin aldehyde	86	85	1.6	95	5.4	83	5.8	93	2.9	102	1.1
p,p' DDT	77	84	1.5	96	5.8	84	6.4	94	2.0	106	1.1
mirex	152	87	1.2	103	4.4	86	6.8	96	2.8	107	2.0
DCB	60	88	1.8	105	3.6	88	9.5	97	2.7	104	0.6

Table III. Recovery of Organochlorine and Organophosphate Pesticides from Spiked Soils Using Carbon Dioxide Only

	amount added (ng/g)	sand n=4		furnaced top soil n=4		river sediment n=4		clay n=4		top soil n=4	
		% recv	RSD, %	% recv	RSD, %	% recv	RSD, %	% recv	RSD, %	% recv	RSD, %
dichlorvos	1040	93	12	57	19	56	62	43	94	62	26
TCMX	60	102	4.3	95	14	89	2.4	109	5.2	95	7.3
diazinon	1030	81	16	5	59	22	85	0	--	3	118
ronnel	51	110	4.6	100	13	88	3.8	107	1.1	102	8.1
parathion	155	103	3.5	77	15	79	13	88	16	87	5.3
methidathion	199	77	17	35	30	25	68	4	91	21	88
tetrachlorvinphos	72	79	16	42	25	34	65	10	56	35	50
endrin	91	104	6.3	98	12	84	5.7	100	2.1	86	8.2
endrin aldehyde	86	95	5.9	43	20	50	25	25	24	41	26
p,p' DDT	77	102	4.5	95	12	77	10	86	15	82	4.3
mirex	152	106	5.8	99	15	85	3.8	101	3.3	88	7.5
DCB	60	105	4.9	99	14	90	7.8	103	4.7	89	8.3

SFE conditions for Tables II and III - 350 atm; 50°C; 2.0 g soil contained in 2 mL vessel; 10-minute static; 10-minute dynamic

Table IV. Comparison of Extraction Methods for Organochlorine Pesticides: Soxhlet vs. Sonication vs. SFE

Compound	Amount Added (ng/g)	Method	Trials N	Found Avg. (ng/g)	Std. Dev. s	RSD %	% Rec. Avg.
TCMX	30	SX	8	24	2.1	8.9	78.0
		SP	7	22	0.79	3.2	81.0
		SFE	9	22	1.2	5.4	74.0
endrin	45	SX	8	44	2.6	6.0	97.0
		SP	7	49	0.5	1.1	108.0
		SFE	9	44	1.5	3.5	97.0
endrin aldehyde	43	SX	8	35	1.3	3.7	81.0
		SP	7	30	0.95	3.1	71.0
		SFE	9	36	1.2	3.3	84.0
p,p' DDT	38	SX	8	33	4.3	13	87.0
		SP	7	31	0.57	1.8	81.0
		SFE	9	38	0.52	1.4	99.0
mirex	76	SX	8	71	8.1	11	94.0
		SP	7	80	1.2	1.5	105.0
		SFE	9	74	2.2	3.0	97.0
DCB	30	SX	8	29	1.1	3.7	98.0
		SP	7	31	0.57	1.8	104.0
		SFE	9	29	0.50	1.7	96.0

Table V. Comparison of Extraction Methods for Organophosphate Pesticides: Soxhlet vs. Sonication vs. SFE

Compound	Amount Added (ng/g)	Method	Trials N	Found Avg. (ng/g)	Std. Dev. s	RSD %	% Rec. Avg.
dichlorvos	520	SX	8	333	28	8.4	64
		SP	6	375	42	11	72
		SFE	5	318	13	4.0	61
diazinon	515	SX	8	479	24	5.1	93
		SP	6	493	27	5.4	96
		SFE	9	433	13	3.0	84
ronnel	25	SX	8	26	1.4	5.2	104
		SP	6	27	2.4	9.0	106
		SFE	9	25	1.2	5.0	98
parathion	78	SX	8	22	20	92	28
		SP	6	77	1.2	1.6	99
		SFE	9	73	0.88	1.2	94
methada-thion	100	SX	8	108	5.7	5.3	108
		SP	6	100	4.8	4.8	100
		SFE	9	100	3.4	3.2	106
tetrachlo-vinphos	36	SX	8	42	4.7	11	117
		SP	6	41	1.3	3.2	113
		SFE	8	39	2.5	6.3	109

Table VI. Quantification of Organochlorine Pesticides in Soil Sample #1 - SFE vs. Sonication

	Supercritical Fluid n=4		Sonication n=3	
	Amount Avg. (ng/g)	RSD %	Amount Avg. (ng/g)	RSD %
TCMX	95%	4.1	93%	12
p,p' DDE	44	7.1	36	15
p,p' DDD	43	8.6	39	8.4
p,p' DDT	453	5.0	431	17
DCB	97%	2.1	102%	2.6

TCMX and DCB added as surrogates prior to extractions - results expressed as % recovered.

Table VII. Quantification of Organochlorine Pesticides in Soil Sample #2 - SFE vs. Sonication

	Supercritical Fluid n=6		Sonication n=3	
	Amount Avg. (ng/g)	RSD %	Amount Avg. (ng/g)	RSD %
TCMX	76%	14	68%	11
heptachlor	14	40	16	17
aldrin	81	9.7	114	6.3
dieldrin	327	9.3	344	2.4
alpha chlordane	429	8.4	483	4.7
gamma chlordane	80	9.0	88	6.5
endrin	1418	4.6	1524	2.5
endosulfan II	54	3.0	58	6.2
endrin aldehyde	29	84	45	3.3
endrin ketone	2601	14	2675	9.3
DCB	90%	5.9	132%	6.9

TCMX and DCB added as surrogates prior to extractions - results expressed as % recovered.

Table VIII. Quantification of Organochlorine Pesticides in Soil Sample #3 - SFE vs. Sonication

	Supercritical Fluid n=6		Sonication n=3	
	Amount Avg. (ng/g)	RSD %	Amount Avg. (ng/g)	RSD %
TCMX	80%	1.3	96%	4.8
aldrin	32	19	33	4.7
alpha chlordane	23	14	20	17
endrin	273	24	312	7.7
endrin aldehyde	17	36	31	14
endrin ketone	60	12	88	14
DCB	93%	15	112%	8.3

TCMX and DCB added as surrogates prior to extractions - results expressed as % recovered.

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SFE IN A PRODUCTION ENVIRONMENTAL LAB

Mark L. Bruce, Enseco, 4101 Shuffel Dr. NW, North Canton, OH 44720 and Michael Miille, Enseco, 2544 Industrial Blvd., West Sacramento, CA 95691.

ABSTRACT

High temperature and high flow rate extractions have produced good analyte recovery from dry and wet clay matrices for TPHs and PCBs. Rugged methods combined with automated SFE systems should be able to reduce extraction cost and turn-around time for solid environmental samples.

INTRODUCTION

Supercritical Fluid Extraction is making in-roads to the production environmental laboratory. Researchers and regulatory agencies have expended much effort producing extraction methods for environmental applications. The process of moving SFE technology from the research lab to the production environmental lab has been slowed by a combination of requirements unique to this laboratory segment.

Solid environmental matrices range from amorphous clays to zeolites. Soil samples are most the common, but the composition is highly variable. Many analytes are covered by federal and state regulations. For example, the US EPA 40 CFR Appendix IX list from 7/91 has about 150 semivolatile compounds that must be extracted by SFE if it is to completely replace existing sonication and Soxhlet methods. Since environmental samples are often heterogeneous, the question of sub-sample representativeness must be addressed. SFE is easiest with small samples while statistical concerns recommend large samples. Highly automated instruments are required to meet through-put expectations. Working in the environmental field requires heightened awareness to health & safety and environmental issues. Using reagents and solvents that are or may be perceived as detrimental is discouraged. Lastly, all methods require federal, regional or state approval before they can be used.

The goal of method development for a production environmental lab is to establish a single set of extraction conditions that work for as wide a range of solid matrices as practical. The method should emphasize high through-put and low cost at client defined data quality objectives.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Supercritical Fluid Extractor
- Suprex, PrepMaster and AP44
- 1, 5, 10 mL extraction vessel

Gas Chromatograph
- Hewlett Packard 5890
- Electron Capture Detector
- Column RTX-5, 30 m, 0.32 mm ID, 0.5 μ DF

Infrared Spectrophotometer
- Perkin-Elmer, 710
- Buck Scientific Oil in Water Analyzer
- 10 mm, 3 mL quartz cell

Solvents
- Hexane, EM Science

CO_2, SFC grade with 1500 PSIA Helium headspace with dip tube, Scott Specialty
Tetrachloroethene, J.T. Baker - Oil & Grease

EXPERIMENTAL

There are several supercritical fluid extraction parameters to optimize. They are extraction time (static & dynamic), CO_2 pressure, CO_2 flow rate, extraction temperature, analyte trap, modifier amount & type and amount of sample. Solid matrices such as loam, humus and various clays (kaolin, Fuller's earth, montmorillonite) were examined. Fractional factorial experiment designs were used to investigate and optimize these parameters as well as measure method ruggedness. Also, the issues of matrix variability, automation, environmental pollution and regulatory acceptance have been considered.

Total Petroleum Hydrocarbon analyses were performed using draft Method 8440. PCB analyses were performed by GC-ECD with modified Method 8081.

RESULTS AND DISCUSSION

TPHs

Draft Method 3560 states that a small amount of water in the sample improves analyte recovery. However, high moisture content may cause two types of problems. First, if water is liberated from the sample during the extraction, some common SFE restrictors may plug which then stops the extraction. Second, water reduces TPH recovery for some matrices under the SFE conditions specified in the draft method (Dec 1992). There are two approaches to handling water. 1) Mix an absorbent into the sample, allow sufficient interaction time and extract below the temperature where the drying agent releases water. 2) Use a restrictor that tolerates water and extract at a high enough temperature to dry the sample during the extraction process.

Use of a drying agent is the primary suggestion in 3560. The drying agent quickly absorbs free water so that the restrictor is protected. However, there can be sufficient water remaining on the surface of the matrix that TPH recovery is reduced unless the drying agent is allowed to *interact* with the sample for a long time. The EPA has determined that overnight drying is sufficient when using magnesium sulfate monohydrate as the drying agent. The results of our time study are consistent with this recommendation. Figure 1 shows how TPH recovery improves as the interaction time between the sample and Hydromatrix (diatomaceous earth) increases. For this difficult *sample* Hydromatrix is not sufficiently active to achieve acceptable results in a reasonable time frame. Using a more active drying agent such as magnesium sulfate accelerates the process but after three hours (the minimum allowed in 3560) TPH recovery is still low. The last bar in Figure 1 shows that the motor oil analyte is completely recovered from the *sample* when water content was near 0%. Thus, the draft 3560 (Dec 1992) conditions work well with dry samples but require an overnight drying step for wet samples. As a production lab overnight drying is not a desirable method requirement. We sought other ways to address the analyte recovery problems from wet samples.

Extractions of dry motor oil spiked kaolin show significant extraction time reduction by elevating the extraction temperature from 80 to 150°C. Flow rate and pressure changes do not affect extraction efficiency when varied from 1.2 to 6 ml/min and 340 to 500 atm. When motor oil spiked Fuller's earth is extracted wet (50% moisture) the temperature effect is still strong but flow rate becomes equally important. Higher flows improve extraction efficiency. Parameters were varied as follows, pressure 340 450 atm, CO_2 flow rate 3.5 7 mL/min and extraction temp 120 150°C. Figure 2 shows the results

from the factorial design experiments. Raising the temperature from 120°C to 150°C improved recovery about 25%. Raising the flow rate from 3.5 to 7 ml/min increased recovery about 25% as well. These results are summarized in Figure 2. The higher temperature and flow rate removed water from the sample quickly, presumably this allowed the supercritical CO_2 greater access to the analytes on the clay surfaces. These high temperature and high flow rate extractions have produced good analyte recovery from wet clay matrix spiked samples. Table 1 summarizes this data. The wet sample (3g) was mixed with 1.5g of Hydromatrix and extracted immediately. The Hydromatrix soaks up any free water and disperses the sample to prevent it from turning into a *brick* during the course of the extraction. The moisture from the sample is blown out of the extraction vessel through the restrictor and analyte trap to waste. The restrictor and analyte trap can tolerate up to 5 g of water.

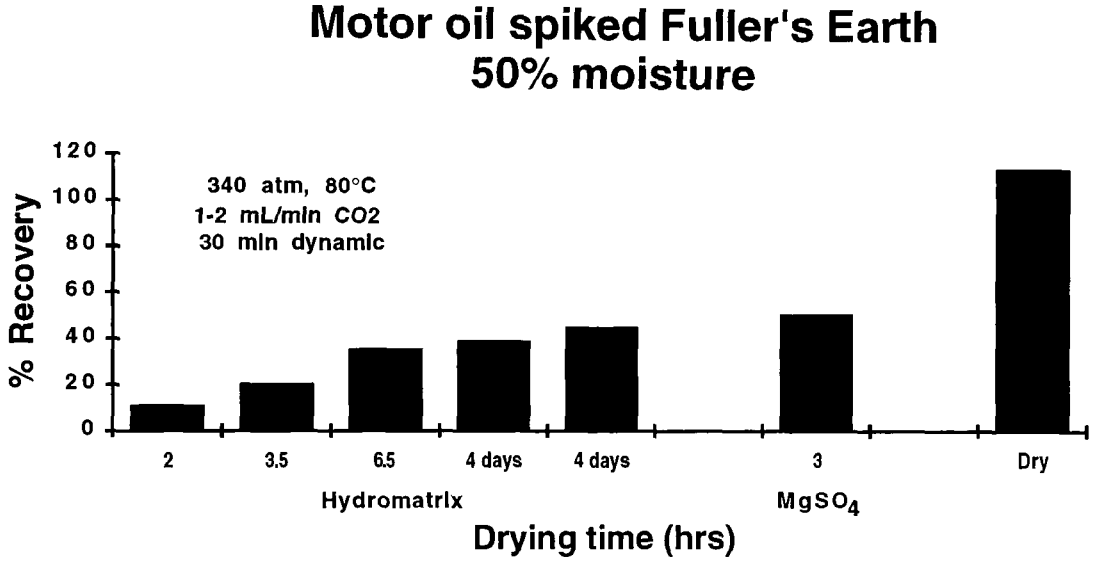

Figure 1 Drying Agent Time Study.

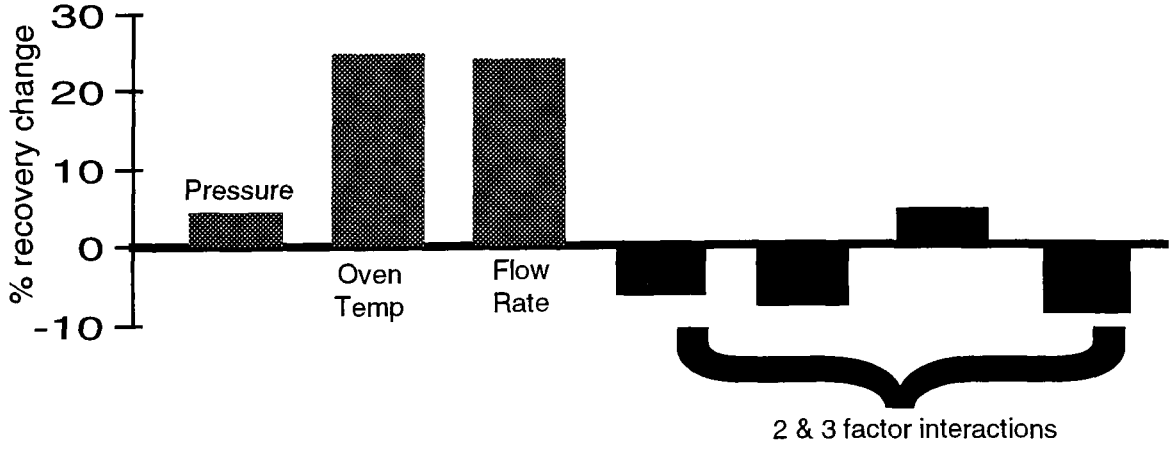

Figure 2. Factorial design results for wet kaolin.

Table 1 TPH Recovery from Wet Clays - High Temperature and Flow Extraction.

Matrix	Analyte	% Recovery
Fuller's Earth	Diesel	84
	Motor Oil	99
Montmorillonite KSF	Diesel	95
	Motor Oil	80
Montmorillonite K10	Diesel	91
	Motor Oil	94

340 atm, 150°C, 6.5 mL/min CO_2, 25 min dynamic, Hydromatrix drying agent

PCBs

A similar water effect has been seen when extracting polychlorinated biphenyls (PCBs). Increasing temperature improves PCB recovery from dry clays. Increasing flow rate and temperature improves PCB recovery from wet clays but eventually further increases in flow rate have no effect. Figure 3 shows the factorial results for dry kaolin using the following SFE conditions; pressure 380 450 atm, CO_2 flow rate 4 7 ml/min and extraction temp 120 - 150°C. Increasing the temperature from 120°C to 150°C improved PCB recovery about 17%. The other factors showed no significant effect.

Water was added to the same spiked kaolin (50% moisture). The sample was extracted under less severe conditions; pressure 350 450 atm, CO_2 flow rate 2 - 4 ml/min and extraction temp 80 150°C. Under these conditions (Figure 4) both flow rate and temperature significantly effect analyte recovery. Increasing the flow rate further in the next factorial experiment shows no recovery increase (Figure 5). The extractions conditions were; pressure 380 - 450 atm, CO_2 flow rate 4 - 7 ml/min and extraction temp 120 - 150°C.

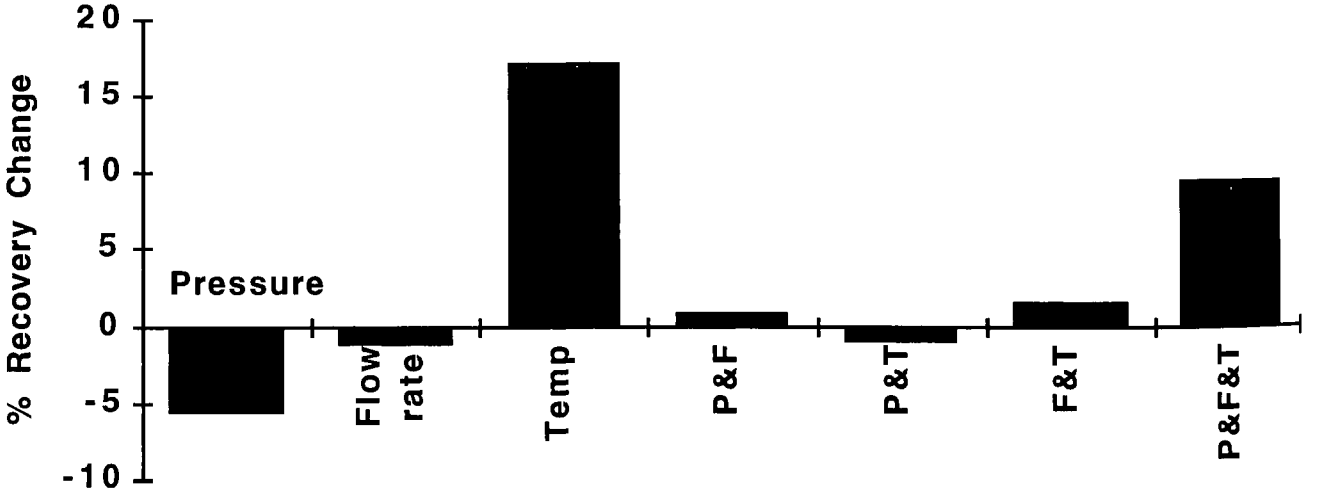

Figure 3 Extraction of Dry Kaolin Spiked with PCB 1254.

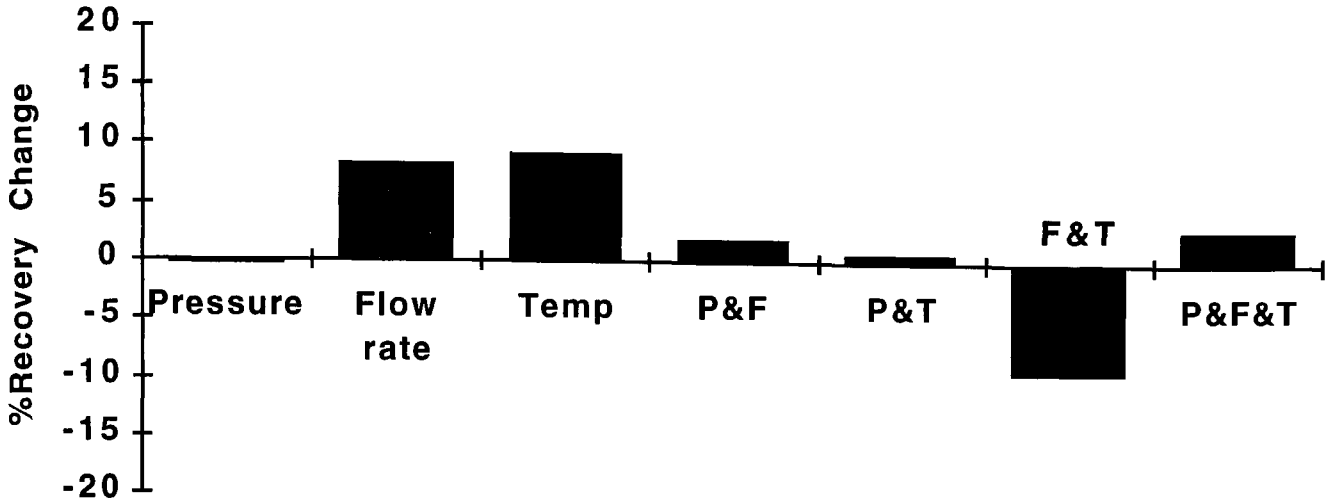

Figure 4 Extraction of Wet Kaolin Spiked with PCB 1254.

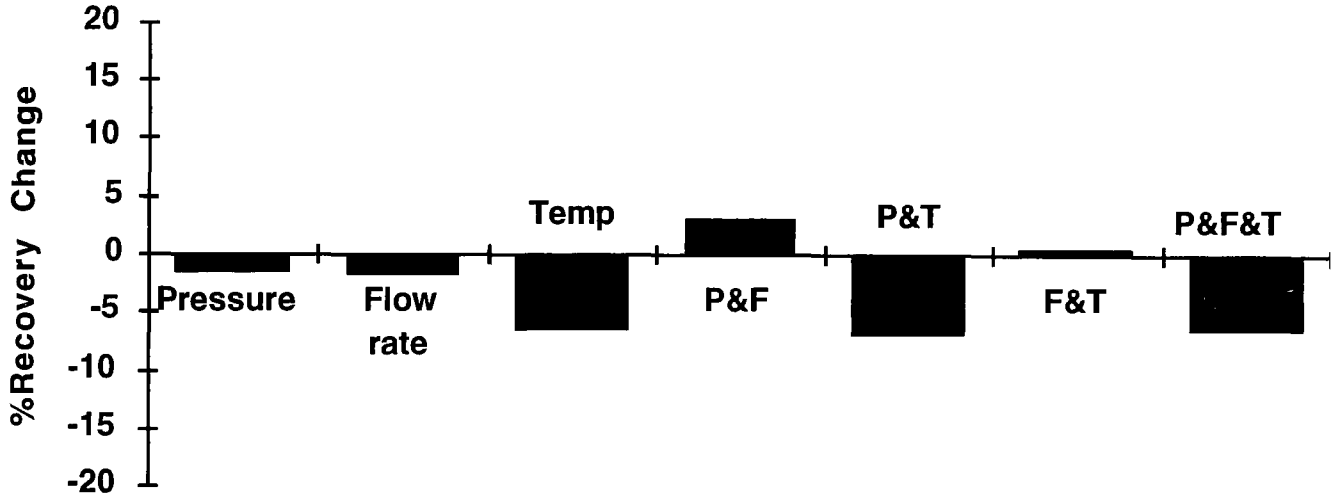

Figure 5 High Flow Extraction of Wet Kaolin Spiked with PCB 1254.

Real samples with *native* PCB analytes were extracted with the following conditions; pressure 350 - 450 atm, CO_2 flow rate 2 - 4 ml/min and extraction temp 80 150°C. A humus and cement flakes sample with 4.5 ppm PCB 1260 was studied. The sample results are shown in Figure 6. The standard deviation of replicate runs was 15%. Since no calculated effects were much larger than 15%, there were no significant effects or factors. The %RSD for all extractions was 15%. Thus, SFE was very rugged for this sample but the precision was limited by sample homogeneity.

The next sample was sandy soil with 29.2 ppm PCB 1242. The standard deviation of replicate runs was 4.5%. Since no calculated effects were much larger than 4.5%, there were no significant effects or factors. The %RSD for all extractions was 5.8%. Thus, SFE was rugged for this sample. See Figure 7 for these results.

The last sample was a standard reference material from National Research Council Canada. It was marine sediment HS-1 with 0.02 ppm PCB 1254. The standard deviation of replicate runs was 19.9%. Since no calculated effects were larger than 19.9%, there were no significant effects or factors. The concentration of the extract was near the GC instrument detection limit where precision is poor. Further concentration of the extract should produce better precision. The %RSD for all extractions was 16.8%. These results are summarized in Figure 8.

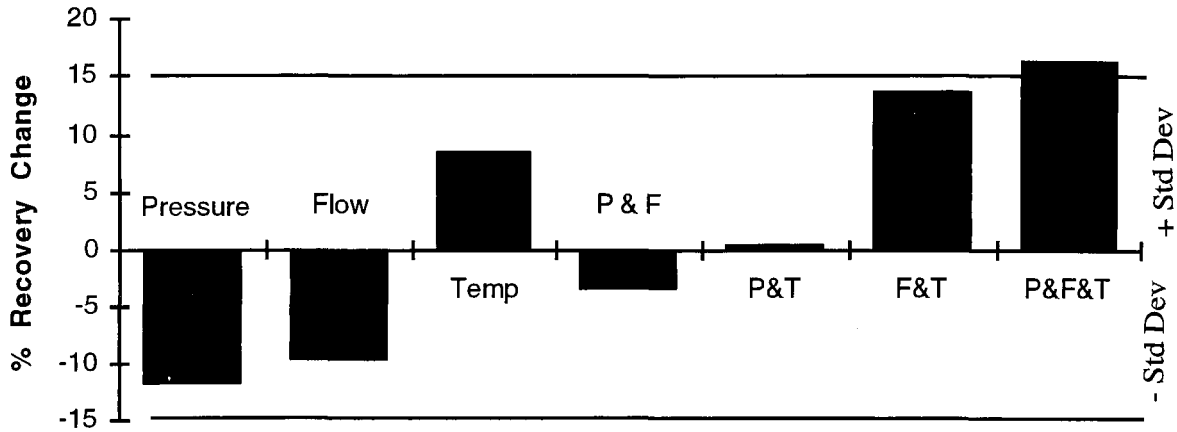

Figure 6 Humus & cement flakes, 4.5 ppm PCB 1260.

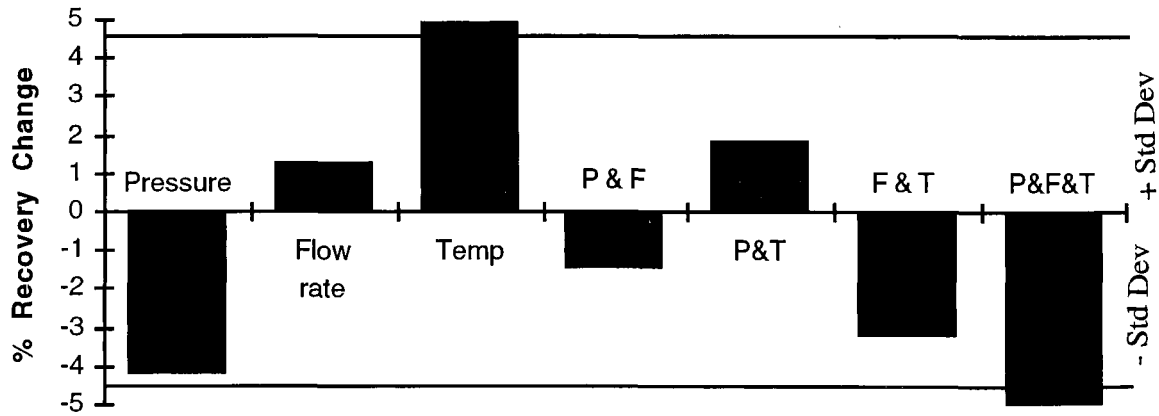

Figure 7 Sandy soil, 29.2 ppm PCB 1242.

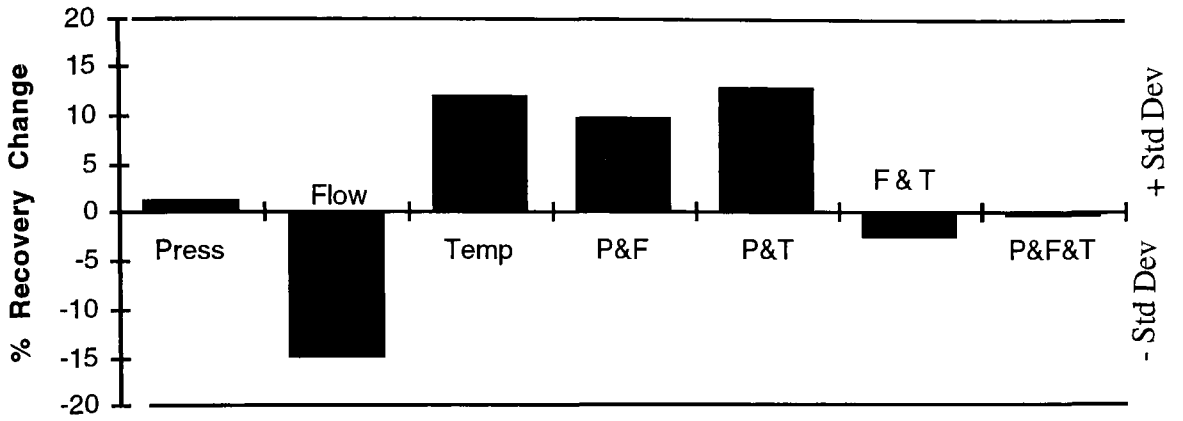

Figure 8. Factorial design results for HS-1.

CONCLUSION

TPHs and PCBs can be efficiently recovered from spiked clay (dry & wet) as well as many real samples. The use of high extraction temperatures and high flow rates has reduced the need for organic co-solvents (modifiers). Extraction is typically complete in 10-30 minutes. The use of automated SFE systems should reduce labor and solvent costs while reducing extraction turn-around time.

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PREEXTRACTION HOLDING TIMES FOR NITROAROMATICS AND NITRAMINES IN SOILS

T.F. Jenkins, Research Chemist, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire 03755-1290; C.L. Grant, Professor Emeritus, Chemistry Department, University of New Hampshire, Durham, New Hampshire 03824; and K.F. Myers and E.F. McCormick, Chemists, U.S. Army Engineer Waterways Experiment Station, Environmental Laboratory, Vicksburg, Mississippi 39180.

ABSTRACT

Studies were conducted to investigate the maximum acceptable preextraction analytical holding times (MHTs) for nitroaromatic and nitramine explosives in soils. Initial experiments were conducted using three soils fortified with two nitramines, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and four nitroaromatics, TNB (1,3,5-trinitrobenzene), TNT (2,4,6-trinitrotoluene), 2,4-DNT (2,4-dinitrotoluene) and tetryl (N-methyl-N,2,4,6-tetranitroaniline). Fortification was accomplished using aqueous solutions, and spiked concentrations were in the low µg/g range. Additional studies were conducted with field-contaminated soils from the Crane Naval Surface Warfare Center. These soils had been field-contaminated with HMX, RDX, TNT, and TNB. Fortified samples were held for periods up to eight weeks in the dark at room temperature (22°C), under refrigeration (2°C), or frozen (–15°C). Field-contaminated samples were held in the dark up to eight weeks under refrigeration.

Whether fortified or field-contaminated, the two nitramines (HMX and RDX) were stable over the eight-week test period at all storage temperatures. For the fortified soils, however, nitroaromatics were reasonably stable when frozen, degraded rapidly at room temperature, and more slowly under refrigeration. TNB and tetryl were the least stable of the four nitroaromatics tested, with losses ranging from 67% to 99% when stored under refrigeration for seven days. In contrast, TNT and TNB, at very similar concentrations to those in the fortified samples, were quite stable under refrigeration for four field-contaminated soils. When these field-contaminated soils were subsequently fortified with TNT and TNB, rapid degradation under refrigeration was again observed for the added nitroaromatics. We conclude that studies using fortified soils can produce very different estimates of MHTs compared to those using field-contaminated soils.

INTRODUCTION

Several years ago, the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) developed a laboratory method for the determination of nitroaromatic and nitramine explosives in soil (1). This method was collaboratively tested (2) and subsequently given preliminary acceptance by the EPA as SW846 Method 8330 (3). One criterion that was not experimentally evaluated during this method development process was an acceptable preextraction sample holding time. Lacking available experimental data, the EPA method established a preextraction hold time of seven days for soil (3). This holding time was chosen to be consistent with those for other organics in a soil matrix and for contractual compliance.

Subsequently, a study was conducted at Oak Ridge National Laboratory to provide the data necessary to recommend appropriate maximum preextraction holding times (MHTs) for soils contaminated with nitroaromatic and nitramine explosives (4). In their study, soils were fortified with two nitroaromatics (TNT and 2,4-DNT) and two nitramines (RDX and HMX) and stored at either room temperature (+20°C), refrigerator temperature (+4°C), or freezer temperature for periods up to a year. Soil fortification was accomplished using an acetonitrile solution of the analytes (2 mL in 2 g of soil) and the acetonitrile was not removed prior to the onset of the study. While the effect of this large amount of acetonitrile on the soil biota is unknown, storage of soils under acetonitrile does not mimic the manner in which normal soil samples are stored prior to analysis for nitroaromatics and nitramines. In fact, acetonitrile is the extraction solvent of

choice for analysis of soils for these analytes (1, 3). While the study was carefully done and the statistical treatment of the data extensive, we feel the Oak Ridge study suffers a flaw and the resulting MHT estimates may not be appropriate for customary soil sample storage procedures. Nevertheless, based on their results, they recommend storage of RDX, HMX, and 2,4-DNT contaminated soils at 4°C (refrigerator) with a MHT of six weeks, and TNT contaminated soils at –20°C (freezer), also with a MHT of six weeks.

To our knowledge there is no standard procedure for the estimation of MHTs for organic contaminants in soil. The Oak Ridge study used a modified version of an ASTM method developed for MHT estimation for water samples (5). According to this protocol, MHT is defined as the "maximum period of time during which a properly preserved sample can be stored before such degradation of the constituent of interest occurs or change in sample matrix occurs that the systematic error exceeds the 99% confidence interval (not to exceed 15%) of the test about the mean concentration found at zero time." The zero time mean concentration and standard deviation are estimated from an appropriate number of samples (usually ten) analyzed immediately after collection. If an analyte concentration is less than one order of magnitude higher than the criterion of detection, a bulk sample is fortified and the zero time mean and standard deviation are redetermined. Concentrations are then measured after various time intervals using a number of replicates based on the percent relative standard deviation (RSD) of the zero time results. The average concentration found at each analysis point is plotted versus time on linear graph paper and the "best graphical fit" to the data points is drawn. A MHT is the point where the "best fit" line intersects the two-sided 99% confidence interval about the zero time mean. Note that the number of replicates used in the confidence interval calculation is the number used for each time interval measurement rather than the ten replicates used to estimate the zero time mean. While the ASTM protocol allows use of field-contaminated waters for MHT estimation, common practice for soils is the use of fortification, as was done in the Oak Ridge study. Experiments on the stability of 1,2-dibromoethane (EDB) (6) and polyaromatic hydrocarbons (PAHs) (7) in soils casts doubt on the ability of fortification to mimic analyte-soil interactions where contamination has been in place for extended periods. For nitroaromatics and nitramines this is particularly germane since these contaminants have been in place in some cases for over 50 years.

In the following study, we reexamine the issue of MHTs for soils contaminated with nitroaromatic and nitramine explosives with emphasis on (a) avoidance of organic solvent addition during soil fortification and (b) comparison of stability of fortified soils to field-contaminated soils.

EXPERIMENTAL

Chemicals

All standards and test solutions were prepared from Standard Analytical Reference Materials (SARMs) obtained from the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, Maryland. Aqueous standards and test solutions were prepared in reagent grade water obtained from a Milli-Q Type I Reagent Grade Water System (Millipore Corp.). Methanol used in the preparation of HPLC eluent and acetonitrile used for soil extraction were HPLC Grade from Alltech and Baker, respectively. Eluent was prepared by combining equal volumes of methanol and water and vacuum filtering through a nylon membrane (0.45 μm) to degas and remove particulate matter.

Analyte spiking solutions

All analyte spiking solutions were prepared in water. SARMs for 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (TNB), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine (HMX), and N-methyl-N,2,4,6-tetranitroaniline (tetryl) were placed in individual brown glass jugs, reagent grade water was added, and the contents were stirred at room

Table 1. Physical and chemical properties of test soils.

Soil	Property			
	pH	% Clay	Total Organic Carbon (%)	Cation Exchange Capacity, meq/100g
Windsor	6.2	30	1.1	3.5
Charlton	6.0	20	1.8	7.3
Fort Edwards	8.4	70	0.5	>150.0
Crane A	8.6	12	0.5	15.7
Crane B	8.4	1	0.9	3.2
Crane C	7.9	9	1.5	9.5

temperature for a week. The solutions were then filtered through 0.45 μm nylon membranes into clean, brown glass jugs. No solvents other than water were used in the preparation of these solutions.

The concentration of analyte in each aqueous spike solution was determined against standards prepared in methanol or acetonitrile (1, 3) diluted 1:1 with reagent grade water prior to analysis. A multianalyte spiking solution was prepared by combining appropriate volumes of all of the individual, aqueous-based, analyte solutions with the exception of tetryl and filtering through a 0.45 μm nylon membrane.

Soils

Blank test soils were obtained locally from Vermont (Windsor), New Hampshire (Charlton), and New York (Fort Edwards). These soils were air-dried, ground with a mortar and pestle, and passed through a 30-mesh sieve (590 mm). Some physical and chemical properties of these soils are presented in Table 1. Replicate 5.0 ± 0.1 g subsamples of each blank soil were placed in individual 20-mL glass scintillation vials.

Three field-contaminated soil samples (designated A, B, and C) from the Rockeye site at the Naval Surface Warfare Center, Crane, Indiana site were selected from a large group of samples on the basis of field screening for explosives residues. These soils were not dried or sieved, but they were homogenized by hand and rocks or other large particles were removed. They were stored in glass jars at 4°C in the dark. These soils contained measurable concentrations of HMX, RDX, TNT, TNB, two isomeric microbiological transformation products of TNT, 2-amino-4,6-dinitrotoluene (2-AmDNT) and 4-amino-2,6-dinitrotoluene (4-AmDNT) and 3,5-dinitroaniline (3,5-DNA), which is a microbiological transformation product of TNB (8, 9). Selected properties of these soils are shown in Table 1.

Soil wetting and analyte spiking

Prior to the onset of the experiment, previously air-dried test soils were rewetted. Because the water holding capacity for each soil varied, the amount of water added to each soil was varied such that after spike additions were also made, there was no evidence of freestanding water. For the three initially blank soils, 0.20 mL of reagent grade water was added to the Windsor sandy loam and 1.00 mL was added to the Fort Edwards Clay and Charlton silty loam. For the field-contaminated soil from Crane, 0.50 mL of reagent grade water was added. After water addition, all soils were allowed to stand at room temperature in the dark for three days to allow microbiological activity to reestablish (4).

Fortification of the three blank soils was made by adding 1.00 mL of a combined aqueous spiking solution to each vial. An identical study was conducted separately for tetryl since the transformation products of tetryl interfered analytically with the other nitroaromatics of interest. Except for the soils designated as day

zero exposure and those to be stored frozen, the spiked soils were immediately placed in the appropriate storage temperature in the dark. The zero day samples and the samples to be frozen were permitted to stand for two hours after fortification to allow time for the analytes to interact with the soils prior to either extraction or freezing. The vials containing the field-contaminated soil were treated and stored in an identical manner as described above except that no fortification was made. Initial analyte concentrations in the field-contaminated soil ranged from 0.3 to 1.6 μg/g.

Soil respiration

To ensure that the rewetted, fortified soils had regained microbial activity, three vials of each soil were placed in separate 250-mL Erlenmeyer flasks enclosed with a two-hole rubber stopper. Air was drawn through two aqueous NaOH scrubbers, through an Erlenmeyer containing a given soil, and into a CO_2 collection tube containing standard aqueous NaOH. The CO_2 evolved from the soils was collected as carbonate over a period of two weeks and the carbonate level determined by back titration with 0.5 N HCl. The results indicated that resumption of microbial activity had occurred in the rewetted soils.

Soil holding time test parameters—fortified soils

Three storage conditions were examined: room temperature (22 ± 2°C), refrigerator (2 ± 2°C), and freezer storage (−15 ± 2°C). Portions stored under these conditions were extracted after 0, 3, 7, 14, 28, and 56 days of storage and the analyte concentrations determined. Because of expected variability among replicates, triplicates were analyzed for each temperature /time combination.

Soil holding time test—field-contaminated soils

Experiments with the three Crane soils were initiated within two days of sampling. No spiking took place in the initial portion of this study. Seven 5.00-g subsamples of each field moist soil were immediately extracted and analyzed. A bulk portion of each soil was weighed, air-dried overnight, and reweighed to obtain percent moisture. The dried samples were ground and seven 3.00-g subsamples were extracted and analyzed. This procedure was repeated with a second bulk portion of each soil after eight weeks storage (moist) at 4 ± 2°C in the dark.

Since the results from this study differed greatly from those with fortified soils, an additional study was conducted with the residual portion of these three Crane soils. In this experiment, 42 2.00-g subsamples of moist soil were transferred to 20-mL vials for each of the three Crane soils. Additional samples were used for the determination of percentage moisture after overnight air drying. Twenty-eight of the subsamples for each soil were fortified with an aqueous solution of TNB and TNT of known concentration. The volume of spiked solution varied somewhat from soil to soil in order to prevent free-standing solution, but all subsamples for a given soil received the same volume. Reagent grade water was added to the remaining 14 vials for each soil in amounts that matched the respective volumes of spike solution and served as controls.

One set of seven spiked subsamples and one set of water-treated subsamples from each soil were extracted and analyzed the same day they were prepared. All other subsamples were stored at 4 ± 2°C in the dark until removed for analysis.

Soil extraction and analysis

Soils were extracted and analyzed as described in SW846 Method 8330 (1, 3) with two differences. First the soils were not air-dried prior to extraction, because it was judged that the time required to dry the soil in the vials at room temperature could result in analyte loss and confound the effect of the holding time temperatures. Second, a 5-gram portion of soil was used for the fortified samples instead of the usual sample

size of two grams. This was necessary since the solubility of HMX and RDX in the aqueous spiking solution is limited (4 mg/L and 42 mg/L, respectively) as was the moisture holding capacity of the test soils. Thus to obtain sufficiently high extract concentrations of these analytes without exceeding the moisture holding capacity of the soils, larger soil samples were required.

Data analysis—fortified soils

The mean and standard deviation for each set of triplicate measurements were calculated. Suspect individual measurements were flagged on the basis of extreme values of the % RSD (> 50%) and inconsistencies in the overall pattern for that compound. Each suspect value was checked for possible computation or transcription errors. Twelve individual extreme values were arbitrarily excluded because they produced large distortions of both means and standard deviations. In no case was more than one datum excluded from a triplicate set. These exclusions amounted to less than 1% of the values.

A modified version of the ASTM procedure was used to estimate MHTs where appropriate. To gain degrees of freedom (d.f.) and to fairly represent precision for the entire experiment, pooled standard deviations were calculated for the six sets of triplicates for each soil/storage condition where rapid degradation was absent. This produced more d.f. for the standard deviation than the nine that would have been obtained if we had been able to run ten replicates on day zero as suggested by ASTM. Where a 99% confidence interval exceeded ± 15% of the day zero mean, the limits were set at ± 15% as specified in the ASTM procedure. This procedure worked well for the fortified soils where standard deviations were small, and the results should be very comparable to the standard ASTM procedure.

Data analysis—field-contaminated soils

Analysis of variance (ANOVA) was used to compare mean concentrations for the results for the field-contaminated soils. Rapid degradation of spiked TNB and TNT is depicted graphically; no statistical analysis was required.

RESULTS AND DISCUSSION

Behavior of analytes in fortified soils as a function of holding time

The mean concentrations of the five fortified analytes and transformation products in Windsor soil are presented in Table 2 as a function of holding time and storage condition. Of the six fortified analytes, TNB shows the most rapid rate of degradation. The rate of loss for TNB in Charlton and Fort Edwards soils is even greater (8). For all three soils TNB concentration rapidly decreases at room temperature with only an average of 6.5% remaining in these soils after three days. For refrigerator storage, the rate of disappearance of TNB is slower than at room temperature, but even so, only an average of 15.3% remains after seven days. Further reduction of TNB occurs by 14 days and by 28 days the concentration of TNB is below its detection limit. This disappearance is accompanied by the appearance of an increased level of 3,5-DNA, the expected initial microbiological transformation (reduction) product (9). These changes are shown for Windsor soil stored at refrigerator temperature in Figure 1. On a molar basis, a maximum of 36%, 47%, and 15% of the TNB lost could be accounted for as 3,5-DNA for the Windsor, Charlton and Fort Edwards soils, respectively. It is also interesting to note the slow decrease in 3,5-DNA concentration in all three soils once the TNB precursor is gone. Clearly this is a very dynamic system even under refrigeration. In contrast to the rapid degradation found at room temperature and under refrigeration, TNB is quite stable in the frozen soils (Table 2).

Table 2. Concentrations of analytes and transformation products as a function of holding time and storage condition, Windsor sandy loam.

		Mean concentration (μg/g) ± standard deviation (μg/g)											
		Holding time											
		00 Days		*03 Days*		*07 Days*		*14 Days*		*28 Days*		*56 Days*	
Compound	*Storage*	*X*	*s*	*X*	*s*	*X*	*s*	*X*	*s*	*X*	*s*	*X*	*s*
HMX	Room. temp.	0.373	0.003	0.353	0.007	0.385	0.012	0.377	0.001	0.392	0.009	0.349	0.008
	Refrigerator	0.373	0.003	0.360	0.004	0.375	0.004	0.381	0.009	0.379	0.004	0.350	0.009
	Freezer	0.373	0.003	0.354	0.003	0.377	0.011	0.377	0.005	0.399	0.018	0.354	0.008
RDX	Room. temp.	1.500	0.007	1.355	0.019	1.608	0.005	1.568	0.003	1.622	0.015	1.572	0.016
	Refrigerator	1.500	0.007	1.374	0.006	1.612	0.009	1.590	0.015	1.597	0.006	1.570	0.046
	Freezer	1.500	0.007	1.368	0.008	1.600	0.023	1.575	0.004	1.633	0.025	1.586	0.010
TNB	Room. temp.	0.914	0.004	0.013	0.023								
	Refrigerator	0.914	0.004	0.598	0.020	0.300	0.030	0.090	0.027			0.013	0.001
	Freezer	0.914	0.004	0.885	0.008	0.946	0.037	0.952	0.001	0.937	0.054	0.949	0.010
3,5-DNA	Room. temp.			0.277	0.007	0.274	0.016	0.238	0.007	0.191	0.008	0.127	0.009
	Refrigerator			0.116	0.005	0.220	0.013	0.283	0.003	0.277	0.007	0.255	0.022
	Freezer									0.014	0.024	0.028	0.001
TNT	Room. temp.	0.969	0.005	0.465	0.030	0.067	0.010						
	Refrigerator	0.969	0.005	0.861	0.005	0.777	0.013	0.637	0.043	0.309	0.026	0.086	0.017
	Freezer	0.969	0.005	0.926	0.006	0.975	0.026	0.978	0.003	0.980	0.024	0.954	0.010
4-Am-DNT	Room. temp.			0.109	0.005	0.202	0.006	0.215	0.005	0.211	0.010	0.169	0.004
	Refrigerator			0.025	0.002	0.041	0.006	0.067	0.010	0.124	0.002	0.169	0.003
	Freezer			0.004	0.003								
2-Am-DNT	Room. temp.			0.037	0.002	0.074	0.004	0.088	0.002	0.092	0.000	0.079	0.003
	Refrigerator			0.010	0.004	0.016	0.004	0.031	0.002	0.051	0.002	0.065	0.018
	Freezer											0.004	0.007
2,4-DNT	Room. temp.	0.850	0.002	0.741	0.016	0.716	0.021	0.626	0.006	0.573	0.004	0.419	0.020
	Refrigerator	0.850	0.002	0.802	0.004	0.837	0.007	0.828	0.013	0.772	0.005	0.675	0.015
	Freezer	0.850	0.002	0.799	0.006	0.863	0.020	0.856	0.005	0.857	0.017	0.808	0.007
Tetryl	Room temp.	5.48	0.74	1.63	0.72	0.66	0.42						
	Refrigerator	5.48	0.74	4.15	0.09	2.94	1.01						
	Freezer	5.48	0.74	4.44	0.78	5.10	0.87						

The behavior of TNT in these fortified soils parallels that of TNB except that the rate of disappearance is reduced (Table 2). The expected transformation products, 2- and 4-AmDNT (9), are observed to increase as TNT concentrations decline. The rapid loss of TNT for the room temperature storage condition parallels that observed in the Oak Ridge study (4) and elsewhere for low concentration spiked soils (11, 12). Our results are quite different from those found at Oak Ridge for refrigerated storage, however. We found that for seven days of storage, the concentration of TNT remaining was only 80, 72, and 0%, respectively for Windsor, Charlton and Fort Edwards, while the Oak Ridge study found no significant TNT loss until after day seven for the three soils studied.

When soils were frozen, our modified ASTM criterion showed no significant change for TNT in Windsor or Charlton soils during the 56-day test period. With Fort Edwards soil the TNT concentration reached the lower 99% confidence interval (15% change) after about 20 days. However, the total decrease was still only 16.1% after 56 days.

The behavior of tetryl in these fortified soils parallels that of TNB and TNT. For the Windsor soil, a large reduction in the concentration of tetryl can be seen after only three days at room temperature (Table 2). In

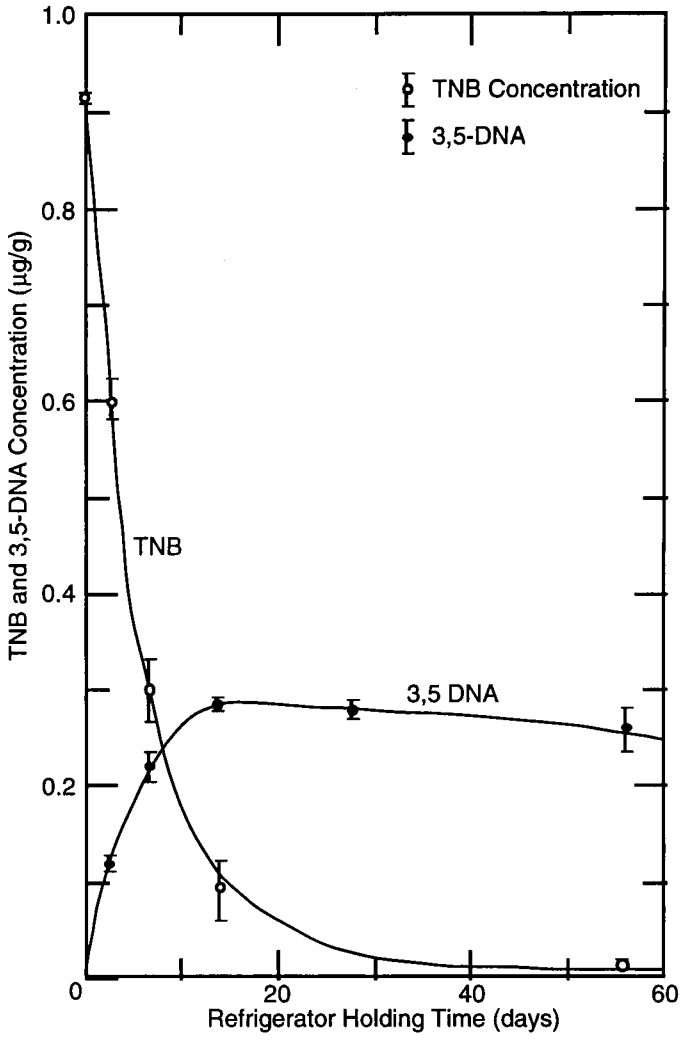

Figure 1. Stability of fortified TNB in Windsor soil.

addition, three apparent transformation products are also evident. After seven days under refrigeration, the tetryl concentration is reduced by about 46% and the same transformation products are seen. Loss of tetryl in the Charlton soil is much more rapid than found for Windsor, both at room temperature and under refrigeration. The same three transformation products observed in the extracts of the Windsor soil are again evident. After seven days under refrigeration, the initial concentration of tetryl is reduced by 97%. The rate of degradation of tetryl in the Fort Edwards clay is even faster than found for the Charlton soil, resulting in over 99% loss of tetryl after seven days of refrigeration. The relative amounts of the various transformation products observed for this soil appear to be different than observed for the Windsor and Charlton soils. One of the reasons for the different behavior for this soil is its pH, which is 8.4 compared to 6.2 for Windsor and 6.0 for Charlton (Table 1). It has been observed elsewhere that hydrolysis products of tetryl were different at acidic and basic pH and that hydrolysis proceeds much more rapidly under basic conditions (13). Perhaps the very rapid loss of tetryl for Fort Edwards clay is partially due to hydrolysis rather than biodegradation. A more thorough discussion of the transformation products of tetryl is presented elsewhere (14). No statistically significant loss of tetryl was observed for freezer storage at −15° C over the seven-day study period for the three soils studied.

The stability of 2,4-DNT in these fortified soils is much greater than TNB, TNT, or tetryl (Table 2). At room temperature an average of 68.4% remained after three days. This increased stability of 2,4-DNT relative to TNT at room temperature agrees with the results from Oak Ridge (4). Under refrigeration an average of 86% remained after seven days of storage. A slow rate of loss continued throughout the study and by 14 days, peaks corresponding to the expected reduction products, 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene, appeared (9). With freezer storage, 2,4-DNT was quite stable. For the Windsor soil, our modified ASTM criterion was exceeded on the low side after 42 days. Once again, this occurred because of a very small pooled standard deviation, and at 56 days the concentration decrease was only 4.9%. Charlton soil showed no significant change during the 56-day test period. However, the Fort Edwards soil produced a significant 2,4-DNT decrease after 30 days and the loss after 56 days was 20.3%. Still, the overall mean recovery relative to day zero for the three soils was 94.2% and the mean for the 56-day time was 90.8%.

The stability of HMX and RDX in these three fortified soils is much greater than TNB, TNT, or 2,4-DNT. This agrees with the results obtained at Oak Ridge (4) and elsewhere (15, 16), where it was demonstrated that RDX does not biodegrade under aerobic conditions. Regardless of storage conditions, no loss of HMX or RDX was observed over the entire 56-day study.

Table 3. Drying and storage effects on explosives concentrations in field-contaminated soils.

(Day 0 = moist, unground; day 1 = overnight air-dry, ground; day 56 = 8 weeks at 4°C in dark at field moisture, then overnight air-dry and ground.)

	Mean Concentration, µg/g dry weight basis						
Soil A	HMX	RDX	TNB	3,5-DNA	TNT	4-Am DNT	2-Am DNT
Day 0	12.2	3.32	0.12	0.16	0.64	0.71	0.54
Day 1	12.4	3.51	0.13	0.17	0.87	0.73	0.57
Day 56	13.3	3.74	0.15	0.12	0.82	0.73	0.52
LSD	NS	NS	0.025	0.032	NS	N	NS
RSD (Means)	8.0%	4.4%	5.1%	6.0%	10.2%	3.5%	3.4%
Soil B							
Day 0	1.69	0.71	0.069	0.15	0.46	0.38	0.17
Day 1	1.48	0.61	0.055	0.12	0.40	0.31	0.16
Day 56	1.19	0.82	0.082	0.15	0.48	0.44	0.21
LSD	NS	NS	0.019	NS	NS	0.05	0.03
RSD (Means)	1.7%	7.8%	7.6%	6.2%	11.1%	3.7%	4.3%
Soil C							
Day 0	0.10	NQ	NQ	0.077	0.12	0.18	0.18
Day 1	0.11	NQ	0.047	0.16	0.47	0.17	0.20
Day 56	0.12	NQ	0.036	0.058	0.35	0.18	0.20
LSD	NS	—	NS	0.060	0.22	NS	NS
RSD (Means)	7.2%	—	14.2%	28.5%	19.1%	6.7%	6.9%

LSD = Least significant difference for means at significance level of 5%. Means that differ are identified by lines connecting them.

NS = No significant difference in the three means at 5% significance.

NQ = Not possible to quantify due to very low concentration.

%RSD (means) = $S_{yp}(100)/\bar{X}\sqrt{n}$ where S_{yp} is the pooled standard deviation from the three sets of seven replicates per mean (n = 7), and $\bar{X}$ is the overall mean of the three sets of seven replicates.

Holding time behavior—field-contaminated soils

Field-contaminated soils from the Crane-Rockeye site (A, B, and C) were analyzed initially, both with and without drying (days 0 and 1) and again after eight weeks of storage (moist) at 4°C in the dark (day 56). None of these samples are believed to have received significant recent explosives contamination; i.e., the contamination occurred several years ago. Results are summarized in Table 3. Analysis of variance (ANOVA) was conducted on each set of replicates for each soil and each analyte. Where means were significantly different (5% significance level), least significant differences (LSDs) were computed. Specific differences in means were identified in Table 3 by lines connecting them.

Neither HMX nor RDX showed any significant differences. In general, precision of the measurements was very satisfactory as shown by the percent relative standard deviations of the means a. Absence of significant differences in the means confirmed nitramine stability observed previously with fortified soils.

The nitroaromatics did produce a few significant differences but, in general, these differences were small in magnitude, were not consistent, and were of no practical importance. A more thorough discussion of the differences observed is presented elsewhere (17). The major observation here is the vastly improved stability of the nitroaromatics in these field-contaminated soils relative to the three fortified soils discussed previously.

The question at this point was whether the improved stability of the nitroaromatics was a reflection of differences in binding for nitroaromatics in aged field-contaminated soils, compared to fortified soil, or just differences in the specific soils studied. To address this question, we spiked TNT and TNB into 42 aliquots of each of the three field-contaminated soils from Crane-Rockeye discussed above and followed the con-

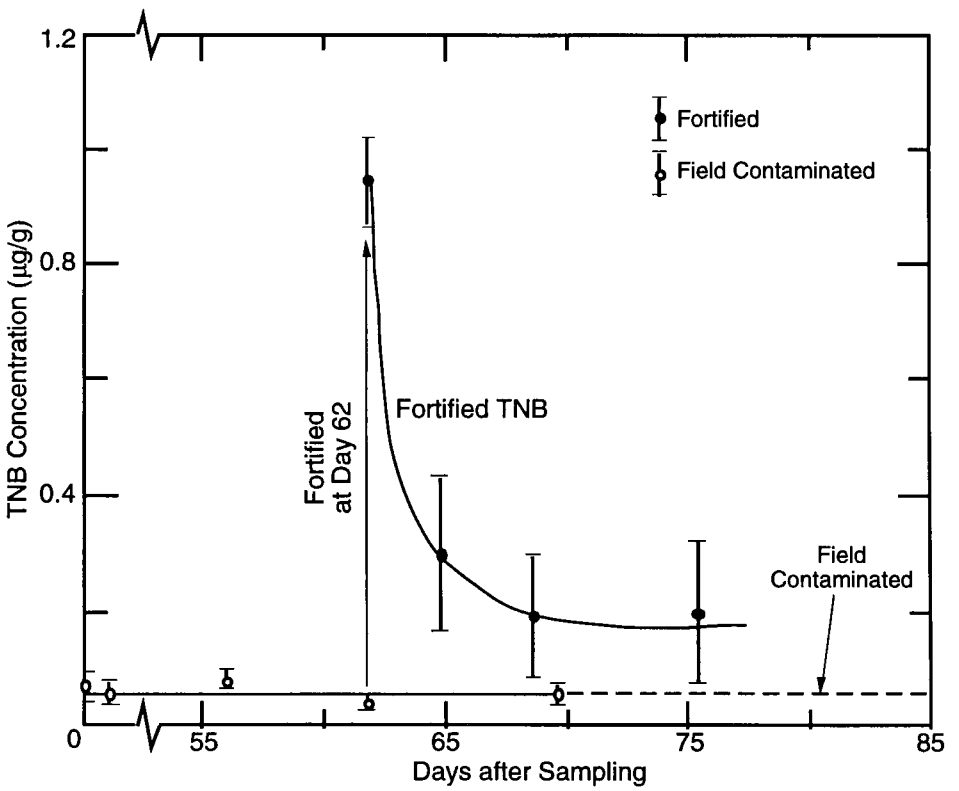

Figure 2. Refrigerator storage effects on TNB for Crane Soil B.

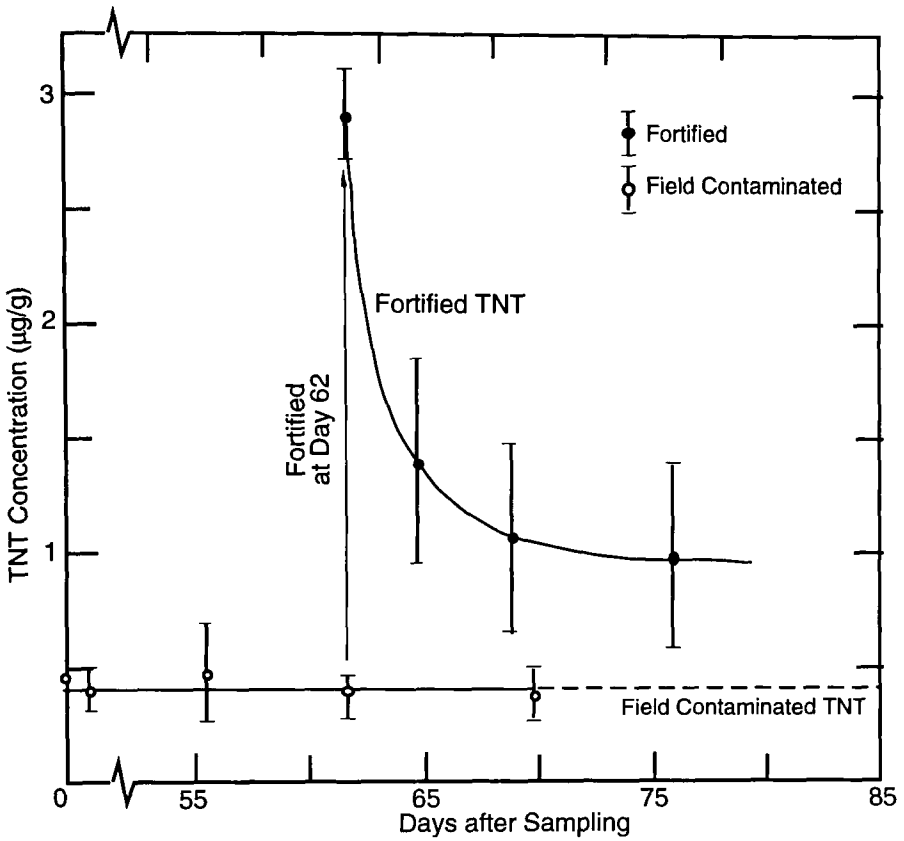

Figure 3. Refrigerator storage effects on TNT for Crane Soil B.

centration changes during storage at 4°C in the dark. Control samples were prepared by adding water to 14 aliquots of each soil in amounts equal to the volumes of aqueous spiking solution used. One set of seven aliquots of each spiked soil and one set of seven aliquots of each water-treated soil were analyzed on the same day they were prepared. The remaining aliquots were immediately placed in storage at 4°C in the dark. Because degradation was found to be slower in soil A than in B and C, the former experiment went 21 days while the latter two lasted 14 days. The second set of water-treated samples for A was analyzed on day 21 while the B and C controls were analyzed on day eight. Results are presented for TNB and TNT in Crane soil B (Figures 2 and 3).

In general, analyte concentrations in the water-treated control samples showed either no change (within experimental error) or a small increase after storage (Figures 2 and 3).

For the fortified, field-contaminated samples from Crane, results were very different from the controls. For all three soils, the concentrations of TNB and TNT declined rapidly as observed for the three fortified soils discussed earlier (Figures 2 and 3). The disappearance was again accompanied by increases in the concentrations of the expected transformation products. These results afford unambiguous evidence of the dramatic differences in the stability of explosives in fortified and field-contaminated soils and cast doubt on the ability of fortified soils to mimic soil-analyte interactions in field-contaminated soils where analytes have been in contact for extended periods.

CONCLUSIONS

The major observation in this study is the large stability differences for nitroaromatics in fortified and field-contaminated soils. Even with avoidance of the addition of unnatural solvents during fortification, fortified soils do not appear to accurately mimic soils contaminated in the field over extended periods of time. This result has implications that extend well beyond the experimental estimation of MHTs. Spiking analytes into various matrices is used by analytical and environmental scientists for many purposes such as (a) estimating the accuracy of analytical procedures via recovery determinations, (b) generating quality control data, and (c) testing the efficacy of remediation treatments. To date there has been only limited acknowledgment (1, 6, 7) that fortification as currently practiced often fails to yield an accurate representation of results to be expected with real samples. We believe that this topic deserves much greater attention in the future.

The results for the nitramines are more consistent. Whether fortified or field-contaminated, RDX and HMX appear stable for at least 56 days when refrigerated. This agrees with the results from the Oak Ridge study (4). Since nitramines and nitroaromatics are often co-contaminants, MHTs will seldom, if ever, be established for nitramines alone. Nevertheless, the MHT estimates for nitramines may be useful in determining the useability of results for samples analyzed outside normal holding times.

Results from fortified soils appear most applicable to freshly contaminated soils such as one might find near the front of a moving groundwater plume. If MHTs are to be established using worst case estimates, the results for the nitroaromatics in the fortified soils in this study may be useful. These results indicate that refrigeration is insufficient to stabilize TNB, TNT, and tetryl. If samples are immediately frozen, however, the nitroaromatics will remain acceptably stable for at least eight weeks.

ACKNOWLEDGMENTS

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Wide-Spread and Systematic Errors in the Analysis for PCBs in Soils

David Eugene Kimbrough, Public Health Chemist II, Rustum Chin, Public Health Chemist III, Janice Wakakuwa, Supervising Chemist, California Environmental Protection Agency, Department of Toxic Substances Control, Hazardous Materials Laboratory - Southern California, 1449 W. Temple Street, Los Angeles California 90026-5698.

Abstract

The analysis of PCBs in soils is one of the most widely performed tests among environmental laboratories. It is a very difficult test and is subject to a great deal of inter-laboratory variance and bias. A new inter-laboratory study, using five soils spiked at four different concentrations with Aroclor 1260, was conducted with two groups of laboratories numbering 20 and 129 respectively. The results of this study are compared with the results of the other studies but show that the bias is concentration dependent. A number of definite patterns of recovery are noted indicating that the large variance and bias was not due to random errors but to wide-spread systematic errors.

Statistically significant differences were found between laboratories depending on the type of extraction equipment, solvents, and clean-up procedures that were used. Results from laboratories using Soxhlet extraction showed significantly more accurate results than did sonication, especially at higher concentrations but with equal precision. Results from laboratories using non-polar solvents showed significantly lower accuracy than more polar solvents with equal precision. Results from laboratories using Florisil@ column clean-up showed signifcantly more accurate and precise results at lower concentrations than laboratories using no clean-up procedure.

Other significant variables that affect the accuracy of the analysis of PCBs in soils is the linear dynamic range, calibration range, and detector drift of the gas chromatographic instrument. There were three types of errors: one was calibrating the instrument within the linear dynamic but analyzing samples above and below this range. The second was calibrating the instrument outside the linear dynamic range. The third was to allow excessive drift in the detector. Each of these errors produced a charateristic pattern of biased results. The net result was a large inter-laboratory variance and biases.

An Evaluation of Gas Chromatography/Ion Trap Mass Spectrometry for Analysis of Environmental Organochlorine Pesticides

Gary Robertson, U.S. EPA, Environmental Systems Monitoring Laboratory, Las Vegas, NV 89193
James Barron, U.S. EPA, Office of Solid Waste and Emergency Response, Washington, D.C. 20460

The U.S. EPA is continually making efforts to improve the quality of analytical data and supporting documentation used for making decisions about environmental contamination. A research project evaluating the use of Gas Chromatography/Ion Trap Mass Spectrometry (GC/ITMS) for the analysis of organochlorine pesticides is being conducted by the Environmental Monitoring Systems Laboratory-Las Vegas and the Analytical Operations Branch of the Office of Solid Waste and Emergency Response. The adoption of a mass spectrometric method for the detection of pesticides would provide the same assurances of identification and quantitation as the Contract Laboratory Program (CLP) analysis for semivolatile compounds. This would reduce the costs involved in data review, and provide the data user a more reliable product.

The research has concentrated on the CLP list of organochlorine pesticides. Instrumental operating conditions and detection limits for pesticides on the GC/ITMS have been established. Minor modifications in the sample concentration step of the CLP method have been developed to increase detectability. The effects of interferences have been evaluated using samples containing both synthetic and native interferences. Results of these studies, which show GC/ITMS to be a promising technique, will be discussed, and a comparison will be made to current CLP quantitation limits. Planned additional research will also be discussed.

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RAPID AND COST-EFFECTIVE ANALYSIS OF 2,3,7,8-TCDD USING THE "DIOXIN RISc®" IMMUNOASSAY TEST KIT

R. Allen, T. Stewart, D. Reynolds, S. Friedman, EnSys, Inc.
Research Triangle Park, North Carolina 27709

ABSTRACT

Current methods for detecting low levels of Dioxin are expensive and laborious. We have developed a rapid and sensitive enzyme immunoassay, DIOXIN RISc®, for the detection of 2,3,7,8-TCDD in a variety of matrices. The immunoassay is designed to incorporate sample processing protocols which are routinely used in research and analytical laboratories. However, many of the steps used in processing dioxin samples can be eliminated because of the inherent specificity and affinity of the immunochemical reagents. The test easily detects ppt to ppq levels of 2,3,7,8-TCDD in samples which have been extracted and taken to dryness. The immunoassay shows less than 0.01% cross-reactivity with PCBs, PAHs, Chlorophenols and Chlorinated Aromatic Pesticides. The immunoassay recognizes 2,3,7-TriCDD (20%) and 2,3,7,8-TCDF (5%) but does not significantly cross-react with other Dioxin and Furan Congeners. DIOXIN RISc® offers a simple, rapid, reliable and cost-effective alternative to current methods for dioxin analysis.

AUTOMATED SOXHLET EXTRACTION AND CONCENTRATION OF SEMIVOLATILE ANALYTES IN SOIL SAMPLES

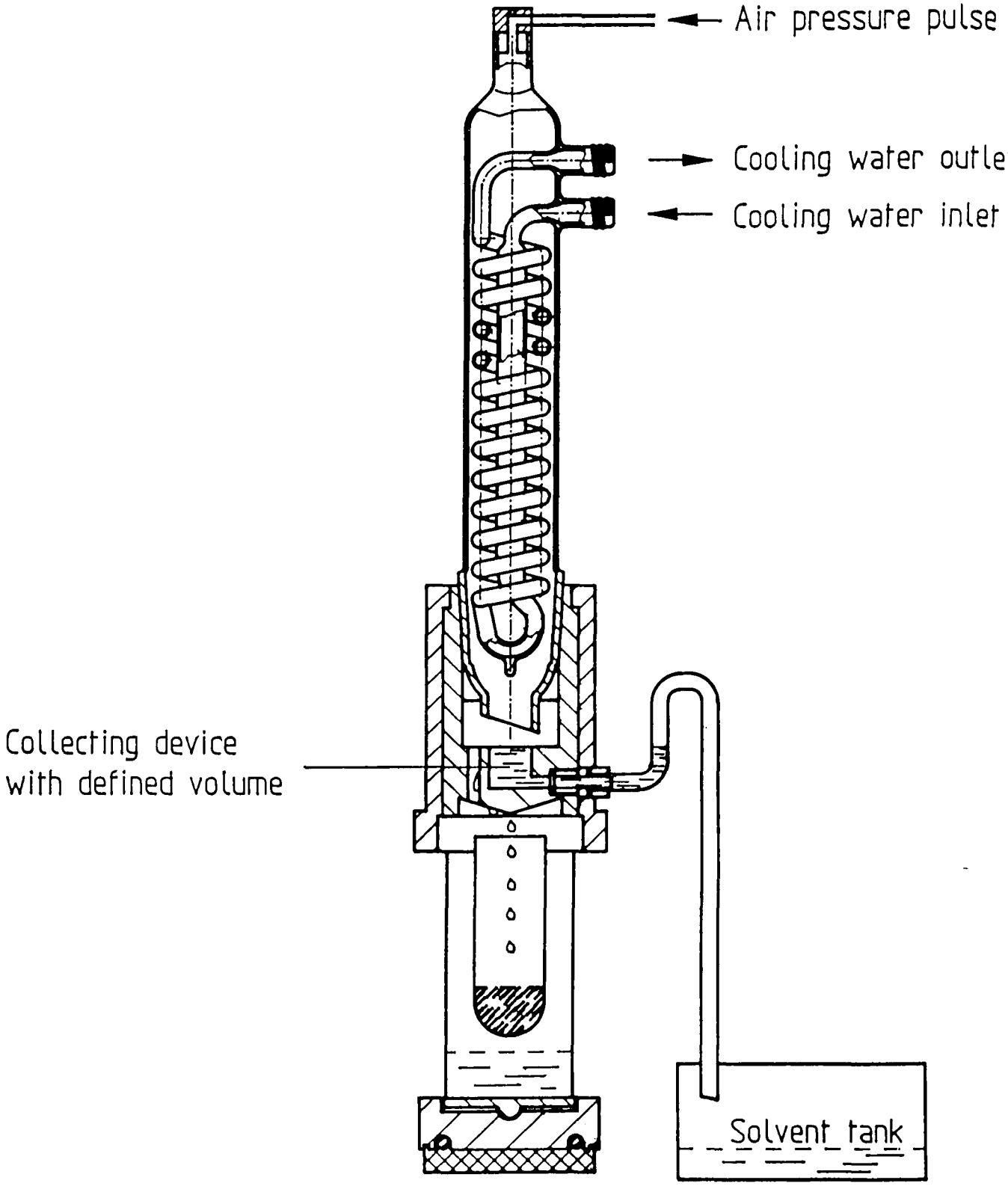
E. E. Conrad, K. P. Kelly,
ABC Instruments (a division of Laboratory Automation, Inc.), Columbia, MO 65202

INTRODUCTION

US EPA Draft SW-846 Method 3541 describes an automated Soxhlet technique which reduces solvent consumption and speeds up sample processing relative to traditional Soxhlet extraction, such as SW-846 Method 3540. Compared to the traditional method, this newer technique uses half the solvent or less and requires under three hours to complete compared to 16 hours or longer. Some laboratories have avoided the Soxhlet extraction because of the long processing times required under promulgated Soxhlet methods. With faster and more automated Soxhlet extraction available, the advantages of decreased solvent consumption and reduced labor investment make Soxhlet extraction a more attractive choice when compared with other techniques such as ultrasonication extraction (e.g. SW-846 Method 3550).

The automated technique is similar to traditional Soxhlet extraction, but extraction occurs in two distinct stages with this procedure. First there is an initial boiling time, during which the sample is immersed in boiling extraction solvent. The second stage resembles traditional Soxhlet-type extraction, with condensate dripping through the sample thimble; however, the stream of extraction solvent is continuous rather than soaking the thimble with batches of condensed solvent. The technique used in these experiments follows the chemistry of Method 3541, but it provides a higher degree of automation by eliminating the need for operator intervention during extraction. Between the two extraction stages and following the extraction, solvent volume is automatically reduced in increments by diverting measured portions of the solvent condensate to a collection tank rather than allowing it to return to the extraction vessel (see Figure). This allows automated concentration of the extract to a small volume. Experiments are reported here using spiked samples to investigate automated Soxhlet extraction and evaporation recoveries of semivolatile analytes.

An additional advantage of the technique used for this work is automated collection of nearly all solvent used during the sample preparation process. Without operator intervention required, the system diverts condensed solvent vapors to a collection tank where the spent solvent is available for recycling or appropriate disposal. This reduces emissions of hazardous chemicals into the atmosphere.


Air pressure pulse
Cooling water outlet
Cooling water inlet
Collecting device
with defined volume
Solvent tank

PROCEDURES

The extraction instrument (ABC Instruments Soxtherm) was programmed with parameters appropriate to Method 3541. Heater temperature was 160° C for samples extracted with a 1:1 mixture of acetone and hexane or methylene chloride. Operation of the instrument was unattended and run time was slightly over two hours, including evaporation. Ten grams of sand or prepared soil mixture (clay soil and sand) was spiked with analytes at one or more levels using solutions in acetone or methanol. Samples were contained in preextracted single-thickness paper thimbles (33 mm diameter). A stainless steel holder suspended the extraction thimble and sample in the glass extraction beaker.

Solvent reduction parameters were chosen to produce final volumes that facilitated further sample processing. Concentrated extracts were removed from the extraction beakers and the concentrate was further evaporated using the microSnyder technique and/or a nitrogen blowdown to produce final volumes as low as 1 mL. Hexane solvent exchange was employed for mixtures that were analyzed using electron capture detection (ECD). Analytes in processed samples were quantitated using gas chromatography and results were compared to chromatograms obtained from the spiking solutions used.

EXPERIMENTAL PROGRAM

Various subgroups of semivolatile analytes were selected for spiking. Since the method includes an evaporation step, analytes which would reflect losses during reduction of concentrates to small volumes were included. Adequate control of the final concentrate volume is necessary to obtain good recoveries of such analytes. The instrument uses gaskets located between the glass extraction beaker and the upper portion of the extraction apparatus to ensure operation with minimal solvent leakage. Some gaskets are prone to cause sample contamination, thus more than one gasket type was investigated.

EVALUATION OF A QUANTITATIVE IMMUNOASSAY FIELD SCREENING METHOD FOR DETERMINATION OF PENTACHLOROPHENOL IN SOIL AND WATER

Mary C. Hayes, Scott W. Jourdan and David P. Herzog, Ohmicron Environmental Diagnostics, 375 Pheasant Run, Newtown, Pennsylvania 18940

ABSTRACT

Analysis of environmental samples for pentachlorophenol (PCP) using EPA approved extraction and measurement methods is typically costly, time consuming and requires specialized equipment. Immunoassay technologies have the potential to quickly and inexpensively screen for PCP in both soil and water. In the summer of 1993, a demonstration and evaluation of immunoassay screening methods for determination of PCP in soil and water was conducted under the EPA EMSL, Las Vegas, Nevada, Superfund Innovative Technology Evaluation (SITE) Program by PRC Environmental Management, Inc. The Pentachlorophenol RaPID Assay®, a quantitative immunoassay for PCP, utilizing a three point calibration curve, was one of the methods evaluated. The accuracy and precision of the RaPID Assay on water and soil samples from two contaminated sites is compared to the same parameters for a conventional confirmatory laboratory using EPA approved analytical methods.

INTRODUCTION

Pentachlorophenol (PCP) is a wood preservative which has been used extensively by the wood treating industry since the 1950's. PCP is a regulated chemical, is included in the EPA Extremely Hazardous Substance List, and is reported in the EPA Toxic Substance Control Act Inventory. PCP is included as a target compound of many EPA approved analytical methods. These analytical methods use solvent extraction and gas chromatography for separating PCP from other compounds in the sample. Analyzing samples for PCP using these methods is typically costly and time consuming.

The Environmental Monitoring Systems Laboratory (EMSL) of the US EPA identified the need for effective, accurate, low cost screening technologies that could provide near real-time analytical data. Immunoassay technologies were selected for a demonstration, each with the potential to quickly and inexpensively screen PCP in both water and soil samples. Administrative and technical support for the demonstration was contracted to PRC Environmental Management, Inc. of Kansas City, KS. (PRC).

The purpose of the demonstration was to evaluate each of the field screening technologies for accuracy and precision in detecting high and low levels of PCP in soil and water samples. Each technology was also evaluated for the length of time required for analysis, ease of use, portability, and operating costs. The accuracy and precision of each

technology was compared to results obtained by a confirmatory laboratory using a GC/MS EPA analytical methods (Method 8270). Statistical comparisons were used to determine the highest data quality level that each technology could attain in field applications. For the purposes of this demonstration, three primary data quality levels were defined. (1) Level 1 data quality provides only an indication of contamination. This data is not necessarily analyte specific. (2) Level 2 data quality provides analyte specific data. To provide an accuracy check, verification analysis for at least 10 percent of the samples by an EPA-approved method is necessary. (3) Level 3 data quality provides formal or confirmatory analysis. The method is considered analyte specific and generally involves second-method confirmation on 100 percent of critical samples.

The PCP RaPID Assay, and the RaPID Prep Soil Collection and Extraction Kits (Ohmicron Environmental Diagnostics) were evaluated as one of the immunoassay methods. The demonstration took place in August of 1993 at a Superfund site. Recently, the results of this evaluation were presented in a Draft Technical Evaluation Report prepared by PRC and submitted to the US EPA. A summary of the RaPID Assay results is presented here.

DESCRIPTION OF DEMONSTRATION

At the time of the demonstration, soil and water samples were collected from two PCP contaminated sites, the former Koppers site near Morrisville, North Carolina and the Winona Post site, Winona, Missouri. A previous investigation found levels of PCP ranging from non-detect to several parts per thousand in water and soil at both sites. For the demonstration, 53 soil and 5 ground water samples were collected from the Koppers site and 45 soil and 5 surface water samples were collected from the Winona Post site.

To evaluate the field screening technologies under field conditions, the demonstration of immunoassay tests were conducted at the Koppers site. The immunoassays were performed on-site in a portable trailer. Samples collected at the Winona Post site were sent overnight to the Koppers site for the demonstration. Samples collected from each site were mixed thoroughly for homogeneity and then split for analysis by each immunoassay technology and by the confirmatory lab, the US EPA Region 7 Laboratory. Analysis of the demonstration samples was completed within 9 days of sample collection for each of the immunoassay technologies. Turnaround times for samples analyzed by the confirmatory lab ranged from 14 to 30 days.

Each immunoassay method was demonstrated by a designated PRC operator. A one day training session was given by an Ohmicron technical representative for the operator to familiarize him with the PCP RaPID Assay and the RaPID Prep Soil Collection and Extraction Kits.

STATISTICAL ANALYSIS OF DATA

This demonstration consisted of comparisons of various groups of data. Non-detectable concentrations were eliminated from the comparison. Outlier tests were then applied to eliminate the six poorest correlating non-zero data points. Each data group was then analyzed in a similar fashion. For the immunoassay methods, two data sets were created, one for soil samples and the other for water samples. In addition, each water and soil data set was composed to two subsets, one produced by the samples taken from Koppers site and one produced from the samples collected at Winona Post site. A third subdivision involved the grouping of the site-specific data sets into results greater than 100 ppm or less than 100 ppm PCP The 100 ppm level represented a regulatory or action level for the demonstration

The data generated by quantitative immunoassay methods was subjected to linear regression analysis to compare concentration results of the immunoassay to those given by the confirmatory lab, considered the "true" concentration of PCP for each sample. Another statistical method used for assessing intermethod accuracy was the Wilcoxon Signed Rank Test. This test can be used to evaluate whether two sets of data differ significantly. Both the Wilcoxon Signed Rank Test and linear regression analysis were used to determine the level of quality data (e.g. Level 1, 2 or 3) produced by each of the quantitative immunoassays

Calculating linear regression makes it possible to determine whether two sets of data are reasonably related, if so, how closely. When a linear regression is calculated, results are expressed in an equation ($y = mx + b$) that can also be visually expressed as a line drawn through an x-y plot of the datasets. The y-intercept (b), the slope of the line (m), and the correlation coefficient (r^2) determined by linear regression were used to assess quality of data generated by the immunoassays. The r^2 expresses the mathematical relationship between the two data sets. If r^2 is one, then the two data sets are directly related. Lower r^2 values indicates less of a relationship. To meet Level 3 requirements, r^2 was required to be 0.85 to 1 and the slope and y-intercept had to be statistically the same as their ideal values. If the r^2 was between 0.75 and 1, and the slope and/or the y-intercept was not equal to the ideal value, the technology was considered inaccurate but capable of producing Level 2 quality data. Data placed in the Level 1 category had r^2 values less than 0.75, the data was not statistically similar to the confirmatory lab, based on parametric testing, or the results failed to meet the developer's performance specifications.

Field soil and water duplicate samples were analyzed during the demonstration to compare the precision of each immunoassay technology to the precision of the confirmatory lab. The Dunnett's Test and Wilcoxon Rank Sum Test were used to determine intermethod precision for quantitative immunoassays.

IMMUNOASSAY METHOD

The RaPID Prep™ PCP Sample Extraction Kit was used to process all soil samples. The PCP RaPID Assay produced quantitative results for water and diluted soil extracts. Water samples are pipeted directly into the immunoassay reaction tube. Soil samples are extracted in a special device with a methanol solvent for five minutes prior to filtration, dilution and subsequent introduction into the reaction tube. This immunoassay produces quantitative results by comparing the optical density (O.D.) of the colored reaction byproduct of unknown soil extracts and waters to the color produced by PCP calibrators in a standard curve run simultaneously (Figure 1). Absorbance readings are transformed to PCP concentrations using a log-logit algorithm programed into the RPA-I™ RaPID Photometric Analyzer. The detection range for water is 0.06 to 10 ppb. The detection limit for soil 100 ppb to 10 ppm. Samples giving concentrations above the upper detection limit were diluted until the O.D. of the diluted unknown fell within the O.D. range of the kit calibrators. The additional dilution factors were then applied to the PCP result.

SUMMARY OF RESULTS

A summary of intermethod accuracy, as determined by linear regression analysis is presented in Table 1. The combined soil data set (Figure 2) and the combined water data sets (Figure 3), both fell into the Level 2 data quality category. Separation of these data sets by site and by concentration produced some data groupings of Level 1 data quality category. Lower r^2 on these data groupings suggest a possible concentration and/or site effects on the two methods. Possibilities for these differences include: 1) technique variability in handling or preparing extracts for each of the technologies; 2) extraction efficiency between the immunoassay method and the more vigorous EPA extraction method (especially at concentrations >1000 ppm); and 3) sample size differences used in analysis by immunoassay and the confirmation lab. By grouping, the assay produced Level 2 quality data for water samples at the Koppers site and soil samples at the Winona Post site. The assay produced Level 1 quality data for water samples at the Winona Post site and soil samples at the Koppers site.

INTERMETHOD ACCURACY ON FIELD SOIL SAMPLES

The RaPID Prep PCP Sample Extraction Kit package insert indicates that the kit system is expected to give less than 100% quantitative recovery on soil samples at the short extraction time called for in the procedure. In house studies on three soils types including clays and loams fortified with PCP to final concentrations of 1.0, 1.5 and 5 ppm gave spike recovery results that ranged from 63 to 83%. Greater analyte recovery can be achieved if extraction time is extended from five minutes up to thirty minutes. If RaPID Assay PCP concentrations are used as screening results for recognition of 100 ppm as shown in Figure 4, a 70 ppm cutoff can be imposed to correct for the diminished

extraction efficiency with the short extraction time. When this is done, the false negative rate drops to 6 in 84 (7%) from 7 in 84 (8%) while maintaining the same false positive rate (4%).

A typical user of Ohmicron's kits would be advised to make a constant additional dilution prior to analysis if a regulatory or action level of 100 ppm was being targeted. This would reduce the frequency of additional sample dilution and re-assays and improve precision and accuracy by placing the decision point in the middle of the immunoassay calibration curve. Users are instructed to make simple calculations for factors affecting extraction efficiency as well as analytical confidence (precision) as shown in Figures 5 and 6. When an analytical confidence factor of 0.7 is applied to the data in Figure 2 to minimize false negatives at the 100 ppm level, the false negative rate drops to 3 in 84 (4%) while the false positive rate changes by just 1 in 84 to 5% in this data set. This treatment is shown in Figure 4.

The ability of the RaPID Prep system to recover 5 ppm spikes in a variety of soil samples was excellent as shown in Table 2. This was the case for these blank field soils notwithstanding the somewhat lower recoveries of PCP from some randomly selected clay and loam samples tested in our laboratories. Unfortunately the reference method was not used to demonstrate recovery on these same samples so no comparison can be made for this classic test of method accuracy.

The precision of Ohmicron's kits on field soil and water was similar to that of the confirmatory lab's precision as demonstrated on the performance of both methods on blind duplicates of the same sample in Table 3. A recently completed AOAC Collaborative study of the Ohmicron Atrazine RaPID Assay kit with drinking and surface waters showed the immunoassay to possess precision equivalent to EPA Method 507 for drinking water analysis at similar atrazine concentrations.

CONCLUSION

Overall, the accuracy and precision of Ohmicron kits was very good despite the fact that soil data sets were not corrected for extraction efficiencies. Intermethod accuracy on the total soil and water data sets, placed the Ohmicron kits in Level 2 data quality category. Technologies that produce Level 2 quality data can be used to guide field work and sampling efforts. These technologies will provide data, or can be corrected to provide data, which corresponds to confirmatory results. Since many of the data groupings produced by Ohmicron kits were found to be linear, the results could be corrected mathematically. If 10 or 20 percent of the soil samples are sent to a confirmatory lab for comparison of analyte concentrations, then the results from the other 80 to 90 percent can be corrected for any bias and reported with analytical confidence. This approach could result in significant savings in analytical costs.

This information is presented with the permission of Mr. Larry Jack, EPA, EMSL, Las Vegas, NV, sponsor of the Superfund SITE Demonstration.

Figure 1. Pentachlorophenol RaPID Assay calibration curve

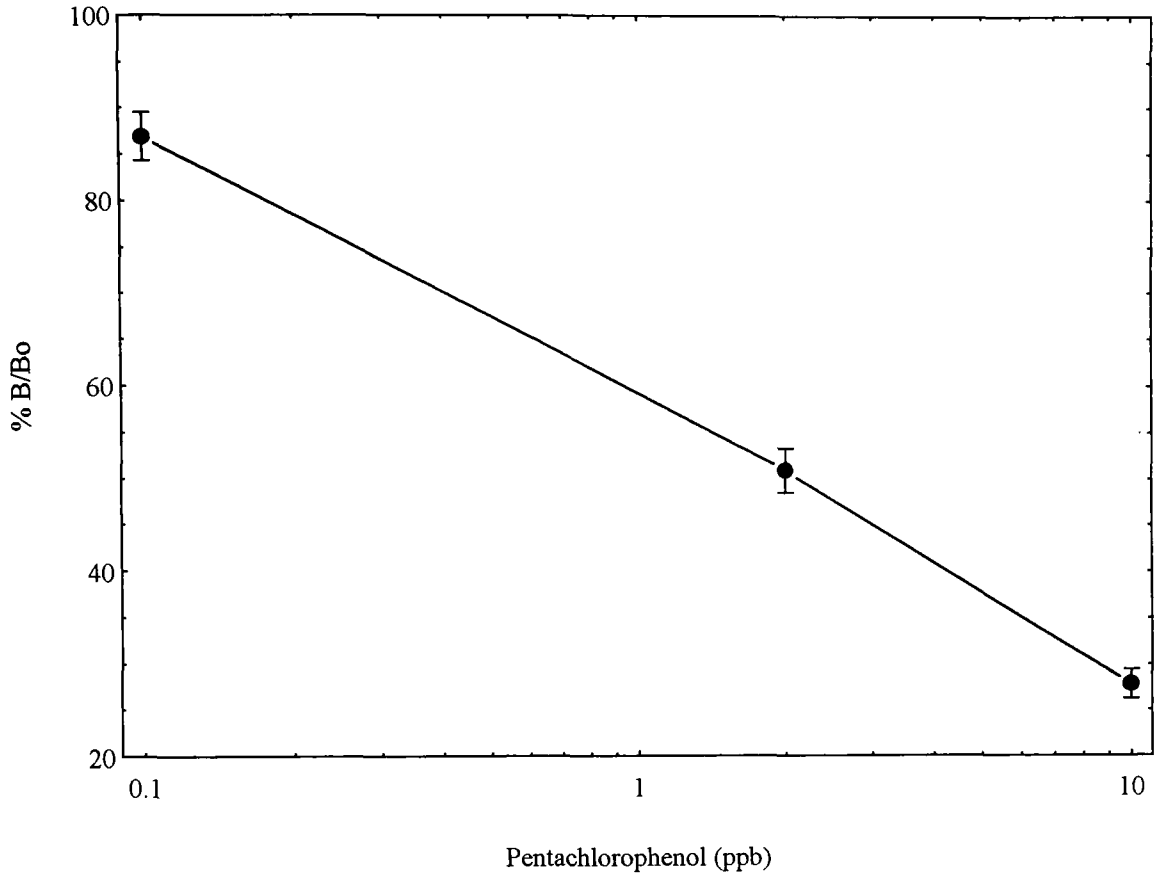


Figure 2. Total soil data set

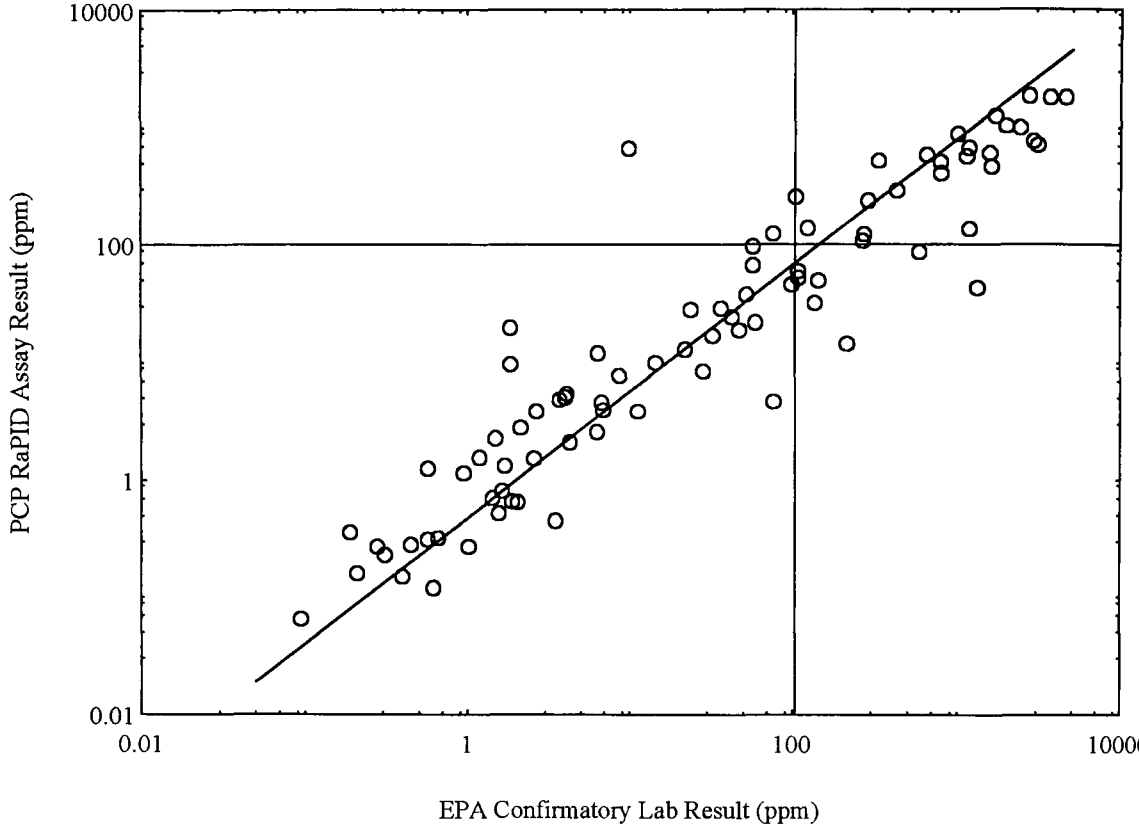


Figure 3. Total water data set.

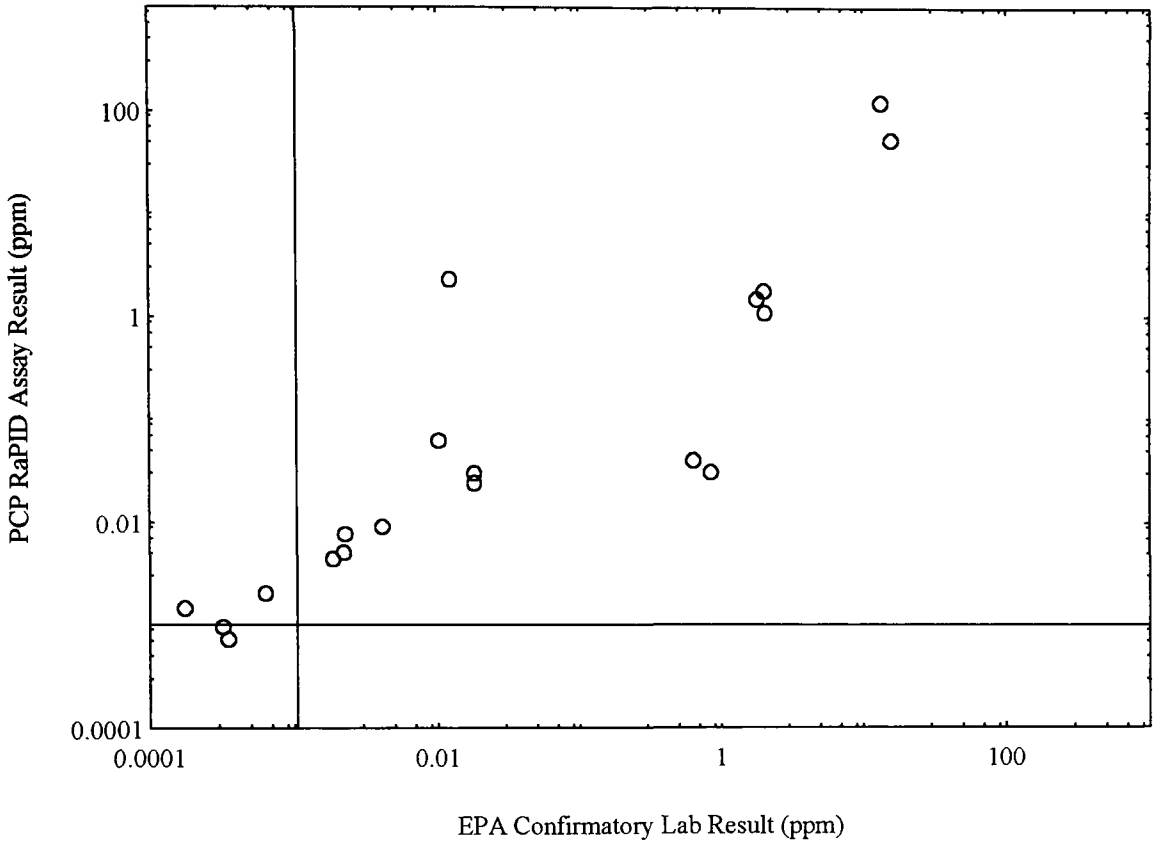


Figure 4. Total soil data set showing cutoffs for extraction efficiency and analytical confidence factors.

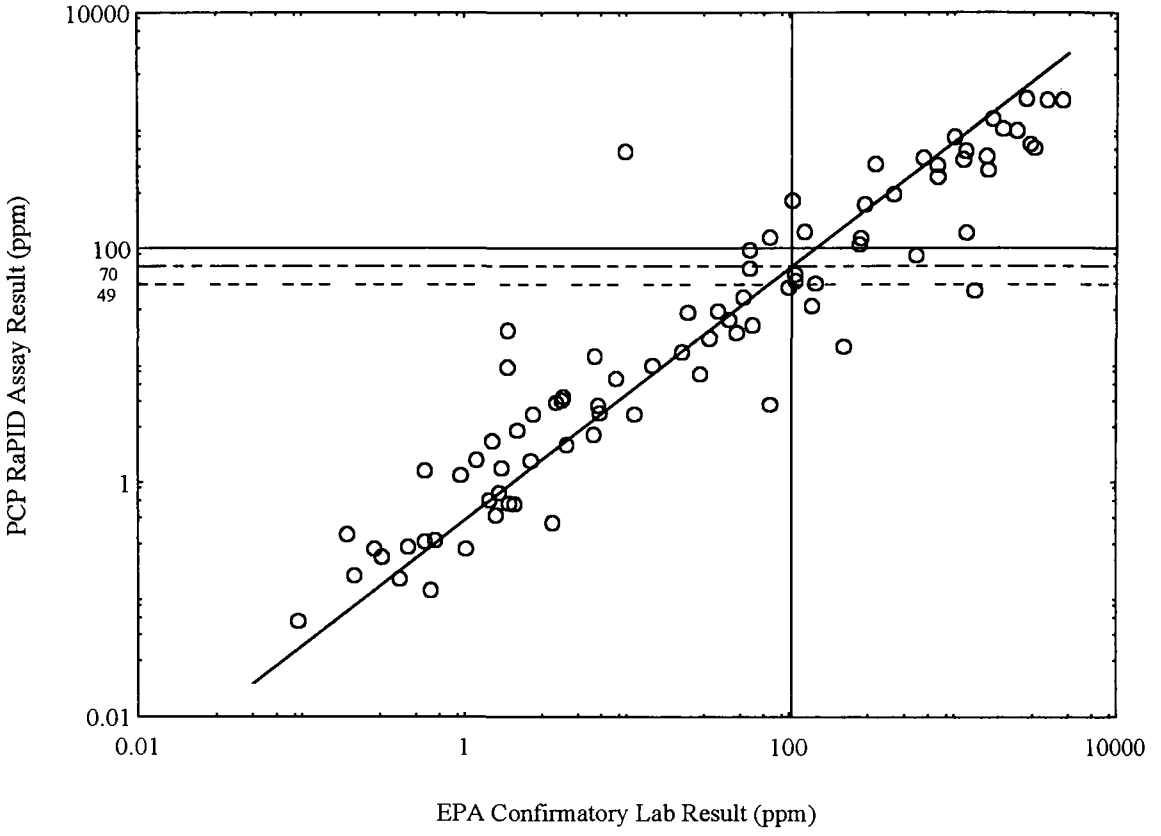


FIGURE 5. CALCULATION OF A CUTOFF CONCENTRATION

WORKSHEET

Required Detection Limit	_____	(*A*)
Cross-Reactivity Factor (from Table 1)	_____	(*B*)
Extraction Recovery Factor	_____	(*C*)
Analytical Confidence Factor (from Table 2)	_____	(*D*)
Cutoff Concentration A × B × C × D	_____	(*E*)

Example -

To optimize the PCB RaPID Assay system for detection Aroclor 1260 at 10 ppm in soil:

Required Detection Limit	10 ppm (*A*)	A *Detection Limit* of 10 ppm of Arochlor 1260 is assumed for this example. See *Detection Limit* in text above.
Cross-Reactivity Factor (from Table 1)	0.81 (*B*)	Since the PCB to be detected in this example is Aroclor 1260, the *Cross-Reactivity Factor* obtained from Table 1 of the PCB RaPID Assay Performance Characteristics is 0.81.
Extraction Recovery Factor	0.85 (*C*)	The *Extraction Recovery Factor* of 0.85 is obtained from the RaPID Prep Sample Extraction kit package insert. Preferably, this factor would be obtained from a spiked matrix determination.
Analytical Confidence Factor (from Table 2)	0.80 (*D*)	By examining Table 2 for PCB in Soil it can be observed that an *Analytical Confidence Factor* of 0.8 is estimated to yield 96.1% negative results at a PCB concentration of 5 ppm Arochlor 1260 (0.5 × *Detection Limit*[10 ppm Arochlor 1260]). In this example it is judged that a 3.9% "false positive" rate would be acceptable for samples at 5 ppm. It is also noted that at 10 ppm (*Detection Limit*) the estimated rate of positive results is 88% while at 20 ppm (2.0 × *Detection Limit*) the incidence for false negative results is estimated to be <0.1%.
Cutoff Concentration	5 ppm (*E*)	Performing the calculation A×B×C×D the result is 5.5 ppm. In this example the *Cutoff Concentration* used for the PCB assay result (after correction for dilution) was rounded down to 5 ppm to be conservative.

FIGURE 6. ESTIMATING REQUIRED ANALYTICAL CONFIDENCE LIMITS

PENTACHLOROPHENOL RaPID ASSAY CHARACTERISTICS

Table 1 - Cross- Reactivity Factors for Pentachlorophenol RaPID Assay

Compound	*Cross-Reactivity Factor*
Pentachlorophenol	1.00
2,3,5,6-Tetrachlorophenol	0.54
2,3,4,6-Tetrachlorophenol	0.15

Table 2 - Analytical Confidence Factor Data

Pentachlorophenol in Water

Analytical Confidence Factor	@ 0.5 × Detection Limit		@ 1.0 × Detection Limit		@ 2.0 × Detection Limit	
	% Negative	% Positive	% Negative	% Positive	% Negative	% Positive
0.9	99.4	0.6	26.6	73.4	<0.1	>99.9
0.8	97.0	3.0	10.6	89.4	<0.1	>99.9
0.7	89.4	10.6	3.0	97.0	<0.1	>99.9
0.6	73.4	26.6	0.6	99.4	<0.1	>99.9
0.5	50.0	50.0	<0.1	>99.9	<0.1	>99.9

Pentachlorophenol in Soil

Analytical Confidence Factor	@ 0.5 × Detection Limit		@ 1.0 × Detection Limit		@ 2.0 × Detection Limit	
	% Negative	% Positive	% Negative	% Positive	% Negative	% Positive
0.9	95.9	4.1	33.3	66.7	<0.1	>99.9
0.8	90.4	9.6	19.2	80.8	<0.1	>99.9
0.7	80.8	19.2	9.6	90.4	<0.1	>99.9
0.6	66.7	33.3	4.1	95.9	<0.1	>99.9
0.5	50.0	50.0	1.5	98.5	<0.1	>99.9

Note - The shaded data achieves false positive rates of around 10% or less at 0.5 × Detection Limit and less than 5% false negative rates at 2.0 × Detection Limit.

TABLE 1

SUMMARY OF INTERMETHOD REGRESSION ANALYSIS

	N	r^2	Y-int	Slope
All Data	84	.81	28	.43
All Data <100 ppm	46	.76	.55	.71
All Data >100 ppm	33	.68	71	.43
Koppers All Data	48	.65	-3.4	.37
Koppers <100 ppm	32	.61	1.5	.57
Koppers >100 ppm	13	.60	-110	.39
Winona All Data	33	.90	34	.51
Winona <100 ppm	15	.69	-3.8	1.2
Winona >100 ppm	20	.75	98	.46

N = Number of data points
r^2 = Coefficient of correlation
Y-int. = Y-axis intercept of the regression line

TABLE 2

PCP RAPID ASSAY
SOIL MATRIX SPIKE SAMPLE RESULTS

Sample No.	Amount Found in Orig. Sample (ppm)	Amount Added to Matrix Spike Sample (ppm)	DETN 1 (ppm)	% Recovery	DETN 2 (ppm)	% Recovery
ARD26020	0.13	5.0	3.60	70	4.21	82
ARD26029	ND	5.0	4.57	91	4.65	93
ARD26039	ND	5.0	5.50	110	6.23	125
ARD26051	ND	5.0	5.20	104	4.74	95
ARD26086	1.86	5.0	8.46	123	8.68	126
ARD26090	ND	5.0	5.87	117	4.95	99
ARD26095	ND	5.0	6.31	126	4.94	99

Average % Recovery of 5 ppm spike (n = 14) = **104%**

TABLE 3

SOIL FIELD DUPLICATE SAMPLE RESULTS
PCP RAPID ASSAY SYSTEM AND EPA METHODS 8270A AND 8151A

	PCP Rapid Assay			EPA Methods		
Sample No.	Original Sample Result (ppm)	Field Duplicate Sample Result (ppm)	Relative Percent Difference (%)	Original Sample Result (ppm)	Field Duplicate Sample Result (ppm)	Relative Percent Difference (%)
ARD26001	1.61	2.53	44	4.42	4.18	6
ARD26011	55	64	15	106	112	6
ARD26020	0.13	ND	NA	0.10	0.09	11
ARD26030	8.3	8.6	3	28.6	29.0	1
ARD26040	19	10	62	400	34.4	168
ARD26048	11,800	11,700	1	26,100	30,260	15
ARD26050	1.17	1.46	22	2.16	1.25	53
ARD26055	748	670	11	3,135	3,003	4
ARD26058	2.92	2.16	30	3.53	9.13	88
ARD26059	1,800	2,200	20	9,600	10,260	7
ARD26073	123	125	2	74.8	78.2	4
ARD26074	649	690	6	836	1,520	58
ARD26086	1.86	7.21	118	6.59	688	4
ARD26087	29	20.2	36	34	51.8	41
AVERAGE			**28** (n=13)			**33** (n=14)

Screening for Low Level Chlorinated Pesticides Using Solid Phase Extraction

Lydia Nolan, Chemist, Robert Shirey, Chemist, Research and Development, Supelco, Inc., Supelco Park, Bellefonte, Pennsylvania 16823

ABSTRACT

The US Environmental Protection Agency has continued in its efforts to develop and implement new methods designed to assist in the determination and identification of potentially hazardous abandoned waste disposal sites. The Quick Turnaround Methods (QTM) procedures are being developed as screening methods to allow quick decisions to be made about the extent and nature of hazardous contamination at a given site. The main emphasis of these methods is to provide rapid, on site sample preparation and analysis. For this reason, solid phase extraction (SPE) has been the main focus for semivolatile sample preparation of aqueous samples.

This study will present results of extractions using an octylsilane modified, silica-based SPE tube that provides reproducible results as well as the extremely low background levels required for analysis of these compounds. The polymerically bonded phase provides sufficient capacity to prevent breakthrough of analytes up to the 250 ng per 100 mL sample level. Five lots of tubes were tested with twenty target analytes and statistically analyzed for variability. Recoveries of spiked reagent water samples ranged from 91% to 110%, with variability below 10% except for endosulfan II and endrin ketone. Results also indicate that the pesticides method requires an exceptionally inert sampling system as well, since sample concentrations are as low as 10 ng per 100 mL of water. The effect of sampling system interferences on the reliability of extraction data will also be demonstrated. The study analysis shows that these tubes can be used, with a low background sampling system, to meet the proposed extraction performance criteria for this method.

INTRODUCTION

The main emphasis of the CLP QTM methods is to provide rapid, on-site sample preparation and analysis. For this reason, SPE has remained a major focus for semivolatile sample preparation of aqueous hazardous waste samples. An octylsilane-modified, silica based SPE cartridge has been named in the draft procedure released 3/92. Octadecylsilane modified, silica-based cartridges were approved for the extraction of organochlorine pesticides from drinking water in EPA Method 508 [1] and various published studies have cited their use for organochlorine pesticides in other matrices [2,3,4]. Performance of a polymerically bonded octylsilane phase cartridge, as specified in the draft procedure, was evaluated in this study.

Sample volumes are limited to 100 mL, and can be introduced directly into the SPE tube from the sample collection bottle using a novel Teflon® line sampling system and a vacuum source. The tubes are first conditioned to wet the packing and solvate the phase, maximizing interaction of hydrophobic analytes with the stationary phase. The sample pH is adjusted and methanol added to maintain conditioning of the adsorbent bed. The sample is introduced to the conditioned tube at a rate of 5 mL /minute. Sampling is completed in 20 minutes and the packing is dried using direct nitrogen purge. The extraction solvent is allowed to soak into the dried bed and eluted into a glass receiving vial. The eluates are dried to a constant 1 mL volume. Extracted samples are ready for analysis using capillary GC with an electron capture detector.

Extractions to analyze background levels of various systems were also run. All cartridge device extractions were performed using a vacuum manifold with disposable Teflon valve liners, reducing extraneous peaks and any possible carryover from sample to sample. Standard polypropylene cartridges with polyethylene frits were extracted and compared to glass cartridges with Teflon frits and Teflon-lined polypropylene tubes with Teflon frits.

The device with the lowest acceptable background levels was used to extract spiked reagent water samples. Recovery results of 5 different bonded lots of material are reported. Effects of sample pH, drying time and analyte capacity on the extraction efficiency of the cartridge were examined. Optimum conditions were then used for the extraction of spiked wastewater and hazardous waste samples.

EXPERIMENTAL

Materials:

Chlorinated pesticides standards were obtained as a custom mix and concentrated system monitoring compound solution from Supelco, Inc. Working solutions were diluted as specified in the draft EPA method procedure. Solid phase extraction tubes contained ENVI™-8 silica based packing material and were extracted using a DL model Visiprep vacuum manifold with disposable Teflon liners. Wastewater and hazardous waste, prescreened field samples, were delivered to the tubes using a Large Volume Sampler system.

Instrumentation:

Samples and standards were analyzed using an HP 5890 Series II capillary gas chromatograph with ECD detector and an HP 7673 autosampler. The capillary column was a PTE™-5 QTM, 15m x 0.53mm ID, 0.5μm film. Temperature program and conditions as described in the draft EPA method procedure. A cold, on-column injector was not used.

RESULTS AND DISCUSSION

The minimum background level for the analytical system was 84 ng/mL. This was determined by spiking the system monitoring compound into 15 mL of extraction solvent solution, reducing the volume with nitrogen purge to 1 mL and comparing all peak areas during the run to the standard peak response. Background analyses of Teflon lined tubes with Teflon frits exhibited high levels of interferences. Pretreatment with heat or solvent rinsing did not produce sufficient reduction of those interferences to allow use of these tubes for the extraction study (see chromatograms in Figure 1). The average background level for glass tubes with Teflon frits was 109 ng/mL, with no interferences coeluting at the same retention times as quantitated peaks. Polypropylene tubes with Teflon frits had slightly higher backgrounds of 191 ng/mL however, the presence of more coeluting interferences would make low level quantitation unreliable. Results are summarized in Figure 2.

The extraction procedure recommended in the draft EPA method was used to determine lot-to-lot reproducibility for five bonding lots of ENVI-8 adsorbent packing. Results are summarized in Table 1. Although overall results were acceptable, anomalies in the recoveries of key compounds were observed during these extractions. Recovery of endrin was occasionally very low, with elevated recoveries of the aldehyde and ketone forms. Assuming pH could be a factor in the conversion of these analytes, extractions were done using a single lot, adjusting the sample to three different pH levels. This factor had little effect on these compounds (Table 2). Suspecting volatility as another possible factor, eluate drying times were also tested. Table 3 represents a side-by-side comparison using two different lots, with reduction in overall recoveries of all analytes when excessive drying occurs. Extraction volumes were reduced to 10 mL to minimize drying times.

Using the low background tube extraction system and reduced extraction volume, wastewater and aqueous hazardous waste samples were prepared. Recoveries are reported in Table 4. As expected, recoveries were lower and more variable than with reagent water samples. Increasing the bed weight did not significantly increase the recovery rates or decrease the co-extractants responsible for the variability.

CONCLUSIONS

SPE tubes with glass cartridges and Teflon frits, packed with ENVI-8 phase material, meet the acceptance criteria outlined in the draft EPA QTM CLP pesticide method released 3/92. The low background extraction system will reduce laboratory interferences and cross contamination. SPE tubes used with a large volume sampler will minimize hands-on sample preparation time, essential for on-site and in-lab screening procedures. The optimized extraction procedure was acceptable for the screening of spiked wastewater and aqueous hazardous wastes examined in this study; however, high levels of coextractants remain in the eluates making very low level analysis difficult. Further study, using other solid phase technologies, are necessary to improve reliability at

the low levels specified in the draft method, especially for complex hazardous waste field samples.

FIGURE 1

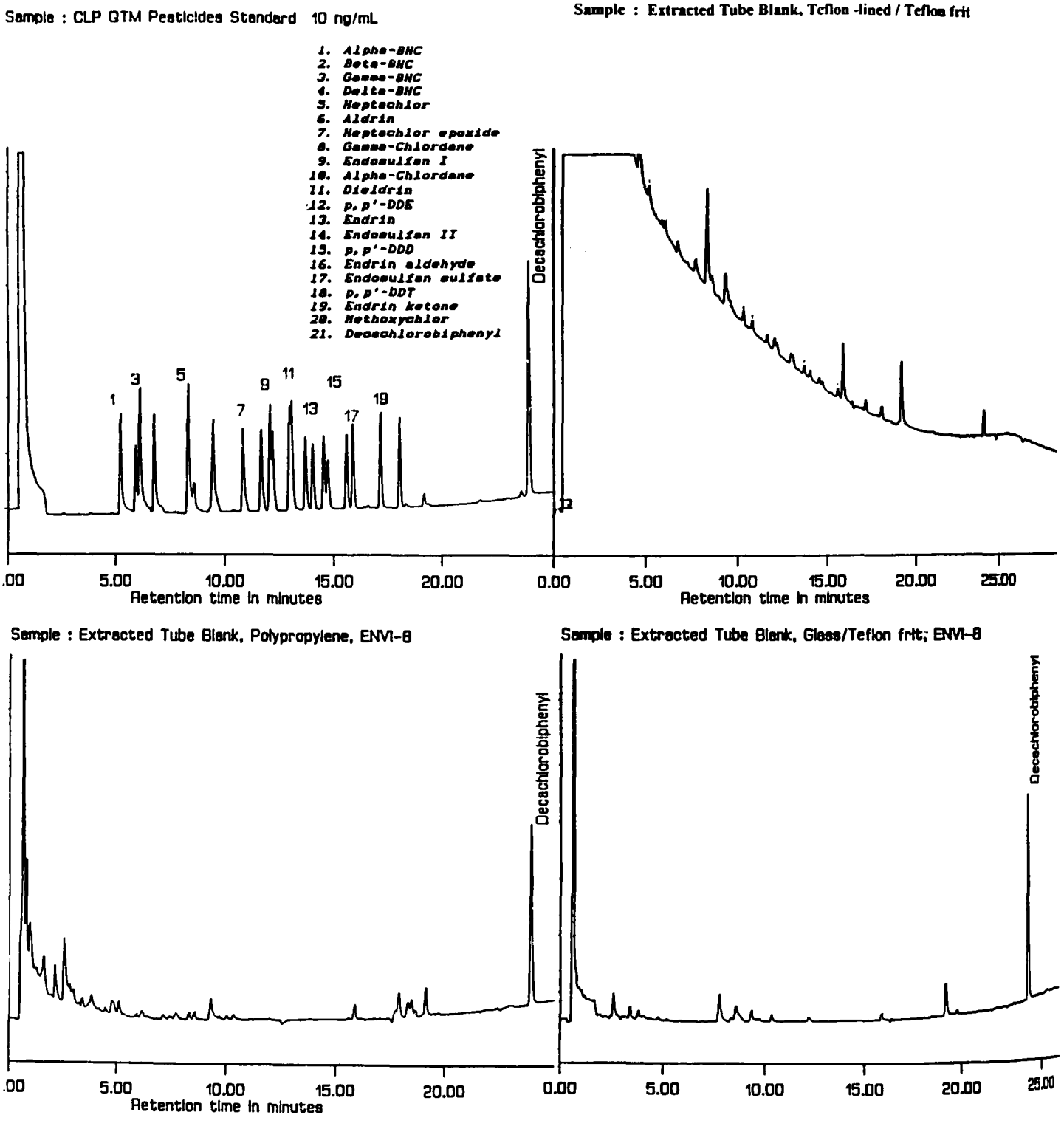

Sample : CLP QTM Pesticides Standard 10 ng/mL
1. Alpha-BHC
2. Beta-BHC
3. Gamma-BHC
4. Delta-BHC
5. Heptachlor
6. Aldrin
7. Heptachlor epoxide
8. Gamma-Chlordane
9. Endosulfan I
10. Alpha-Chlordane
11. Dieldrin
12. p,p'-DDE
13. Endrin
14. Endosulfan II
15. p,p'-DDD
16. Endrin aldehyde
17. Endosulfan sulfate
18. p,p'-DDT
19. Endrin ketone
20. Methoxychlor
21. Decachlorobiphenyl
Decachlorobiphenyl
Retention time in minutes
Sample : Extracted Tube Blank, Teflon -lined / Teflon frit
Retention time in minutes
Sample : Extracted Tube Blank, Polypropylene, ENVI-8
Decachlorobiphenyl
Retention time in minutes
Sample : Extracted Tube Blank, Glass/Teflon frit; ENVI-8
Decachlorobiphenyl

FIGURE 2

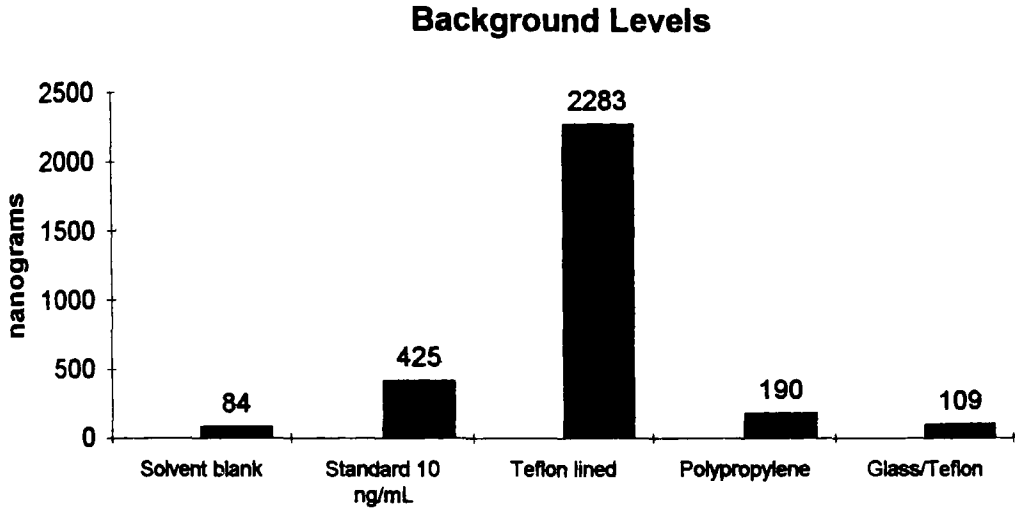

Background Levels
nanograms
2500
2000
1500
1000
500
0
84
425
2283
190
109
Solvent blank
Standard 10 ng/mL
Teflon lined
Polypropylene
Glass/Teflon

TABLE 1
Extraction of CLP QTM Pesticides
Recovery Study

Analytes	SPE Capacity Level High Calibration Standard			SPE Contamination Level Low Calibration Standard		
	Percent recovery	Std dev	Relative Std dev	Percent recovery	Std dev	Relative Std dev
α-BHC	91.4	7.0	7.7	84.6	9.2	10.9
β-BHC	100.1	10.1	10.1	------	------	------
γ-BHC	94.0	6.1	6.4	88.2	10.8	12.2
δ-BHC	92.9	7.2	7.7	85.1	7.3	8.5
Heptachlor	95.0	5.7	6.0	86.6	6.4	7.3
Aldrin	94.9	4.8	5.1	84.7	13.9	16.4
Heptachlor epoxide	96.8	4.2	4.4	96.3	5.6	5.8
γ-Chlordane	97.4	4.5	4.6	85.3	6.3	7.3
Endosulfan I	94.6	4.7	4.9	84.8	8.5	10.1
α-Chlordane	96.4	4.6	4.7	90.2	7.4	8.2
Dieldrin	98.2	3.8	3.9	88.6	6.0	6.8
p,p' - DDE	99.9	4.2	4.2	80.1	7.7	9.6
Endrin	97.9	13.2	13.5	77.8	20.1	25.9
Endosulfan II	98.2	3.8	3.8	90.0	8.0	8.9
p,p' - DDD	104.4	5.4	5.2	98.6	10.9	11.1
Endrin aldehyde	101.0	5.5	5.5	coelute	coelute	coelute
Endosulfan sulfate	104.6	3.9	3.7	96.2	7.9	8.3
p,p' - DDT	107.9	4.9	4.5	95.3	13.4	14.1
Endrin ketone	110.4	14.3	12.9	104.6	29.9	28.6
Methoxychlor	108.4	3.2	2.9	93.4	13.1	14.0
Decachlorobiphenyl (SMC)	101.0	7.0	6.9	72.9	14.0	19.3
	n=10			n=10		

results are average of 5 bonding lots

TABLE 2
Extraction of CLP QTM Pesticides
Effect of pH
High Calibration Standard Recovery

Analytes	Percent recovery		
250 ng/ 100 mL	pH=2	pH=5	pH=7
α-BHC	74.3	77.0	82.4
β-BHC	105.4	100.8	101.8
γ-BHC	75.9	78.7	82.9
δ-BHC	79.0	82.0	85.8
Heptachlor	75.6	77.4	85.4
Aldrin	86.4	83.7	91.1
Heptachlor epoxide	81.6	80.6	87.8
γ-Chlordane	86.0	82.2	89.3
Endosulfan I	70.4	70.1	76.5
α-Chlordane	82.6	78.7	86.0
Dieldrin	81.8	80.1	88.3
p,p' - DDE	88.6	84.4	92.2
Endrin	68.6	48.0	51.5
Endosulfan II	76.5	74.9	80.9
p,p' - DDD	105.2	81.8	95.9
Endrin aldehyde	74.4	90.3	94.6
Endosulfan sulfate	104.9	95.9	99.4
p,p' - DDT	106.2	93.8	104.9
Endrin ketone	120.3	135.3	150.1
Methoxychlor	99.9	93.4	104.8
Decachlorobiphenyl (SMC)	100.5	90.6	96.0

TABLE 3
Extraction of CLP QTM Pesticides
Effect of Drying
High Calibration Standard Recovery

Analytes	Percent recovery		
250 ng/ 100 mL	dry to 1mL	complete dry	percent difference
α-BHC	100.3	73.4	27
β-BHC	122.1	103.6	15
γ-BHC	103.5	79.9	23
δ-BHC	98.2	84.7	14
Heptachlor	103.7	69.6	33
Aldrin	103.7	67.0	35
Heptachlor epoxide	105.0	74.9	29
γ-Chlordane	106.6	72.3	32
Endosulfan I	106.7	72.8	32
α-Chlordane	105.4	72.6	31
Dieldrin	108.2	75.9	30
p,p' - DDE	107.4	71.2	34
Endrin	114.6	79.1	31
Endosulfan II	108.3	84.7	22
p,p' - DDD	114.1	123.1	-16
Endrin aldehyde	105.8	coelute	coelute
Endosulfan sulfate	113.5	93.9	17
p,p' - DDT	116.4	76.0	35
Endrin ketone	106.9	83.5	22
Methoxychlor	116.8	85.9	26
Decachlorobiphenyl (SMC)	116.0	97.7	16
	average % difference		**26**

TABLE 4
Extraction of CLP QTM Pesticides
Effect of Sample Matrix

Analytes	Percent recovery		
100 ng/ 100 mL	deionized water	waste water	hazardous waste
α-BHC	92.4	74.9	80.9
β-BHC	57.0	48.5	79.9
γ-BHC	90.3	107.4	332.3
δ-BHC	90.3	111.4	120.1
Heptachlor	89.7	77.5	91.5
Aldrin	87.3	78.2	192.7
Heptachlor epoxide	94.7	85.7	90.9
γ-Chlordane	94.2	171.2	116.1
Endosulfan I	92.7	94.0	99.5
α-Chlordane	95.3	91.6	135.8
Dieldrin	90.0	94.5	127.7
p,p' - DDE	94.1	94.7	86.2
Endrin	69.0	89.5	136.8
Endosulfan II	93.0	90.2	110.1
p,p' - DDD	88.9	97.0	115.7
Endrin aldehyde	93.8	86.5	75.9
Endosulfan sulfate	90.3	91.1	94.9
p,p' - DDT	87.4	90.7	96.7
Endrin ketone	97.2	98.2	112.6
Methoxychlor	83.9	98.2	104.4
Decachlorobiphenyl (SMC)	72.1	117.7	123.4
	n=3	n=3	n=3

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CONTAMINANT DEGRADATION STUDY AT THE HANFORD SITE 1100-EM-1 OPERABLE UNIT

R.A. Bechtold, Principal Scientist, Westinghouse Hanford Company, Richland, Washington 99352 : K. M. Angelos, Senior Environmental Scientist, Golder Associates Inc., Redmond, Washington.

ABSTRACT

A study of volatile organic contaminant degradation conducted by Westinghouse Hanford Company (WHC) on environmental groundwater samples is presented. WHC is the U.S. Department of Energy's (DOE) Operations and Engineering Contractor for the Hanford Site. A contaminant degradation study was conducted from December 1990 through December 1991 to evaluate the degradation of trichloroethene (TCE) in ground water in the vicinity of Horn Rapids Landfill. The Horn Rapids Landfill is part of the 1100-EM-1 Operable Unit which is one of four operable units within the 1100 Area of the Hanford Site. The 1100 Area was placed on the National Priorities List (NPL) in July 1989. This paper describes work which was part of the Remedial Investigation Phase 2 Supplemental Work Plan for the 1100-EM-1 Operable Unit (DOE-RL 1990a). The objective of this study was to evaluate the degradation of TCE present in the ground water in the vicinity of the Horn Rapids Landfill. Contaminant degradation was studied in ground water from monitoring wells known to have detectable TCE.

The 1100 Area is the central warehousing, vehicle maintenance, and trasnportation operations center for the Hanford Site. This area was designated an NPL site in July, 1989, and is divided into four operable units. The first equipment maintenance operable unit, 1100-EM-1, was assigned the highest RI/FS priority within both the 1100 Area and the Hanford Site as a whole. The Horn Rapids Landfill is a solid waste facility used primarily for the disposal of office and construction waste and the burning of classified documents; asbestos, sewage sludge, fly ash, and potentially, drums of unidentified organic liquids (presumably carbon tetrachloride) were also disposed at this site.

Samples of ground water were collected from three groundwater monitoring wells (MW-11, MW-12, and MW-15) located in the vicinity of Horn Rapids Landfill. The samples were collected by WHC personnel into 40 mL volatile organic analysis (VOA) bottles in sufficient quantity to allow for repeated analysis of the samples at frequencies of 1, 2, 4, 8 and 12 months from the date of collection. The VOA bottles were not preserved with mineral acid as is customary for volatile organic samples so as not to inihibit degradation of the organic compounds. The samples were stored in the dark at room temperature (approximately 25°C) throughout the duration of the study.

Sample analysis was conducted in accordance with the U.S. EPA Contract Laboratory Program, Statement of Work for Organics Analyses, (EPA 1988a) with the exception that the laboratory reported the following compounds to a lower quantitation limit as opposed to the usual quantitation limit of 5 or 10 μg/L: vinyl chloride, 1,1-dichloroethene, 1,2-dichloroethane, and trichloroethene.

Results of the study showed that TCE was degraded by as much as 50% over the life of the study. However, within the first three months of the study, contaminant concentrations remained stable and little or no degradation was observed. Further work is being conducted on comparison of degradation rates to sample holding times in order to develop rationale for extending sample holding times.

INTRODUCTION

This report presents the results of a study conducted from December 1990 through December 1991 to evaluate the degradation of TCE in the ground water in the vicinity of Horn Rapids Landfill. The Horn Rapids Landfill is part of the 1100-EM-1 Operable Unit which is one of four operable units within the 1100 Area of the Hanford Site. The 1100 Area was placed on the National Priorities List (NPL) in July 1989. This report is part of the work described in the draft Remedial Investigation Phase 2 Supplemental Work Plan for the 1100-EM-1 Operable Unit (DOE-RL, 1990a).

The objective of the study was to evaluate the degradation of TCE present in the ground water in the vicinity of the Horn Rapids Landfill. Contaminant degradation was studied in ground water from monitoring wells known to have detectable TCE in low, medium and high concentrations.

STUDY AREA BACKGROUND AND PHYSICAL SETTING

The 1100 Area is the central warehousing, vehicle maintenance, and transportation operations center for the Hanford Site. This area was designated an NPL site in July, 1989, and is divided into four operable units. The first equipment maintenance operable unit, 1100-EM-1, was assigned the highest RI/FS priority within both the 1100 Area and the Hanford Site as a whole.

A detailed description of the regional and physical characteristics of the operable unit may be found in the Phase I Remedial Investigation Report (DOE-RL, 1990b). The Horn Rapids Landfill is a solid waste facility used primarily for the disposal of office and construction waste and the burning of classified documents; asbestos, sewage sludge, fly ash, and potentially, drums of unidentified organic liquids (presumably carbon tetrachloride) were also disposed at this site. Figure 1 shows the location of the 1100-EM-1 Operable Unit and Horn Rapids Landfill.

SAMPLING AND ANALYSIS

Samples of ground water were collected from three groundwater monitoring wells (MW-11, MW-12, and MW-15) located in the vicinity of Horn Rapids Landfill. The well locations are identified in Figure 2. The samples were collected by WHC personnel into 40 mL volatile organic analysis (VOA) bottles in sufficient quantity to allow for repeated analysis of the samples at frequencies of 1, 2, 4, 8 and 12 months from the date of collection. The VOA bottles were not preserved with mineral acid as is customary for volatile organic samples so as not to inihibit degradation of the organic compounds. The samples were stored in the dark at room temperature (approximately 25°C) throughout the duration of the study.

Following sample collection, the samples were cooled and placed into a shipping container for shipment under chain-of-custody to the analytical laboratory. The laboratory used for analysis of the samples was Pacific Northwest Environmental Laboratories Inc. (PNELI) of Redmond, Washington.

Sample analysis was conducted in accordance with the U.S. EPA Contract Laboratory Program, Statement of Work for Organics Analyses, (EPA 1988a) with the exception that the laboratory reported the following compounds to a lower quantitation limit as opposed to the usual quantitation limit of 5 or 10 μg/L: vinyl chloride, 1,1-dichloroethene, 1,2-dichloroethane, and trichloroethene.

RESULTS OF THE STUDY

This section presents the results of the contaminant degradation study for each well sampled. Results for each well were compared beginning with the fourth round of 1100-EM-1 groundwater monitoring data (December 5, 1990) and completing with the 12th month round of analysis data (December 4, 1991). Table 1 presents a summary of the compounds detected and the resulting contaminant concentrations for each of the wells sampled.

Monitoring Well MW-11

For the six sets of analysis data, 1,1,1-trichloroethane (TCA) was detected in four of the analyses. During the December 28, 1990 analysis and the December 4, 1991 analysis, TCA was not detected at a quantitation limit of 5 μg/L. Trichloroethene (TCE) was detected during all six analyses beginning at a concentration of 3 μg/L and then dropping to a concentration of 2 μg/L, where it remained through the completion of the study (see Figure 3). The degradation products, vinyl chloride and dichloroethylene were not detected in any of the samples.

Monitoring Well MW-12

TCA was detected at concentrations of 2 and 1 μg/L during the first five sets of analyses, and during the final set of analysis, was not detected at a quantitation limit of 5 μg/L. TCE was detected during all six analyses, beginning at a concentration of 74μg/L and dropping to a concentration of 36 μg/L during the final analysis set, a reduction of 51% (see Figure 4). The degradation products vinyl chloride and dichloroethylene were not detected in any of the samples.

Monitoring Well MW-15

TCA was detected in all but one analysis at concentrations of 1 μg/L. TCE was detected at its highest concentration at 61 μg/L during the 1/28/91 analysis and at the conclusion of the test, was detected at a concentration of 45 μg/L, a reduction of 26% (see Figure 5). The degradation products vinyl chloride and dichloroethylene were not detected in any of the samples.

Discussion

TCE may be degraded in the environment by a variety of processes including hydrolysis, oxidation, reduction, dehydrohalogenation, volatilization, and biodegradation, however the major process effecting degradation is considered to be biodegradation (Olsen, R.L., et. al., 1990). Biodegradation of TCE generally results in the formation of the halogenated by-products, dichloroethene and vinyl chloride neither of which were detected during this study. In addition, neither dichloroethene nor vinyl chloride have been been detected during routine groundwater monitoring of the wells sampled for this study (DOE, 1990b).

The results of analysis on wells MW-12 and MW-15 indicate that TCE concentrations are reduced as much as 51% over the course of a year under the test conditions established for this study, yet no degradation products were detected. Possible explanations or refutations for the reduced TCE concentrations are summarized as follows:

- Hydrolysis may be a likely reaction pathway since this would result in the formation of intermediate degradation products (alcohols and free chlorine) which would not be detected using the analytical procedure used in this study. The half-life of TCE undergoing hydrolysis degradation is estimated at approximately 11 months which is similar to the half-life of 12 months observed for TCE in the samples analyzed for well MW-12

- TCE may be undergoing oxidation, however for this process to occur oxidizing agents such a peroxides, ozone or chlorine are usually necessary to promote the reaction and these compounds do not occur naturally in groundwater. Because of this oxidation would not be considered the likely process contributing to reduction of the TCE,

- Reduction reactions acting on the TCE present would most likely result in the formation of lesser chlorinated compounds such as dichloroethene which was not detected during this study,

- Biodegradation may be occuring however the common anaerobic reaction products would be dichloroethylene and vinyl chloride which were not detected during this study. In addition, biodegradation half-lifes for TCE are estimated to range from 33 to 230 days (Olsen, R.L., et. al. 1990). A TCE half-life of 365 days was observed for MW-12 during this study,

- Dehydrohalogenation is a possible reaction pathway, however only the chlorinated ethane compounds (1,1,1-TCA) are susceptible to this process since it requires the removal of chlorine and hydrogen atoms from the molecule and the formation of an ethene compound (dichloroethene, DCE). Since DCE was not detected in this study this reaction process is not likely contributing to the reduction of TCE, and

- Volatilization of TCE through the septum seal in the sample containers may be causing the reduction in concentrations, however, laboratory studies on the stability of TCE under similar storage conditions indicate that losses due to volatilization through the container septa are insignificant (Maskarinec, M.P, et. al., 1990).

SUMMARY AND CONCLUSIONS

A contaminant degradation study was conducted at the 1100-EM-1 Operable Unit beginning in December 1990 and completed in December 1991. Three groundwater wells were sampled for volatile organic compounds and the samples were stored unpreserved, in the dark at room temperature and analyzed over the course of a year to determine if degradation of TCE is occurring by analysis for it's degradation products, dichloroethylene and vinyl chloride. Results of the study are summarized below:

- In groundwater monitoring well MW-11, TCE was detected initially at a concentration of 3 μg/L and at the completion of the study, at a concentration of 2 μg/L.

- In groundwater monitoring well MW-12, TCE was detected initially at a concentration of 74 μg/L and at the completion of the study, at a concentration of 36 μg/L, a reduction of 51%.

- In groundwater monitoring well MW-15, TCE was detected at a concentration of 61 μg/L and at the completion of the study, at a concentration of 45 μg/L, a reduction of 26%.

- The degradation products, dichloroethylene and vinyl chloride were not detected in any of the samples analyzed as part of this study,

- The half-life of TCE during this study was 12 months as indicated by the results of analysis on well MW-12, (see Section 4.2).

Results of the study indicate that the half-life of TCE present in the groundwater and analyzed under the storage conditions imposed by this study is approximately one-year as indicated by the results of the analysis for the samples collected from well MW-12. Rapid degradation of the TCE does not appear to be occuring based on the absence of it's degradation products. The reduction in TCE that was observed in this study is likely due to natural hydrolysis that would result in the formation of alcohols and free chlorine which would not be detected by the analytical procedure employed by this procedure.

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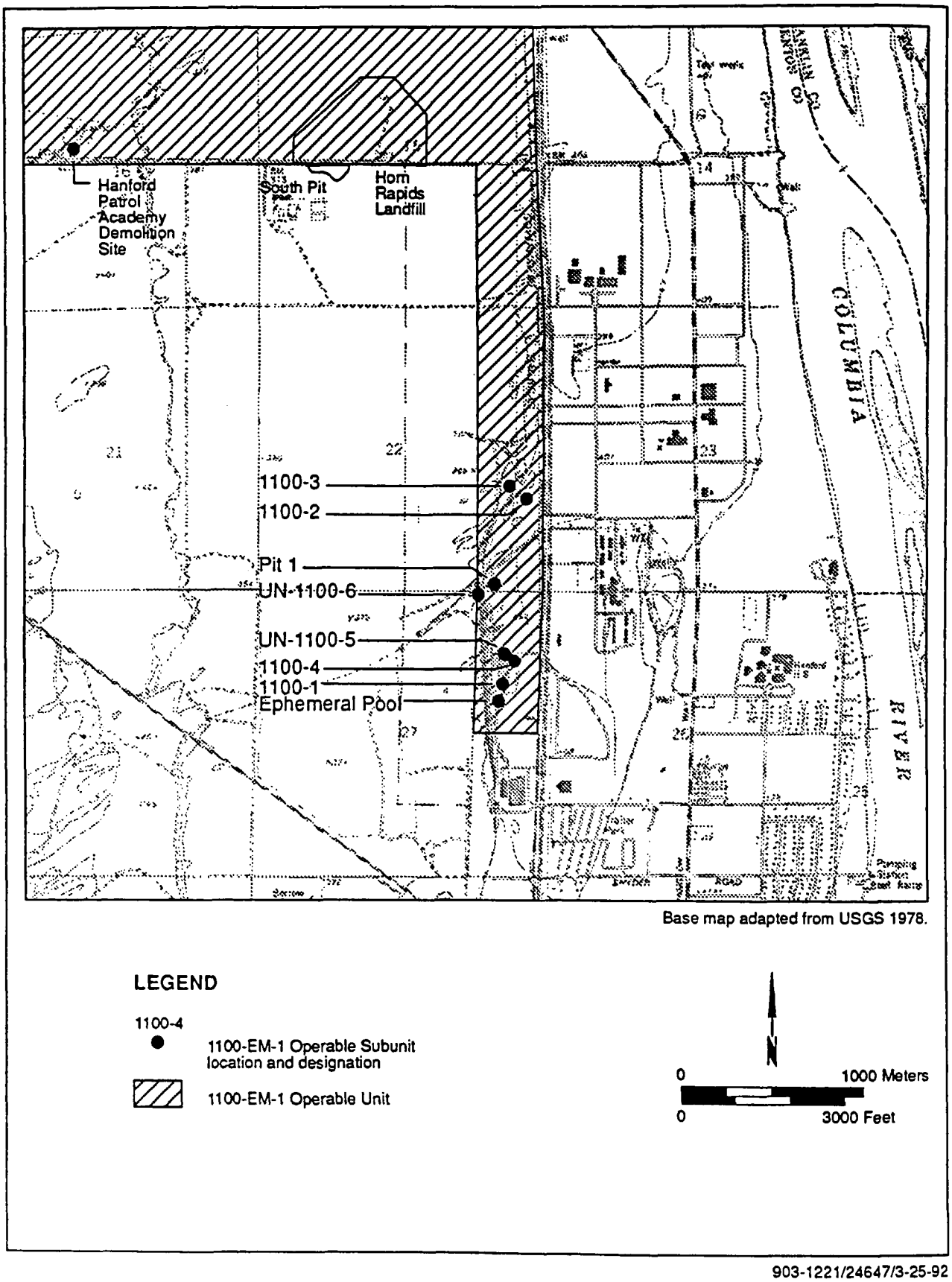

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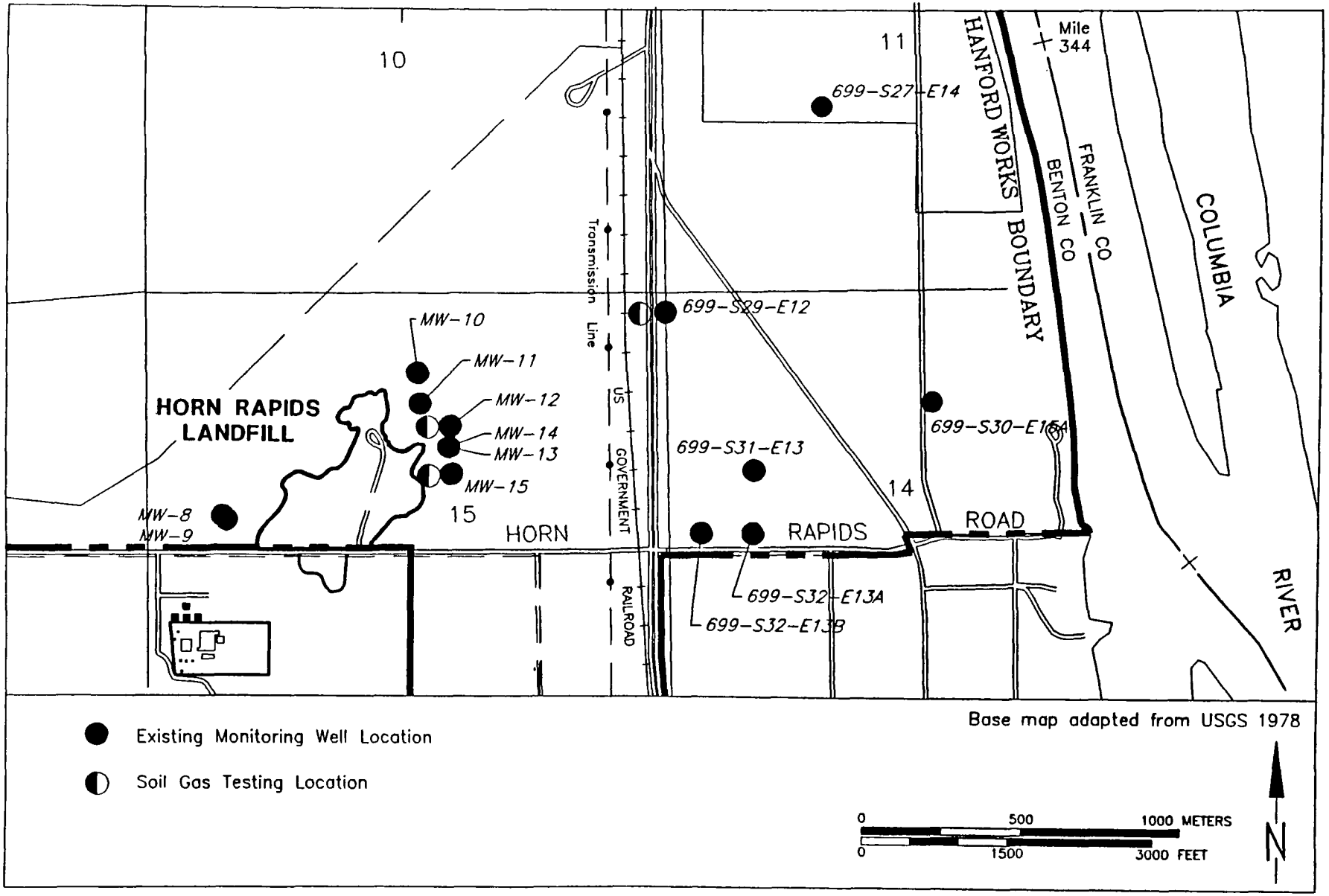
Figure 1. 1100-EM-1 Operable Unit



2/2/91 9031221\31716

Figure 2. Location of Groundwater Monitoring Wells

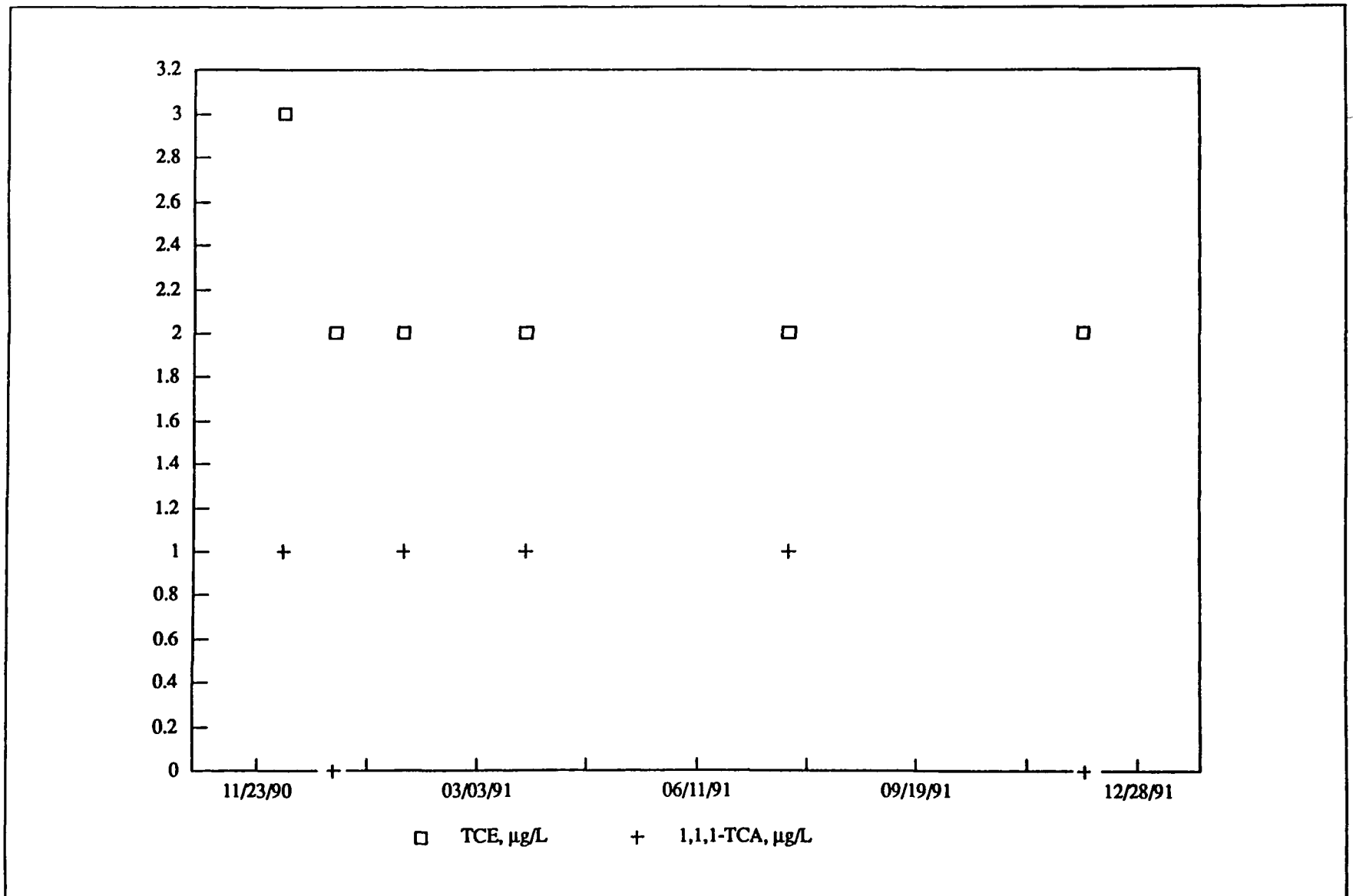


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Figure 3. Degradation Study Results, Groundwater Monitoring Well MW-11

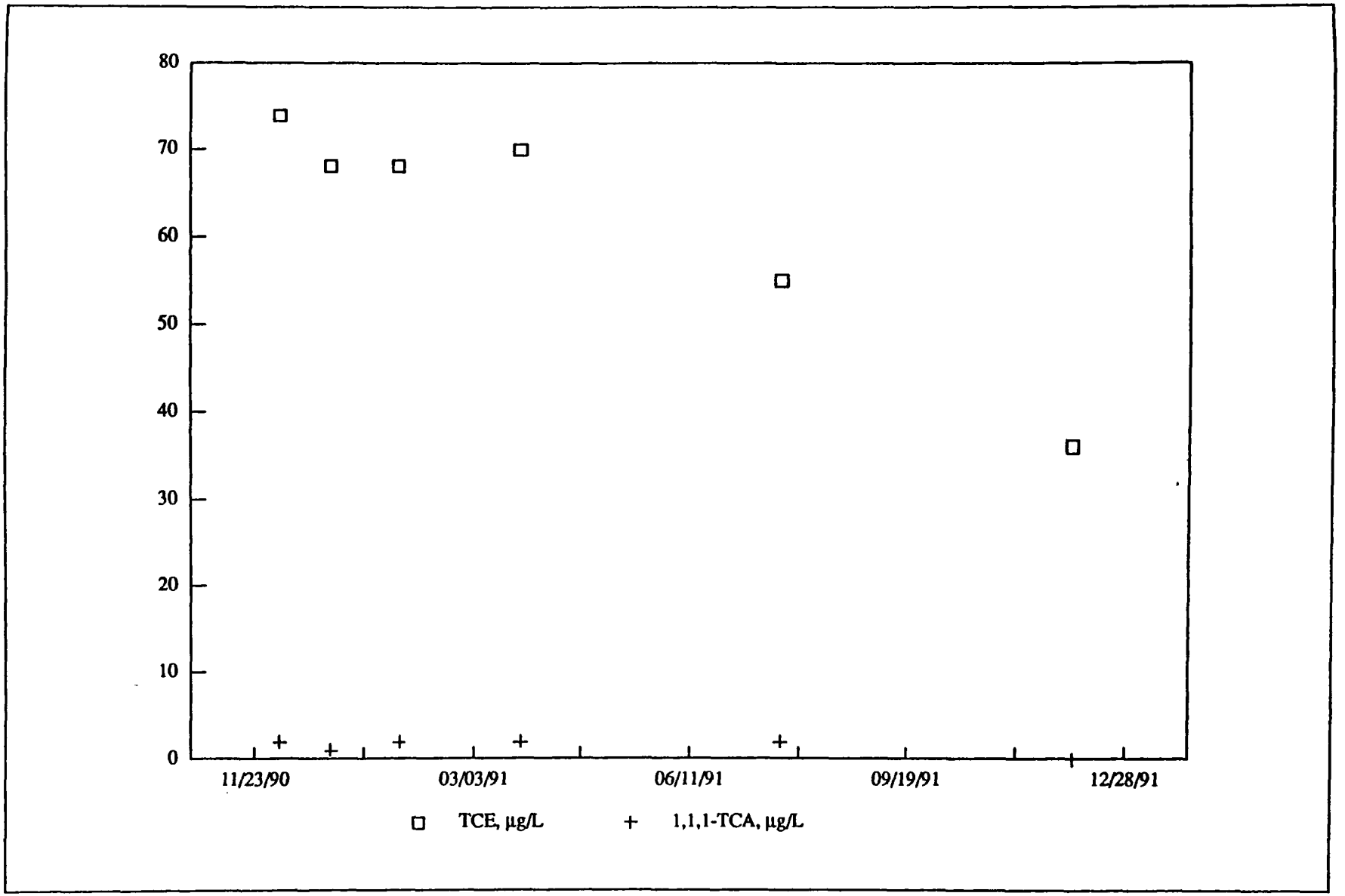

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Figure 4. Degradation Study Results, Groundwater Monitoring Well MW-12

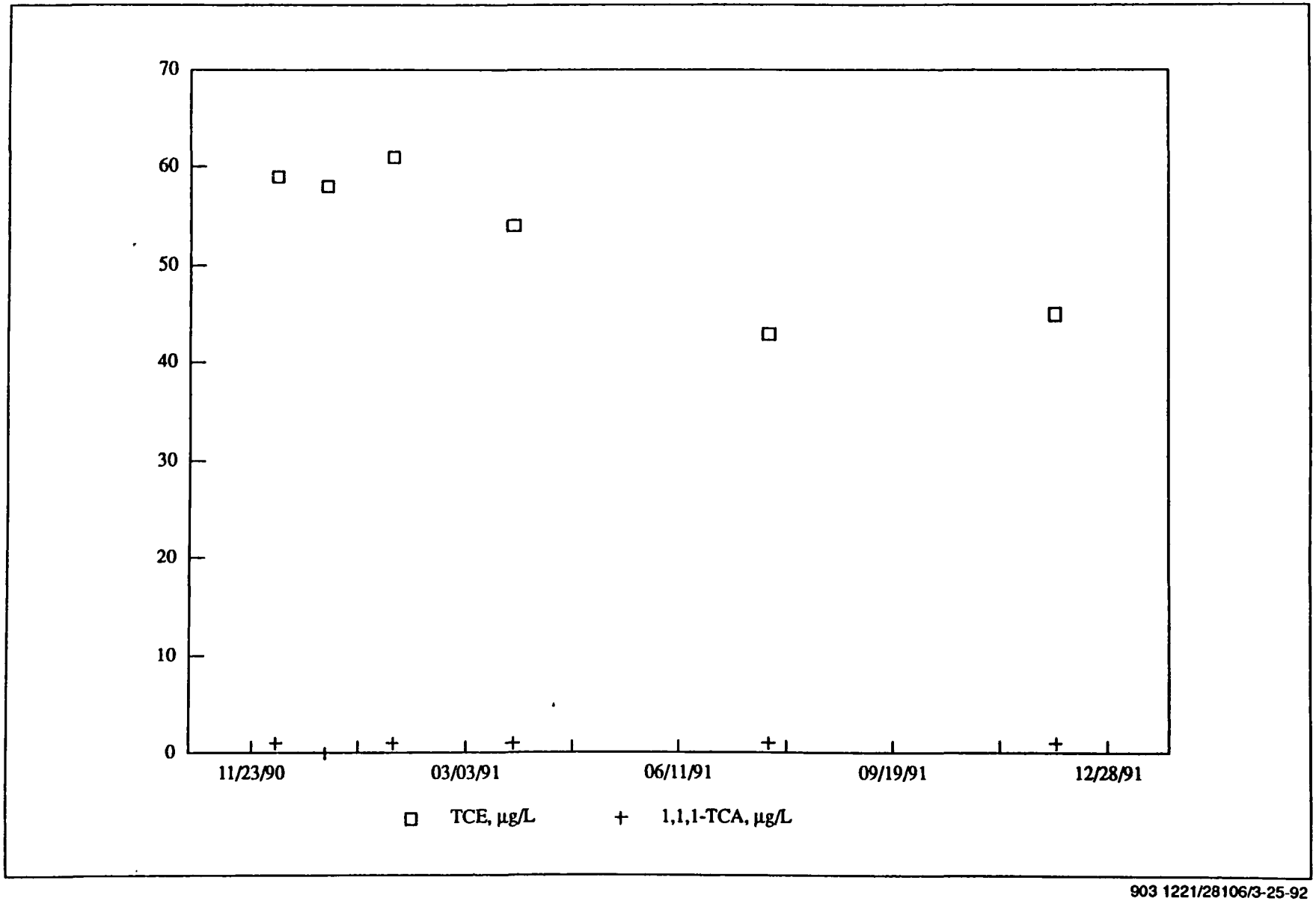

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Figure 5. Degradation Study Results, Groundwater Monitoring Well MW-15

Table 1. TCE Degradation Study Results

WELL:	MW-12					
DATE SAMPLED:	11/26/90					
DATE ANALYZED:	12/05/90	12/28/90	1/28/91	3/25/91	7/23/91	12/4/91
1,1,1-Trichloroethane	2 J	1 J	2 J	2 J	2 J	5 U
Trichloroethene	74	68	68	70	55	36
WELL:	MW-15					
DATE SAMPLED:	11/27/90					
DATE ANALYZED:	12/05/90	12/28/90	1/28/91	3/25/91	7/23/91	12/4/91
1,1,1-Trichloroethane	1 J	5 U	1 J	1 J	1 J	1 J
Trichloroethene	59	58	61	54	43	45
WELL:	MW-11					
DATE SAMPLED:	11/28/90					
DATE ANALYZED:	12/05/90	12/28/90	1/28/91	3/25/91	7/23/91	12/4/91
1,1,1-Trichloroethane	1 J	5 U	1 J	1 J	1 J	5 U
Trichloroethene	3	2	2	2	2	2

U - Indicates the compound was analyzed for but not detected. The value reported is the sample quantitation limit.
J - Indicates the concentration reported is less than the contract required quantitation limit (CRQL) but greater than the instrument detection limit.

THE USE OF AUTOMATED SUPERCRITICAL FLUID EXTRACTION/GC-MS FOR THE QUANTITATIVE DETERMINATION OF PAHS IN SOIL

ABSTRACT

Dr. Joseph M. Levy, Vice President of Technology and Customer Support; Lori A. Dolata, Technical Specialist; Robert M. Ravey, Application Chemist: and Anita Cardamone, Application Chemist, Suprex Corporation, 125 William Pitt Way, Pittsburgh, PA 15238

Supercritical fluid extraction (SFE) has a broad range of applicability, especially with regards to environmental problems. SFE has achieved a significant amount of attention due to the benefits of eliminating toxic, liquid solvent usage, reduction in sample preparation time and an increase in the overall analytical reliability of determinations. SFE/GC-MS is a powerful technique to accurately analyze and quantitate environmental analytes. The off-line transfer of SFE effluents to collection vials adds a considerable amount of flexibility in characterizing complex matrices since a full complement of analytical tools can be used (ie, GC, LC, IR, NMR and UV). Moreover, the advantages of SFE can be further augmented by the development of automation for greater sample throughput which can be especially useful for the volume of samples associated with environmental applications.

This paper will discuss the use of automated SFE methodologies for the determination polynuclear aromatic hydrocarbons (PAH) in soil. Details of method development strategies will be presented. This discussion will focus on the experimental verification of optimized SFE extraction and collection variables to achieve efficient and quantitative extractions of the target analytes in the soil with sequential replicates.

INTRODUCTION

Currently, polynuclear aromatic hydrocarbons (PAH) are extracted from environmental matrices (e.g. soils, sediments) using Soxhlet extraction or sonication sample preparation techniques. Over the past few years, supercritical fluid extraction (SFE) has surfaced as an alternative sample preparation technique offering the distinct advantages of greatly reduced sample preparation times, comparable extraction efficiencies, nontoxic (CO_2) solvent use, and an increase in the overall reliability of the analytical technique (1,2).

As SFE matures as a sample preparation technique, optimized methods will be developed for specific sample matrices and target analytes. In method development strategies, various stages of the entire SFE process need to be investigated. This includes three basic stages: pre-extraction strategies, extraction strategies and collection strategies. In pre-extraction strategies, various sample manipulation techniques such as grinding, freeze-milling or adsorbent addition can be employed to make the sample matrix more appropriate (more surface area or immobilized water) for SFE. Extraction strategies involve optimizing pressures, temperatures, sample size, durations, static/dynamic modes and modifier type and concentration. Collection strategies include off-line or on-line modes, restrictor flow rates, collection temperatures, desorption temperatures, adsorbent

type, and type of wash solvent. Moreover, these strategies need to be optimized for heterogeneous sample matrices to achieve the ultimate goal of the highest possible efficiency in the shortest time with high precision.

EXPERIMENTAL

A stand-alone manual supercritical fluid extraction system (PrepMaster®, Suprex; Pittsburgh, PA), which has been described earlier (2,3), and a sequentially automated supercritical fluid extraction system (AutoPrep-44™, Suprex; Pittsburgh, PA) were used for all of the extraction experiments. Extractions were accomplished with various sizes of extraction vessels (0.5 to 10 mL) using operating conditions that are listed in the text. An off-line collection module, (AccuTrap®, Suprex) was used to perform the cryogenic solid phase trap collection (4-6) for both the manual and automated systems. This collection module included the following components: a VariFlow™ (Suprex) automatically variable restrictor (kept at 50°C) which controlled the CO_2 flow rates (from 1 to 7 mL/minute compressed), a temperature-controlled solid phase trap packed with unibeads and C18 modified silica for analyte trapping, a liquid pump for delivering an appropriate wash solvent for analyte desorption, and a solenoid valve for delivering a stream of nitrogen to purge the adsorbent trap and connecting tubing after desorpton. For this work 1.5 mL of methylene chloride with a flow rate of 2 mL/minute was sufficient to quantitatively wash the adsorbed PAH out from the trap into a GC autosampler vial. After off-line collection, all of the extracted analytes were analyzed using a AutoSystem gas chromatograph (Perkin Elmer, Norwalk, CT) and a Q-Mass benchtop mass spectrometer (Perkin Elmer). A Varian 3400 gas chromatograph (Varian; Sunnyvale, CA) equipped with a capillary split/splitless injection port and flame ionization detection (FID) was used for GC/FID characterization. All of the soil and sediment sample matrices were naturally incurred and characterized by Soxhlet or sonication methods before GC/MS analysis according to Environmental Protection Agency's (EPA) method 8270. The GC conditions for all of the PAH determinations were 60°C (2 min.) programmed to 310°C at 7°C/min. utilizing a 25 m x 0.2 mm i.d. methyl silicone (DB-1) column (J&W Scientific; Folsom, CA).

RESULTS AND DISCUSSIONS

One of the first SFE operational parameters that was investigated for PAH extraction was extraction pressure. Conventionally, most researchers tend to refer to this parameter first when developing a SFE method because of its relation to controlling the solubilizing characteristics of supercritical CO_2. For a PAH contaminated soil, the SFE conditions were 75°C, 40 minutes (5 static/35 dynamic), with a compressed flow of 2.5 ml/minute for a 600 mg sample. The effluent was collected in a solid phase trap (C18/unibeads) at -30°C. Table 1 (7) shows the GC/MS PAH results for this soil at pressures of 250 atm, 350 atm and 450 atm (keeping all other extraction and collection strategies constant). The concentration levels were determined using calibrated external standards and were compared to the acceptance range for each PAH as outlined by EPA method 8270. The highest pressure of 450 atm provided the best agreement with the EPA acceptance range for all of the PAH from two to five fused aromatic rings. The lower molecular weight PAHs (ie, two and three fused aromatic rings) were in fact within the acceptance range

for all three of the extraction pressures. To fall within the acceptance ranges, the higher molecular weight PAH (ie, four and five fused aromatic rings) required higher solubilizing powers. This particular soil sample was contaminated with PAHs at higher levels, which were not apparently tightly associated with the matrix surface. Using the optimized extraction pressure, the levels of precision were determined for the various PAH for 42 replicate runs which are listed in Table 2 using the automated SFE system. The relative standard deviation (RSD) varied from 3.6 to 7.6% for 2 to 4 fused ring PAH. It is also important to note that the determined RSDs represent total system precision including the SFE sample preparation, the off-line cryogenic solid phase PAH trapping, and the GC/FID analytical determination. No additional sample cleanup or work-up was required after SFE and before the GC injection.

Table 1: Off-Line SFE/GC-MS of PAH Contaminated Soil - Effect of Extraction Pressure (7).

Compound	EPA Method 8270 Acceptance Range (PPM)	Concentration Levels (PPM) 250 atm	350 atm	450 atm
Naphthalene	24.2-40.6	23	23	25
Acenaphthylene	14.7-23.5	20	*	22
Acenaphthene	527-737	566	601	614
Fluorene	414-570	445	471	458
Phenanthrene	1270-1966	1682	1978	1911
Anthracene	373-471	357	439	400
Fluoranthene	1060-1500	1028	1459	1571
Pyrene	744-1322	703	1153	1269
Benzo(a)Anthracene	214-290	74	235	284
Chrysene	271-323	74	251	314
Benzo(b,k)Fluoranthene	130-174	<1.0	107	155
Benzo(a)Pyrene	80.1-114.3	<1.0	64	89

Table 2: Automated SFE/GC-FID Determination of PAH in Soil

	Concentration (PPM)								
Analyte	Run #1	Run #12	Run #21	Run #26	Run #31	Run #40	Run #42	Mean	% RSD
Acenaphthene	628	631	636	641	738	726	629	633	5.8
Anthracene	379	340	345	422	393	327	404	373	7.6
Pyrene	858	856	872	864	870	866	818	858	4.6
Benzo(a)Anthracene	239	256	249	246	265	250	237	240	3.6
Chrysene	422	434	431	444	437	437	436	434	4.9

Based upon total sample runs of 42 replicates and Soxhlet/GC-MS target values.

CONCLUSION

SFE technology has undergone a significant evolution over the past two years, particularly in the areas of restrictor technology, solid phase trapping, wrench-free extraction vessel design and sequential extraction vessel feeding. These advances have allowed easier and more reliable analytical use of SFE as a sample preparation tool for routine environmentally related applications.

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ROUND-ROBIN STUDY OF PERFORMANCE EVALUATION MATERIALS FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL: PRELIMINARY ASSESSMENT

Alan D. Hewitt and Thomas F. Jenkins, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire 03755-1290; Clarence L. Grant, University of New Hampshire, Durham, New Hampshire 03824; and Martin H. Stutz, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland 21010

ABSTRACT

A round-robin study of the analysis of soil subsamples vapor-fortified with volatile organic compounds (VOCs) was recently performed by twelve laboratories. Vapor fortification has been proposed as a method of spiking soils with VOCs so that they can be used as performance evaluation materials. Each laboratory was sent two sets of three different vapor-fortified soil subsamples containing trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben), and toluene (Tol). Analyte concentration estimates for these vapor-fortified soils were obtained using SW846 Method 8240. Preliminary analysis of the results showed a range of relative standard deviations from 9 to 22%, with an average of less than 15%. These results confirm that vapor-fortification treatment, followed by confinement in sealed glass ampoules, is a precise means of preparing and storing VOC-contaminated soil subsamples that can be used in quality assurance programs.

INTRODUCTION

The wide use and subsequent improper disposal of petroleum products and chlorinated solvents has made volatile organic compounds (VOCs) one of our most ubiquitous environmental hazardous waste problems (1). Despite the large number of vadose zone soil samples routinely characterized for VOCs, no performance evaluation materials now exist for this matrix (2). Currently the accuracy of soil VOC analyses relies on solution spike and recovery tests. One common practice is to introduce dilute methanol (MeOH) solutions of the analytes of interest into samples after they have been placed in the purge chamber of a purge-and-trap system. This method is of limited utility because (a) it evaluates only the determinative step, (b) it allows no time for natural sorptive processes to occur, (c) it involves a carrier solvent, thereby affecting sorptive interactions, and (d) it does not simulate the manner in which soils become contaminated in the field.

The accuracy of laboratory estimates of analyte concentrations in environmental samples is initially dependent on analytical calibration. Thereafter, accuracy is monitored during routine analysis of real samples by reference to results on accompanying quality assurance (QA) and quality control (QC) samples. For this system to work effectively, QA and QC reference samples must be available in a stable form that effectively mimics real samples and with accurately known concentrations. For VOCs in soils, preparation of such reference materials is very difficult (3, 4).

Vapor equilibration offers a means of fortifying soils that overcomes many of the shortfalls of previous methods (5). This method of soil spiking simulates one process by which vadose zone soils become contaminated. It involves an extended exposure period, it is precise both within and among treatment batches, and it has shown analyte concentration stability for greater than a 60-day holding period for several soils. Moreover, vapor-fortified soils can be used to evaluate both extraction efficiency and determinative accuracy (6, 7).

This treatment method exposes desiccated soils to the vapors of chosen analytes. During exposure, individual soil subsamples are contained in unsealed 1-mL glass ampoules inside a closed desiccator. After treatment, the ampoules are removed from the desiccator and quickly heat-sealed to prevent volatilization losses, which have often compromised previous methods. When used, the sample is analyzed after breaking the ampoule in a closed vessel containing the extraction solvent (i.e., MeOH, water). Performance evaluation materials for the analysis of VOCs in soil, prepared by vapor fortification and sealed in glass ampoules, offer a method by which soil subsamples may be precisely fabricated, distributed, prepared and analyzed without analyte volatilization losses (8, 9).

In this study, 12 laboratories participated in a collaborative evaluation of this vapor-fortification procedure. Duplicate subsamples of three different soils were vapor-fortified with trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben), and toluene (Tol). Each laboratory was directed to extract the six soil subsamples and analyze them within 30 days of receipt using the EPA's SW846, Method 8240 for high-level (> 1 μg/g) VOCs in soil (10). The twelve laboratories that participated in the study are listed in Appendix A. The design and a preliminary assessment of the results of this round-robin study will be presented.

PREPARATION AND DISTRIBUTION OF TEST MATERIALS

Three soil matrices were used in this study. Two of these soils serve as reference matrices for the U.S. Army Environmental Center: a marine sediment from Tampa Bay, Florida (TB), and a composite soil from the Rocky Mountain Arsenal (RMA) in Denver, Colorado. The third soil was from Point Barrow, Alaska (PBA). Clay and organic carbon concentration for these soils are shown in Table 1.

These soils were air-dried, sieved through a 30-mesh screen, and mixed thoroughly before subsampling. Forty subsamples of each soil type were placed into 1.0-mL glass ampoules using a stainless steel spatula and plastic funnel. PBA subsamples were weighed to 1.50 ± 0.01 g, while the RMA soil and TB sediment subsamples were weighed to 2.00 ± 0.01 g.

Vapor fortification was performed after placing twenty ampoules filled with one of the three soil types into a 5.6-L desiccator with a dish of anhydrous $CaSO_4$ for two days. Following desiccation, the $CaSO_4$ was replaced with an open 60-mL glass bottle containing 50 mL of a solution prepared by combining 25 mL of a MeOH stock solution (0.60 g Tol, 0.59 g TCE, 0.50 g TDCE, and 0.35 g Ben diluted to 100 mL) with 25 mL of tetraethylene glycol dimethyl ether (tetraglyme). After seven days of vapor fortification, a desiccator was opened and a 5-mm-diameter glass bead was rapidly placed on top of each ampoule, forming a temporary cap. Then, as quickly as possible, each ampoule was put in a metal tension clamp and the neck was heat-sealed using a propane plumber's torch. A sharp-pointed tip was created when sealing the ampoules to facilitate ease of breaking when preparing for analysis. Details on the development of this procedure and its performance have been documented elsewhere (5–9).

Table 1. Characteristics of soils.

Characteristic	TB	RMA	PBA
% Organic Carbon	0.31	0.05	6.7
% Clay	< 5	NA	20.1

The sequence in which the individual ampoules were sealed after removal from the dessicator was recorded. Sixteen sample sets were prepared by randomly selecting a single fortified soil subsample from each of the six treatment batches. This design allows us to examine batch-to-batch precision, as duplicate samples were prepared in different dessicators. The design also permits evaluation of intra- and interlaboratory analysis precision.

Each sample package contained:

- Eight VOA vials (one extra).
- Seven sealed glass ampoules containing soil [three pairs (1 & 2) of vapor-fortified soils labeled A, B, and C, and one blank soil labeled D for practicing the ampoule-breaking operation].
- A QA ampoule (VOA-2, Ultra Scientific) with MeOH as a solvent and containing certified VOC analyte concentrations.
- Handling and analysis instructions and reporting forms.

SOIL SUBSAMPLES AND QA SAMPLE HANDLING AND ANALYSIS

It was imperative that the procedures used by each laboratory be as consistent as possible to minimize systematic errors. For this reason, very specific handling and analysis instructions were provided. Prior to analysis, the laboratories were requested to calibrate their instrument for the analysis of TDCE, TCE, Ben, and Tol over a range of at least 1 to 100 µg/L. Analysis of both the QA standard and soil subsamples were to be performed within a single day of operation, and within one month of sample receipt. Between receipt and analysis, the entire sample set was to be refrigerated (4°C). All analyses were performed by PT/GG/MS following the general guidelines of SW846, Me > 1 µg/g VOC. The soil subsamples were first dispersed in MeOH, then a portion of the methanolic solution was combined with ≈5 mL of water for PT/GC/MS analysis.

On the day of analysis, the analyst was instructed to make a 1/20 dilution of the QA standard provided using the same MeOH that was to be used for extracting the soil subsamples. A 100-µL aliquot of the 1/20 dilution was added to 4.90 mL of water in the purge chamber of a PT/GC/MS. The results of this analysis should be within ± 20% of the certified concentrations for TCE, Ben, and Tol. If not, the analyst was requested to reanalyze the QA standard and/or consider recalibration prior to continuing.

To prepare a vapor-fortified soils for analysis, 20.0 mL of MeOH was added to one of the supplied VOA vials. An inverted (tip pointing toward the bottom) ampoule was placed into the solution and the vial quickly capped. The ampoule tip was then broken by shaking and the soil dispersed for approximately two minutes by hand agitation. A practice soil subsample ("D") was included to allow the analyst a chance to determine how hard to shake the VOA vial when breaking the ampoule. We recommended that the analyst wear rubber gloves and that the strength of shaking be increased slowly, and not increased further once the ampoule was broken. Our experience has shown that only a portion of the tip has to be broken in order for the soil to be released for extraction. However, if, after two minutes of shaking, soil remains trapped in the ampoule, shaking should be continued until complete dispersion results. Transfer of the methanolic extracts was performed after the soil had settled (approximately 20 minutes) by opening the VOA vial and withdrawing the specified aliquot with the appropriate syringe. Subsample pairs 1 and 2 were to be distinguished throughout.

The ampoules marked "A" and "B" contained vapor-fortified TB sediment and RMA soil, respectively. A 50.0-µL aliquot of the 20.0-mL MeOH extraction solution was transferred with a 100-µL syringe to a 5.00-mL syringe containing 4.90 mL of water. In order to keep a constant volume of MeOH added to the purge-and-trap vessel, 50.0 µL of analyte-free MeOH was also added with a fresh syringe.

Ampoules marked "C" contained vapor-fortified PBA soil. A 10.0-µL aliquot of the 20.0-mL MeOH extraction solution was transferred with a 25-µL syringe to a 5.00-mL syringe containing 4.90 mL of water. In order to keep a constant volume of MeOH added to the purge-and-trap vessel, 90.0 µL of analyte-free MeOH was also added with a fresh syringe.

Each laboratory was asked to provide results of their (a) instrumental calibration for TDCE, TCE, Ben, and Tol, (b) concentration estimates for TCE, Ben, and Tol in the supplied QA standard, along with results for any other analytes detected, regardless of whether the instrument was calibrated for them, and (c) concentration estimates for TDCE, TCE, Ben, Tol, and any other detected analytes, for each of the six fortified soil subsamples. All analyte concentrations were reported in µg/mL. We converted these results to soil concentrations using the masses of the subsamples. In addition, each laboratory was asked to report the date of analysis, the model and manufacturer of their mass spectrometer, purge-and-trap instrument, purge-and-trap column, gas chromatograph, and column.

RESULTS

Table 2 shows the results obtained for the analysis of the QA standard supplied with each sample set. One laboratory failed to report their determined values. The mean values obtained for TCE, Ben, and Tol by the other eleven laboratories were within 4% of the certified concentrations with relative standard deviations of less than 10%.

Table 3 shows a summary of the results obtained for the analysis of three duplicate fortified soil subsamples. Unlike the QA standard, the analysts were not informed of the concentrations present in these soil subsamples. When tabulating these results, some of the data were excluded based on procedural problems identified by the analyst or by the authors. In addition, a few widely discordant values were deleted. No more than four out of twenty-four values were excluded from a set, and in some case no values were excluded. The relative standard deviations (RSDs) obtained for these analytes are remarkably tight, ranging from 9 to 22% with an average of less than 15%. It is important to remember that these means and standard deviations include batch preparation variations for duplicates plus within- and between-laboratory analysis errors.

Table 2. Preliminary assessment of the interlaboratory results for the certified QA standard (Volatiles Mix 2, Ultra Scientific).

Benzene (50.2 µg/mL certified)		
Mean	51.9	
Std Dev.	3.8	(n = 11)
RSD*	7.4%	
Tricholoethylene (50.1 µg/mL certified)		
Mean	51.9	
Std Dev.	3.8	(n = 11)
RSD	7.2%	
Toluene (50.1 µg/mL certified)		
Mean	50.8	
Std Dev.	4.5	(n = 11)
RSD	8.8%	

* Relative standard deviation

Table 3. Preliminary assessment of the interlaboratory results for vapor-fortified soil subsamples.

Soil "A" Tampa Bay sediments (μg/g)

	TDCE	Ben	TCE	Tol
Mean	6.0	7.2	8.6	10.3
Std Dev.	1.2	1.6	1.0	0.96
RSD	20%	11%	12%	9%
n	20	21	21	21

Soil "B" Rocky Mt. Arsenal soil (μg/g)

	TDCE	Ben	TCE	Tol
Mean	11.6	14.0	15.4	19.7
Std Dev.	2.6	1.7	1.7	2.6
RSD	22%	12%	11%	13%
n	24	24	24	24

Soil "C" Pt. Barrow Alaska soil (μg/g)

	TDCE	Ben	TCE	Tol
Mean	41.0	40.7	56.2	67.2
Std Dev.	7.0	5.2	7.6	9.6
RSD	17%	13%	14%	14%
n	22	22	20	20

It is anticipated that, upon thorough statistical analysis of these data, even tighter relative standard deviations around the consensus values will be obtained because there is evidence of systematic calibration error. Furthermore, although not shown here, intra-laboratory results for the subsample duplicates were observed to show mean relative standard deviations that averaged two-thirds to one-half of the inter-laboratory results. This finding, coupled with the close agreement of the batch means, supports the concept that there is little variation between treatment batches for a given soil.

DISCUSSION

Having reliable QA/QC soil subsamples for the analysis of VOCs will not only improve our ability to monitor off-site laboratory performance, but also will allow us to evaluate alternative methods of analysis. This is particularly important for VOCs in soil because of the difficulties encountered when sampling, handling, and storing vadose zone subsamples (11–13). Moreover, performance evaluation materials prepared and handled by the techniques described here provide data on both extraction and determinative operations (14).

This round-robin study has confirmed that vapor-fortification treatment and glass ampoule confinement is a precise means to produce and store soil subsamples contaminated with VOCs for both QA and QC purposes. The subsample concentrations achieved by this method are soil-specific. Once sealed in glass ampoules, analyte concentrations are stable during transportation and preparation for analysis. These features make vapor-fortified soils ideal for assessing the precision and accuracy of sample preparation (extraction) and analysis (determination) procedures.

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APPENDIX A: PARTICIPANTS IN ROUND-ROBIN STUDY

William Saner
U.S. Army Corps of Engineers
New England Division Laboratory
Hubbardson, Massachusetts 01452

Lawrence S. Hall
Data Chem Laboratories
960 LeVoy Drive
Salt Lake City, Utah 84123

Roger Rowan, Assistant Mass Spectrometrist; Don D. Gay, Director
Midwest Research Institute
425 Volker Bl
Kansas City, Missouri 64110

Thomas G. Leuschen, Analyst; Dave E. Splichal, Supervisor
U.S. Army Corps of Engineers
Missouri River Division Laboratory
420 South 18th Street
Omaha, Nebraska 68102

Bobby Jones, Analyst; Richard A. Karn, Team Leader; Karen F. Myers, QA/QC Officer; Ann B. Strong, Group Chief; Linda K. Stevenson, Technician
U.S. Army Engineer Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, Mississippi 39180

Kerry R. Nusekabel, Analyst; John Addams, Supervisor
U.S. Army Corps of Engineers
Ohio River Division Laboratory
11275 Sebring Drive
Cincinnati, Ohio 24534

Gregory G. Lamb, Analyst; Mike Winslow, Supervisor
ESE Laboratory
P.O. Box ESE
Gainsville, Florida 32602

Gretchen Loshbaugh, Analyst; Steve Donvon, Supervisor;
Rust Geotech
PO Box 1400
Grand Junction, Colorado 81502

Steven Heller, Analyst; Suresh Srivasta and Joseph Montanaro, EPA Contacts; Joseph Montanaro, Data Reviewer
EPA Region 1 Service Division
60 Westview Street
Lexington, Massachusetts 02173

David Sherman, Analyst; Mike Urban, Supervisor
Enviro-Tech Research
777 New Durham Road
Edison, New Jersey 08817

Don Dale and Matthew Monagle, Analysts; Chris Leibman , Supervisor; Peggy Gautier, QA & DM Section Leader
MS K484
Los Alamos National Lab
Los Alamos, New Mexico 07545

Chad Pidgeon
U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

ENVIRONMENTAL ANALYSIS USING HPLC WITH ON-LINE PHOTODIODE ARRAY/MASS SPECTROMETER DETECTION

J.P. Romano, M.P. Balogh, R.C. Cotter, E.S. Bouvier, and S. Oehrle, Waters Industrial Division of Millipore Corporation, Milford, MA 01757

ABSTRACT

High Performance Liquid Chromatography (HPLC) is an excellent analytical tool for the analysis of environmentally significant compounds in water matrices. The analytes are measured by photodiode array (PDA) detection in order to provide more meaningful spectral data for environmental monitoring. Mass spectrometer (MS) detection provides information that leads to positive compound identification of these pollutants.

In order to achieve low limits of detection, solid phase extraction combined either off-line or on-line with the chromatographic separation is employed. A good example of this is in the case of the European Economic Community (EEC) Drinking Water Directive which sets a limit of 0.1 µg/l for individual pesticides.

The scope of this study will include the analysis of phenoxyacid herbicides, pesticides, nitroaromatic, and nitramine explosives. A fully integrated HPLC system that includes PDA/MS detection is described. This work also demonstrates the advanced capabilities of a PDA detector that provides excellent sensitivity plus high resolution spectral data for peak identification and peak purity for structurally and spectrally similar compounds encountered when performing environmental analysis. When used simultaneously with MS detection, confirmational information is obtained providing positive compound identification.

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MICROWAVE-ASSISTED EXTRACTION OF ORGANIC COMPOUNDS FROM SOILS AND SEDIMENTS

W.F. Beckert, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119, and *V. Lopez-Avila, R. Young, R. Kim, J. Benedicto,* and *P. Ho,* Midwest Research Institute, California Operations, Mountain View, California 94043.

ABSTRACT

As part of an ongoing evaluation of novel sample-preparation techniques by the U.S. Environmental Protection Agency (EPA), especially techniques that minimize generation of waste solvents, microwave-assisted extraction (MAE) of organic compounds from solid materials was evaluated. Six certified reference materials containing polynuclear aromatic hydrocarbons (PAHs) and some base/neutral/acidic compounds, all of which are pollutants of interest to the EPA, were subjected to MAE in a closed-vessel microwave system with hexane-acetone (1:1) at different temperatures and for different periods of time. For comparison, the same samples were contacted at ambient temperature under quiescent conditions with the same hexane-acetone solvent mixture for time periods equal to those for the microwave extractions, including any cooling times. Two matrices were also heated in a convection oven at 115°C for different time periods with the same solvent and in the same type of vessel as was used for the microwave-extracted samples.

Whereas the average recovery for all analytes extracted at room temperature was about 54%, the average MAE recoveries from the six matrices for 17 PAHs (three of which were deuterated PAHs that were spiked into the matrices) were 72% at 80°C, 78% at 115°C, and 77% at 145°C. The recoveries for the oven-heated samples were similar to those obtained by MAE. MAE was, however, exclusively used in this study because of its easy controllability and convenience. The performance of the MAE technique varied with the matrices and the analytes. Eleven PAHs gave average recoveries ranging from 65% to 111%, and three compounds [benzo(a)pyrene, benzo(ghi)perylene, and fluorene] had recoveries of 51%, 64%, and 62%, respectively. The spiked-compound recoveries by MAE were 77% for anthracene-d_{10}, 104% for benzo(a)anthracene-d_{12}, and 84% for fluoranthene-d_{10}. Additional experiments with 14 phenols and 20 organochlorine pesticides indicated that MAE is a viable alternative to the conventional Soxhlet/Soxtec and sonication extraction techniques.

The main advantages of sample extraction using MAE are reduced extraction time (typical sample preparation time for this

technique is 10 min for extraction and 40 min for extract cooling, centrifugation, and extract concentration) and reduced solvent use (30 mL in the MAE versus 300 mL in the Soxhlet extraction). Up to 12 samples can be extracted simultaneously with one microwave oven, resulting in high sample throughput.

NOTICE

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

DETECTION OF TOXAPHENE IN SOIL BY IMMUNOASSAY

Titan S. Fan and Barbara Young, Millipore Corporation, Bedford MA 01730; Daniel G. Crouse, Roy F. Weston, NJ 08837-3679; and Harry Allen, Environmental Protection Agency, NJ.08837-3679

ABSTRACT

From the mid-1940s until the mid-1980s, toxaphene was one of the most heavily utilized agricultural chemicals world-wide. Past studies performed on the effects of toxaphene have implicated this chemical as a human carcinogen and mutagen. While use this chemical has virtually been eliminated today because of its long half-life, undegraded toxaphene deposits in soil may still be available to living organisms.

The EnviroGard Toxaphene immunoassay test kit is a user-friendly, inexpensive screening test. This test kit was used effectively to detect toxaphene in two Navajo Nation Superfund sites: Nazlini and Whippoorwill. Toxaphene had been used in a sheep dip solution to protect sheep from insects at these sites. There are 136 such sites in The Navajo Nation, and 20 sites will be remediated in 1994. Thirty soil samples were collected from the Nazlini site and analyzed by both the EnviroGard Toxaphene test kit and by EPA Method 8081. The soil samples were split and extracted with methylene chloride/acetone using a Soxhlet apparatus (SW-846 method 3540) for GC/ECD analysis and with 90% MeOH for 2 minutes with an EnviroGard soil extraction kit for immunoassay analysis. The correlation of these methods was excellent. The R value was 0.996.

INTRODUCTION

Toxaphene is a complex mixture of polychlorocamphenes. It was used on armyworms, cutworms and grasshoppers in cotton, corn and small grains. It was also used widely on cattle and sheep as dips for scabies. Toxaphene is carcinogenic in laboratory animals, and accumulates in the animals tissues. This insecticide was banned in November, 1982. One of the major concerns was that toxaphene had become widespread in the Great Lakes and the Mississippi Delta regions, both with large human populations that consumed fish from the contaminated water. During the 1960s and 1970s toxaphene was used in the United States in larger quantities than any other insecticide. In the three years before its ban over 30,000 tones of toxaphene was applied in the southern states. Cleaning up the toxaphene contaminated sites has become an important task for the Environmental Protection Agency. To clean up these sites, the first step is to determine the size of the contaminated area and the contamination level. An easy to use field test kit would be very useful to detect the level of toxaphene in the soil. The second step is to remediate the contaminated soil. This field kit would also be useful for monitoring the progress of remediation. The EnviroGard Toxaphene Test Kit was used successfully in the field at two bioremediation sites in the Navajo Nation The results are reported in this paper.

METHODS

Description of the Immunoassay:

Polyclonal antibodies were produced in rabbits immunized with a proprietary derivative of Cyclodiene chemically bound to a carrier protein. The antibody was coated on the inner wells of polystyrene tubes. When toxaphene is present in the sample, it competes with the toxaphene-enzyme conjugate for a limited number of antibody binding sites. Since there are the same number of antibody binding sites on every test tube and each test tube receives the same number of toxaphene-enzyme conjugate molecules, a sample that contains a low concentration of toxaphene allows the antibody to bind many toxaphene-enzyme conjugate molecules. Therefore, a low concentration of toxaphene produces a dark blue solution. Conversely, a high concentration of toxaphene allows fewer toxaphene-enzyme conjugate molecules to be bound by the antibodies, resulting in a lighter blue solution.

The protocol for the commercially available EnviroGard Toxaphene in soil test kit (part # ENVR 000 30, Millipore Corp., Bedford, MA) is as follows:

A) Soil sample extraction:
A field-portable, fast methanol extraction of soil samples is utilized with this immunoassay. Five grams of a well homogenized soil sample are weighed with a portable balance and transferred into a disposable extraction bottle containing three stainless-steel mixing balls. Ten ml of 90% methanol in water are added and the bottle is shaken vigorously by hand for 2 minutes. The soil is allowed to settle for at least one minute, then a filtration cap is placed on the extraction bottle. After pumping air into the bottle with a syringe, the bottle is inverted over a glass collection vial. The filtered extract is allowed to drip into the vial, which is then tightly capped and stored under refrigeration, in the dark, until analyzed.

B) Assay protocol:
1. Add 250 ul of assay diluent to each test tube. Add 50 ul of each calibrator (0.5, 2.0 and 10 ppm) and sample extracts to the corresponding test tubes. Let the test tubes incubate for 15 min before adding 200 ul of conjugate to each tube.

2. Shake the test tube rack and incubate for 5 minutes. Vigorously shake out the test tube contents into a sink or suitable container. Wash the tubes four time with laboratory-grade water, removing any unbound compounds.

3. A clear solution (500 ul) of chromogenic substrate (3,3,5,5-tetramethylbenzidine hrdrochloride) is then added to the tubes and incubated for 5 minutes.

4. Assay results may be instrumentally recorded by adding 500 ul of 1N HCl stop solution to each tube and reading the optical density (OD) at 450 nanometers(nm) minus a 600 nm reference wavelength.

Immunoassay Validation Procedures:

1. Matrix effects/Determination of the Lower Limit of Detection: For these tests, eight control soil samples were subjected to triplicate extraction and triplicate assays of each extract, in order to determine the varibility associated with toxaphene-free soils. The mean color development due to these samples minus 2 standard deviations was determined and defined to equal the loweset concentration of toxaphene in soil detectable by the immunoassay.

2. False positive/False Negative Testing: Four soil samples were spiked with toxaphene at 0.4 ppm and four at 4.0 ppm, and compared to a 2 ppm toxaphene calibrator in triplicate assays. The rate of occurrence of "false positives" and "False negatives" was determined.

3. Assay of Toxaphene-Spiked Soil Samples: Three toxaphene-free soils were spiked at two levels with toxaphene, in triplicate, and assayed along with three toxaphene calibrators. The rate of correct interpretation of the samples was determined.

4. Cross-Reactivity Studies: A large number of compounds structurally related to toxaphene were tested for their reactivity in this immunoassay. The compounds were prepared in methanol and run as samples in the EIA.

5. Tests with Field Samples: Thirty contaminated soil samples from Navajo Superfund Nazlini site were tested by EnviroGard Toxaphene test kits and split samples were extracted according to Method 3540 (Soxhlet extraction) and analyzed by SW-846 method (8081) with GC/ECD. The extent of agreement between the EIA and GC was assessed.

RESULTS AND DISCUSSION

Validation Procedures:

1. Repeated testing of toxaphene-free soils resulted in an overall mean %Bo of 88.1, with a standard deviation (SD) of 4.3. The mean minus 2 SD equals 79.5% Bo. Reading 79.5%Bo off the graph of toxaphene gives an approximate lower limit of detection of 250 ppb toxaphene in soil.

2. An exercise was conducted to determine the rate of false negative and false positive assay calls when soils were spiked to 0.4 or 4 ppm toxaphene and compared to 2 ppm calibrator. Any sample with an OD greater than the OD of the 2 ppm calibrator was called "<2 ppm". Any sample with an OD equal to or less than the OD of the 2 ppm calibrator was called'≥2 ppm". Out of 48 samples run, there were no false positive calls and zero false negative calls.

3. The 6 results of three soils spiked with 1.0 and 10 ppm toxaphene showed a mean recovery of 98%.

4. Table 1 summarizes the results of cross-reactivity testing conducted with the Toxaphene EIA. The extent of cross-reactivity is displayed in two ways: The concentration of compound that corresponds to the lower limit of detection (LLD) in the assay, and the concentration of the compound required to inhibit 50% of the color developed by negative control (50%Bo).

Chlordane, endrin, endosulfan endosulfan II, dieldrin, heptachlor aldrin have cross reactivities at ppb levels while toxaphene, gamma-BHC, alpha-BHC and delta-BHC have ppm levels.

5.Tests conducted with thirty field samples showed very good agreement between EIA and GC as shown in Figure 1.

CONCLUSIONS:

All of the validation procedures run within our laboratory have demonstrated the ability of the toxaphene in soil test kit to effectively screen for toxaphene in soil samples. The combination of its ease of use and low cost per sample can allow for increased rates of sampling, potentially resulting in improved characterization and mapping of polluted sites as demonstrated at the Nazlini site. The use of complex, expensive chromatographic techniques may then be used for quality control and confirmation.

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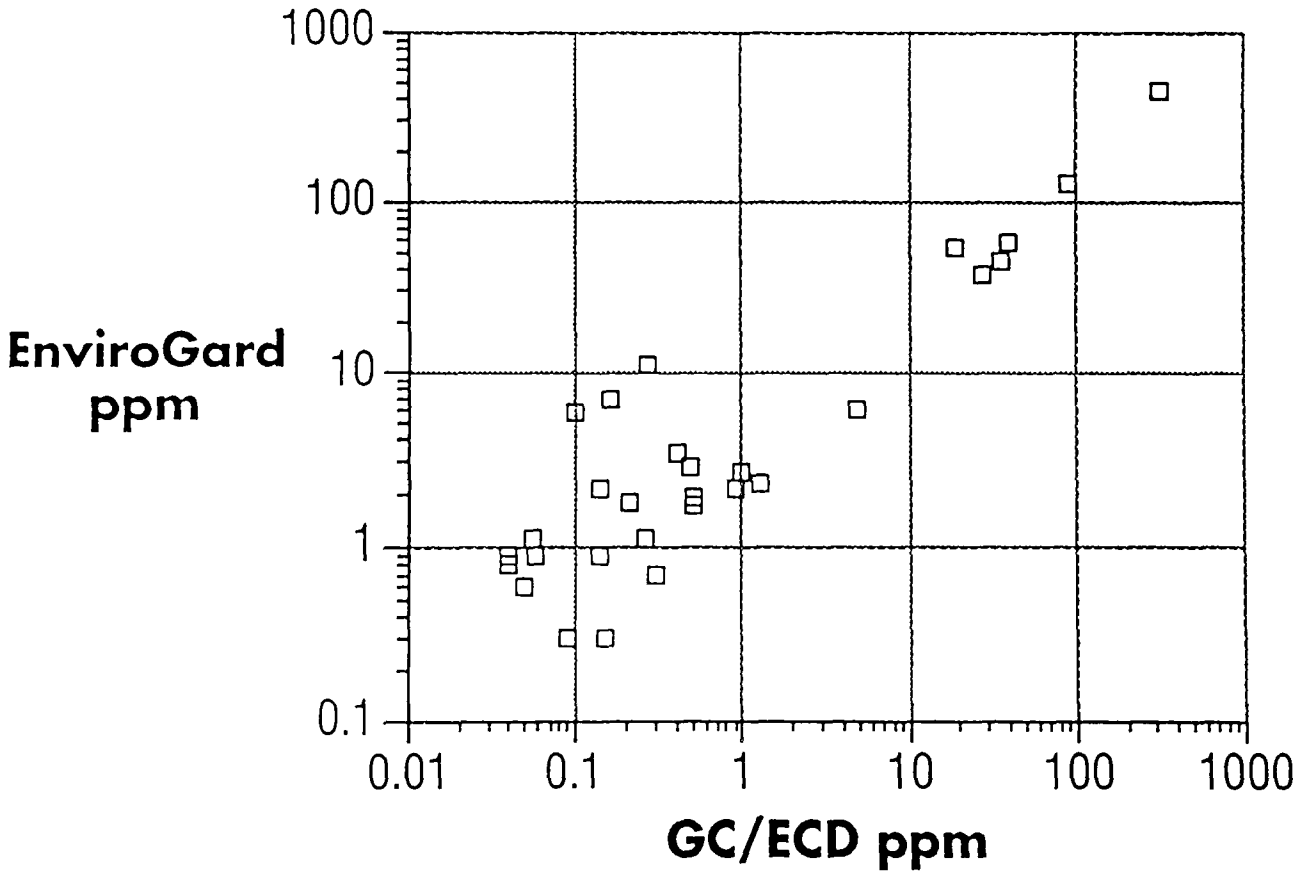
Toxaphene in Soil



Cross-Reactivity Studies

Compound	LLD	IC50
Toxaphene	0.2 ppm	2.8 ppm
Chlordane	14 ppb	76 ppb
Endrin	6 ppb	22 ppb
Endosulfan	6 ppb	36 ppb
Endosulfan II	6 ppb	28 ppb
Dieldrin	6 ppb	42 ppb
Heptachlor	6 ppb	34 ppb
Aldrin	20 ppb	116 ppb
Gamma-BHC	0.6 ppm	4.6 ppm
Alpha-BHC	2 ppm	19 ppm
Delta-BHC	2 ppm	40 ppm

Conc. in Soil
Gamma–BHC = Lindane

DETECTION OF DDT AND ITS METABOLITES IN SOIL BY ENZYME IMMUNOASSAY

Karen A. Larkin, Research Scientist, Jonathan J. Matt, Research Scientist, and Bruce S. Ferguson, Chief Scientific Officer, ImmunoSystems, Subsidiary of Millipore Corporation, 4 Washington Avenue, Scarborough, Maine 04074; Helen L. Beasley, Experimental Scientist, Division of Plant Industry, CSIRO, PO Box 7, North Ryde, NSW 2113, Australia; John H. Skerritt, Principal Research Scientist, Division of Plant Industry, CSIRO, GPO Box 1600, Canberra, ACT 2601, Australia

ABSTRACT

DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane) is a highly persistent, environmentally toxic organochlorine insecticide. It has been very heavily applied for many decades in countries around the world. The combination of its liberal use and its long-term soil persistence has resulted in the existence of many soil sites contaminated with DDT and its major metabolites, DDD and DDE. Conventional analytical techniques for detection of these compounds in soil are costly and time-consuming. Therefore, an enzyme immunoassay (EIA) has been developed to detect DDT and its metabolites in soil. Rabbit polyclonal antibodies prepared against a DDT derivative are pre-coated to polystyrene test tubes. Soil extracts and DDT-enzyme conjugate are added to the tubes and compete for antibody binding sites on the tubes. Excess conjugate is washed away and a substrate solution is added; subsequently, the amount of color developed in the tube is inversely proportional to the concentration of DDT in the sample. This field-portable screening test utilizes a rapid and simple methanol extraction of soil and can detect DDT and its metabolites at levels as low as 0.1 ppm. Assay results can be obtained within 30 minutes. EIA validation data and correlation with a gas-chromatographic method will be presented.

INTRODUCTION

The potency of DDT as an insecticide was discovered in 1939 by Dr. Paul Muller, working at what is now Ciba-Geigy AG in Switzerland (1). DDT became highly valued for its low cost, its potential to help control insect-borne disease, and for its persistence after application, and was very heavily used world-wide, from 1942 to 1972. Although there is no solid evidence of lasting harm to humans due to routine exposure to DDT, other ill effects of the compound eventually became apparent. DDT accumulates in the fat of living organisms and becomes concentrated in animals at the top of the food chain. This proved detrimental to species of predatory birds, in which thinning eggshells and other reproductive problems were directly attributed to DDT and certain of its metabolites. DDT was also found to be acutely toxic to fishes. Consequently, the use of DDT is currently either banned or severely restricted in many parts of the world. (2) Because DDT and its metabolites are so persistent in soil, with half-lives estimated to be 15 to 20 years (3), residues are still very much a concern, even in areas where the pesticide is no longer used.

Most commonly, DDT and other organochlorine pesticides are quantitated by costly gas-chromatographic (GC) methods involving either electron capture detection (ECD) or mass-spectroscopy. These methods must be preceded by time consuming extraction and clean-up procedures which utilize large volumes of solvents. The need exists for a fast, cost-effective screening method for "total DDT" (the sum of *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE) in soil.

There have been a number of studies published recently utilizing enzyme immunoassay to detect various pesticides in soil, including atrazine (4,5), chlordane (6), and metolachlor (7). Antibodies for the detection of DDT have been reported previously (8-11). The objective of the following work was to couple a fast soil extraction protocol with a simple immunoassay test, together capable of providing accurate estimations of total DDT isomers in soil.

METHODS

Description of the Immunoassay:

Polyclonal antibodies were produced in rabbits immunized with a proprietary derivative of DDT chemically bound to a carrier protein. The antibody was coated on the inner walls of polystyrene tubes at various concentrations and titered against serial dilutions of a DDT-derivative conjugated to horseradish peroxidase enzyme, until the optimum combination was obtained. Various immunoassay protocols were tested, with the final choice being a simultaneous competitive format. This finished immunoassay possesses the desired reactivity with *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE, and can detect all three compounds with sensitivities in the range of 0.1 ppm in soil.

The protocol for the commercially available DDT in Soil Test Kit (part #ENVR 000 31, Millipore Corp., Bedford, MA) is as follows:

1. A sample extract or calibrator (25 µL) containing DDT is added to an antibody-coated test-tube containing 500 µL of an assay diluent. 100 µL of DDT-enzyme conjugate is added and the tubes are mixed and incubated at ambient temperature for 15 minutes.

2. The tubes are then washed with tap or laboratory-grade water, removing any unbound compounds.

3. A clear solution (500 µL) of chromogenic substrate (3,3,5,5-tetramethylbenzidine hydrochloride) is then added to the tubes and incubated at ambient temperature for 10 minutes. In the presence of bound DDT-enzyme conjugate, the clear substrate is converted to a blue color. Since there are the same number of antibody binding sites on every test tube and each test tube receives the same number of DDT-enzyme conjugate molecules, a sample that contains a low concentration of DDT allows the antibody to bind many DDT-enzyme conjugate molecules. Therefore, a low sample concentration of DDT produces a dark blue solution, while a high sample concentration of DDT allows fewer DDT-enzyme conjugate molecules to be bound by the antibodies, resulting in a lighter blue solution.

4. Assay results may be instrumentally recorded by adding 500 µL of a 1 N HCl stop solution to each tube and reading the optical density (OD) at 450 nanometers (nm) minus a 600 nm reference wavelength. (Alternatively, a battery-operated differential photometer may be used in field situations.) Results are interpreted by comparing the OD of samples to the OD of *p,p'*-DDT calibrators provided in the test kit.

Soil Sample Extraction:

A field-portable, fast methanol extraction of soil samples is utilized with this immunoassay. Five grams of a well-homogenized soil sample are weighed with a portable balance and transferred into a disposable extraction bottle containing three stainless-steel mixing balls. Five mL of methanol are added and the bottle is shaken vigorously by hand for 2 minutes. The soil is allowed to settle for at least 1 minute, then a filtration cap is placed on the

extraction bottle. After pumping air into the bottle with a syringe, the bottle is inverted over a glass collection vial. The filtered extract is allowed to drip into the vial, which is then tightly capped and stored under refrigeration, in the dark, until analyzed.

Immunoassay Validation Procedures:

1. Matrix Effects/Determination of the Lower Limit of Detection: For these tests, eight control soil samples were subjected to triplicate extraction's and triplicate assays of each extract, in order to determine the variability associated with DDT-free soils. The mean color development due to these samples minus 2 standard deviations was determined to equal the lowest concentration of *p,p'*-DDT in soil detectable by the immunoassay.

2. False Positive/False Negative Testing: Eight soil samples were spiked with *p,p'*-DDT at 0.2 and 2.0 ppm, and compared to a 1 ppm *p,p'*-DDT calibrator in triplicate assays. The rate of occurrence of "false positives" and "false negatives" was determined.

3. Assay of DDT-Spiked Soil Samples: Three DDT-free soils were spiked at two levels with *p,p'*-DDT, in triplicate, and assayed along with three *p,p'*-DDT calibrators. The rate of correct interpretation of the samples was determined.

4. Cross-Reactivity Studies: A large number of compounds structurally related to DDT were tested for their reactivity in this immunoassay. The compounds were prepared in methanol and run as sample extracts in the EIA.

5. Tests With Samples Containing Incurred Residues of DDT: Two separate field site studies were conducted. In each of the below cases, extent of agreement between the EIA and GC was assessed.

Forty-seven soil samples from a site in Kansas were extracted using the immunoassay protocol. These methanol extracts were analyzed by both immunoassay and in-house gas-chromatography:

A Perkin-Elmer (PE, Norwalk,CT) AutoSystem GC with a PE-608 column (30 m, 0.53 mm i.d., 0.80 µm film thickness, methyl phenyl cyanopropyl silicone) was used, under the following conditions:

- oven: 190 °C to 260°C at 10°/min., held for 3 min.
- injector: packed, converted to megabore capillary, using direct flash vaporization, held at 200°C.
- injection size: 1 µL
- detector: ECD held at 350°C, with argon/methane make-up
- carrier gas: helium, at 7 mL/min.

Thirty-two soil samples from a site in Florida were each split into two aliquots. One aliquot was extracted and analyzed by the EIA protocols; the other aliquot was sent to an independent laboratory (APPL Laboratories, Inc., Fresno, CA) where it was extracted by EPA Method 3550 and analyzed by GC with EPA Method 8080.

RESULTS

Standard Curve: The useful range of the DDT immunoassay was determined by running *p,p'*-DDT over a wide span of concentrations. Data were normalized against the negative control (neat methanol) run in each assay by calculating the %Bo of each sample. Percent Bo equals the OD of the sample or calibrator divided by the OD of the negative

control, multiplied by 100. The graph in Figure 1 shows the standard curve for *p,p'*-DDT soil extracts, as well as those for *p,p'*-DDD and *p,p'*-DDE. Because the *p,p'*-DDT curve is most linear from 0.1 to 10 ppm, calibrators of 0.1, 1, and 10 ppm were used during the EIA validation process. Calibrators for the commercially available DDT in Soil Test Kit were chosen to be 0.2, 1, and 10 ppm, to avoid potential false positive interpretations due to soil matrix effects. The range of the EIA can be easily expanded by diluting sample extracts in methanol prior to running them in the immunoassay. For example, samples known to contain 100 ppm or more can be characterized by diluting the sample extracts 1:100 in methanol prior to assay. Due to this 1:100 dilution, the above kit calibrators would then represent 20, 100, and 1000 ppm, and the soil samples can be described in relation to these levels.

Caution must be used with soil samples which contain greater than 1000 ppm DDT; the limited solubility of the compound in methanol may adversely affect extraction efficiency. In this case, it is recommended that the volume of methanol used to extract 5 grams of soil be increased to 20 mL from 5 mL. This is a 1:4 dilution factor which must be factored into the sample interpretation. For example, for a site with a clean-up action level of 2000 ppm, soils should be extracted with 20 mL of methanol and extracts should be diluted 1:500 in methanol. Due to this 1:2000 dilution (1:4 during extraction and 1:500 of the extract) the kit calibrators would represent 400, 2000 and 20,000 ppm total DDT in soil.

Soil Extraction: The soil extraction method used with the DDT in Soil EIA is not expected to be 100% efficient for all samples. Preliminary trials showed negligible differences in total DDT recovery from selected contaminated samples when the extraction times were increased from 2 minutes to 24 hours. Because the objective of this method development was to create a fast, field portable screening test, the 2 minute extraction time was deemed sufficient. As noted above, highly contaminated samples may suffer decreased extraction efficiencies due solely to the problem of solubility. Increasing the volume of extraction solvent helps to solve this problem.

Validation Procedures:

1. Repeated testing of DDT-free soils resulted in an overall mean %Bo of 93.4, with a standard deviation (SD) of 6.0. The mean minus 2 SD is equal to 81.4% Bo. Reading 81.4% Bo off the graph of *p,p'*-DDT in Figure 1 gives an approximate lower limit of detection of 0.044 ppm *p,p'*-DDT in soil.

2. An exercise was conducted to determine the rate of false negative and false positive assay calls when soils were spiked to 0.2 or 2 ppm *p,p'*-DDT and compared to a 1 ppm calibrator. Any sample with an OD greater than the OD of the 1 ppm calibrator was called "<1 ppm". Any sample with an OD equal to or less than the OD of the 1 ppm calibrator was called "≥ 1 ppm". Out of 48 samples run, zero false positive calls resulted (i.e. all of the 0.2 ppm spikes were called "< 1 ppm"). Six false negative calls resulted (i.e. 6 of the 2 ppm spikes were called "< 1 ppm"). This rate of "false negatives" was unacceptable. To correct the situation, calibrators in the commercial EIA kit contain *p,p'*-DDT at concentrations that are 75% of that stated on the calibrator labels. Calculations from the data generated in this section of the validation indicated that this would have eliminated all the false negative calls in the data set without creating any false positive calls.

3. The analysis of soils spiked with 0.25 and 2.5 ppm *p,p'*-DDT showed 100% correct calls of all runs of all replicate spikes.

4. Table 1 summarizes the results of cross-reactivity testing conducted with the DDT EIA. The extent of cross-reactivity is displayed in three ways: the concentration of compound in soil that corresponds to the lower limit of detection in the assay (81.4% Bo), the concentration of the compound in soil required to inhibit one-half of the color developed by negative control tubes (50% Bo), and the % cross-reactivity.

This data shows that the immunoassay is well equipped to measure the total of the *p,p'*-isomers of DDT and its metabolites. The *o,p'*- forms of DDT and DDE are recognized very poorly by the antibody, while *o,p'*-DDD is somewhat more reactive. Because the reactivities of all these components are not identical, and because at least three of them are normally found in contaminated soils in varying proportions, this EIA cannot be used accurately as a quantitative measuring device, but instead is intended as an effective screening tool.

Chloropropylate and DDA are far better recognized by this polyclonal antibody than is DDT. This should not be of concern to most soil analysts, as DDA (the major metabolite of DDT in living organisms) is not prevalent in soil and chloropropylate is a discontinued acaracide with limited persistence.

Chlorobenzilate and dicofol can be detected with approximately the same sensitivity as the *p,p'*-DDT isomers, making the EIA useful to analysts looking for one of these compounds rather than, or in addition to, DDT.

The remainder of the chemicals on the list are mildly reactive, and demonstrate the affinity of this polyclonal antibody for compounds containing a terminal phenyl group with a chlorine in the *para*- position.

5. Tests conducted with two groups of soil samples containing incurred residues of DDT showed very good agreement between EIA and GC, both on split soil extracts and on split soil samples.

Table 2 summarizes the data on the Kansas site soils, for which GC data was generated on the same extracts used in the EIA. There were 4 disagreements between the two techniques. Three of these involved samples containing less than 0.2 ppm total DDT. Of the four disagreements, three were called more positive by EIA than by GC, which is the preferred type of error. These samples may well contain a cross-reacting compound which was not tested for in the GC protocol. The fact that some of the samples which were called "<0.1 ppm" by GC were called ">0.1 ppm" by the EIA prompted the change of the lowest kit calibrator in the commercial product from 0.1 to 0.2 ppm.

Table 3 summarizes the data from the Florida site soils, which was a test of the extraction protocol as well as the immunoassay, because soil samples were split and extracted by either the simple EIA protocol or by official EPA methods in an independent analytical laboratory. Please note that these data were generated after the lowest calibrator in the commercial kit was changed to 0.2 ppm from 0.1 ppm. There were a total of five disagreements in this data set, all of which involved the EIA calling positive samples <u>more</u> positively than did the GC. This indicates that the EIA extraction protocol is sufficient for these low-level DDT soil samples, and that a slight trend for over-estimation of DDT content exists. However, all of the GC "not detectable's" (less than 0.05 ppm total DDT isomers) were correctly interpreted as containing less than the 0.2 ppm kit calibrator.

CONCLUSIONS

All of the validation procedures run within our laboratory have demonstrated the ability of the DDT in Soil Test Kit to effectively screen for total DDT in soil samples. The undesirable rate of false negatives seen in the second validation parameter have been corrected in the commercial test kit by lowering the concentration of *p,p'*-DDT in the calibrators to 75% of their nominal value. The potential for false positives due to unknown matrix effects from field-site soils was decreased by raising the lowest kit calibrator level to 0.2 ppm.

This DDT in Soil immunoassay possesses great applicability as a field screening tool. Its 0.2 ppm detection limit should prove more than adequate for measuring tolerable levels of soil contamination under most federal or state guidelines and regulations. The combination of its ease of use and low cost per sample can allow for increased rates of sampling, potentially resulting in improved characterization and mapping of polluted sites. The use of complex, expensive chromatographic techniques may then be limited to quality control and confirmations.

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FIGURE 1

EIA REACTIVITY OF p,p' DDT, DDD, AND DDE

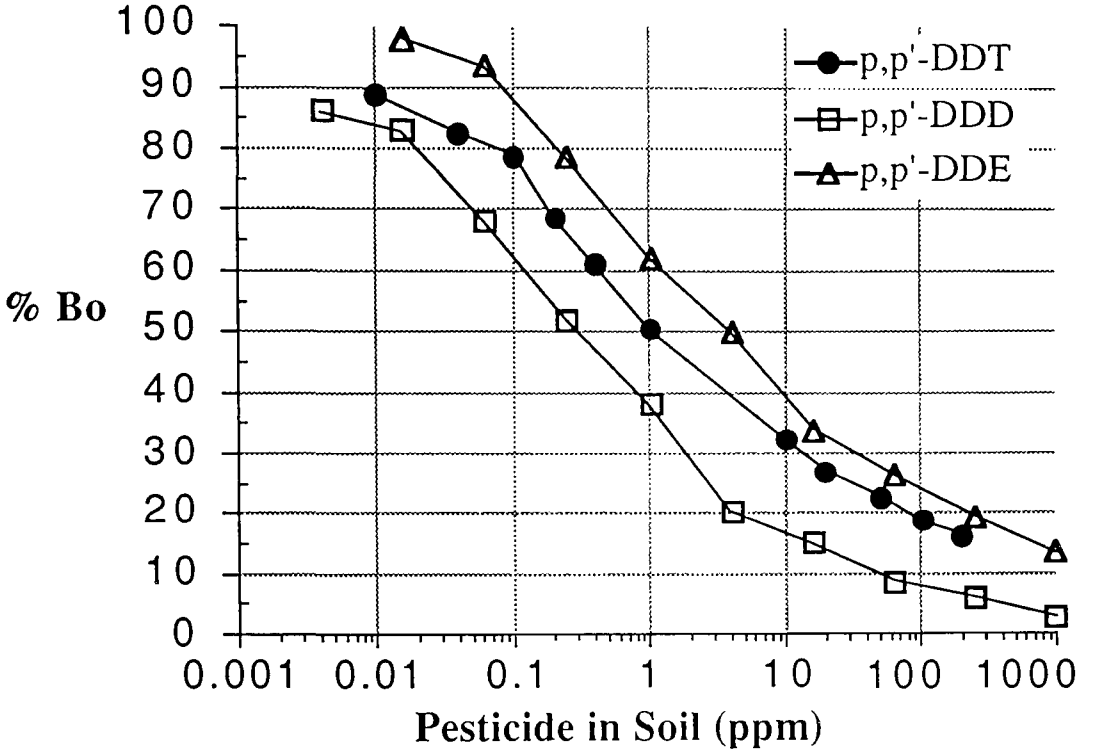

TABLE 1

CROSS-REACTIVITY STUDIES

Compound	PPM in Soil LLD	IC50	% C.R.*
p,p'-DDT	0.04	1.25	100
p,p'-DDD	0.01	0.3	417
p,p'-DDE	0.18	3.6	35
o,p'-DDT	4	93	1.3
o,p'-DDD	0.4	11	11
o,p'-DDE	3	93	1.3
DDA	0.002	0.04	3125
Chloropropylate	0.007	0.08	1562
Chlorobenzilate	0.03	0.35	357
Dicofol	0.14	2	63
Chloroxuron	24	220	0.6
Monolinuron	25	710	0.2
Thiobencarb	5	52	2
Tebuconazole	7	95	1.3
Neburon	17	280	0.4
Tetradifon	1.2	14	9
Diclofop	70	> 1000	<0.1

The following are not detected at 100 ppm:

2,4-D	Chlortoluron	Diuron
Dicamba	Chlorbromuron	MCPB
Chlordane	4-chlorophenoxyacetic acid	MCPA acid
Lindane	2,4-Dichloronitrobenzene	Linuron
Diflubenzuron	Mecoprop	

*% C.R. = % cross-reactivity = the IC50 of *p,p'*-DDT divided by the IC50 of the cross-reactant, x 100.

TABLE 2

KANSAS FIELD SITE RESULTS

Sample ID	GC Total DDT (ppm)	Immunoassay Interpretation (ppm ranges)	Agreement? (YES/NO)
61701	18	> 10 < 50	YES
61702	12	> 10 < 50	YES
61703	11	> 10 < 100	YES
61704	30	> 10 < 50	YES
61706	0.44	> 0.1 < 1	YES
61707	0.47	> 0.1 < 1	YES
61708	0.40	> 0.1 < 1	YES
61709	0.33	> 0.1 < 1	YES
60801	41	> 10 < 100	YES
60802	52	> 10 < 100	YES
60803	40	> 10 < 100	YES
60804	79	> 10 < 100	YES
60807	0.18	> 0.1 < 1	YES
60808	0.23	> 0.1 < 1	YES
60809	0.18	> 0.1 < 1	YES
01	1140	> 500 < 5000	YES
02	2755	> 500 < 5000	YES
03	245	> 50 < 500	YES
04	850	> 100 < 1000	YES
05	1832	> 500 < 5000	YES
06	1185	> 1000 < 5000	YES
07	14,375	> 5000 < 50,000	YES
08	5025	> 5000 < 50,000	YES
09	460	> 100 < 1000	YES
10	217	> 50 < 500	YES
11	536	> 200 < 2000	YES
12	308	> 50 < 500	YES
13	1316	> 200 < 2000	YES
14	1415	> 1000 < 10,000	YES
15	1204	> 200 < 2000	YES
16	1370	> 1000 < 10,000	YES
17	435	> 50 < 500	YES
18	4800	> 5000 < 50,000	NO
19	755	> 100 < 1000	YES
20	1760	> 1000 < 10,000	YES
21	115	> 20 < 200	YES
22	579	> 100 < 1000	YES
23	129	> 30 < 300	YES
24	115	> 100 < 1000	YES
25	2904	> 300 < 3000	YES
26	1512	> 200 < 2000	YES
27	< 0.1	< 0.1	YES
28	< 0.1	> 0.1 < 1	NO
29	< 0.1	< 0.1	YES
30	< 0.1	> 0.1 < 1	NO
31	0.14	< 0.1	NO
32	0.15	> 0.1 < 1	YES

TABLE 3

FLORIDA FIELD SITE RESULTS

Sample ID	GC Total DDT (ppm)	Immunoassay Interpretation (ppm ranges)	Agreement? (YES/NO)
2	3.6	> 10	NO
3	0.55	> 0.2 < 1	YES
4	2.3	> 1 < 10	YES
5	ND*	< 0.2	YES
6	0.15	> 0.2 < 1	NO
7	0.3	> 0.2 < 1	YES
8	0.1	< 0.2	YES
9	0.8	> 0.2 < 1	YES
10	0.23	> 0.2 < 1	YES
13	0.79	> 0.2 < 1	YES
14	0.58	> 0.2 < 1	YES
15	0.35	> 0.2 < 1	YES
17	ND	< 0.2	YES
20	0.18	< 0.2	YES
21	0.06	< 0.2	YES
22	ND	< 0.2	YES
23	ND	< 0.2	YES
24	1.2	> 1 < 10	YES
25	0.12	< 0.2	YES
26	ND	< 0.2	YES
27	ND	< 0.2	YES
28	0.16	< 0.2	YES
28-17D	0.18	> 0.2 < 1	NO
29	0.69	> 0.2 < 1	YES
30	0.73	> 1 < 10	NO
31	0.68	> 1 < 10	NO
32	ND	< 0.2	YES
33	0.32	> 0.2 < 1	YES
34	0.23	> 0.2 < 1	YES
35	0.52	> 0.2 < 1	YES
36	1	> 0.2 < 1	YES
41F	ND	< 0.2	YES

*ND = not detectable (< 0.05 ppm total DDT isomers).

DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN SOIL BY A MAGNETIC PARTICLE-BASED ENZYME IMMUNOASSAY.

Fernando M. Rubio, Timothy S. Lawruk, Charles E. Lachman and David P. Herzog, Ohmicron Environmental Diagnostics, 375 Pheasant Run, Newtown, Pennsylvania 18940; James R. Fleeker, North Dakota State University, P.O. Box 5516, Fargo, North Dakota 58105

ABSTRACT

Use of immunoassays as field-screening methods to detect environmental contaminants has increased dramatically over the past few years. Immunochemical assays are sensitive, rapid, reliable, cost-effective and can be used for lab or field analysis. A magnetic particle-based immunoassay system has been developed for the quantitation of Polynuclear Aromatic Hydrocarbons (PAHs) in soil. Paramagnetic particles used as the solid-phase, allow for the precise addition of antibody and rapid reaction kinetics. The magnetic particle-based immunoassay is ideally suited for on-site investigation and remediation processes to delineate PAHs contamination. This system includes easy-to-use materials for collection, extraction, filtration and dilution of soil samples prior to analysis by immunoassay. The method detects PAHs, including anthracene, chrysene, fluoranthene, phenanthrene, pyrene and benzo[a]pyrene, at sub-parts per million levels in soil. The assay procedure and detailed performance characteristics including precision, spike recovery and correlation with U.S. EPA methods are discussed.

INTRODUCTION

Polycyclic or polynuclear hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings. The U.S. EPA has selected 16 unsubstituted PAHs as Consent Decree priority pollutants for regulatory purposes. Some of the four, five and six-ring PAHs such as chrysene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene are considered to be possible or probable human carcinogens (U.S. EPA, 1985). The two and three-ring PAHs such as naphthalene, anthracene, and phenanthrene are non-carcinogenic and found as a component of certain grades of fossil fuels.

PAHs are introduced into the environment as a product of natural and fossil fuel combustion. Volcanic eruptions and forest fires are among the major sources of naturally produced PAHs. However, activities attributed to fossil fuel combustion sources, such as automobiles, coking plants, asphalt production, and manufacturing facilities that use fossil fuels, have dramatically increased the quantity of PAHs in the environment. Wood

preserving sites that use creosote as a preservative, petrochemical waste disposal sites, and leaking underground fuel storage tanks, have also contributed to the widespread contamination of PAHs in the environment.

The large number of sites contaminated with PAHs in soil and groundwater and the reenactment of key environmental legislation (Safe Drinking Water Act, Superfund Amendment Reauthorization Act) has led federal and state agencies to mandate their clean-up. The federal and state agencies have set various regulatory levels for PAHs in soil, however the usual concentrations of interest are 1 ppm and 10 ppm. The analysis of PAHs contamination in environmental samples is typically performed by GC/MS or HPLC methods which are accurate and precise but can be time-consuming and expensive. This poster describes a magnetic-particle solid-phase immunoassay method in soil samples. Immunoassays have the advantage of being rapid and less expensive than GC/MS or HPLC, as well as field-portable.

The principles of enzyme linked immunosorbent assays (ELISA) have been described (Hammock and Mumma, 1980). Magnetic particle-based ELISA's have previously been described and applied to the detection of pesticide residues (Itak et al, 1993; Lawruk et al, 1993; Itak et al, 1992; Lawruk et al, 1992; Rubio et al, 1991). These ELISA's eliminate the imprecision problems that may be associated with antibody coated plates and tubes (Harrison et al, 1989; Engvall, 1980) through the covalent coupling of antibody to the magnetic particle solid-phase. The uniform dispersion of particles throughout the reaction mixture allows for rapid reaction kinetics and precise addition of antibody. The PAHs magnetic-based ELISA described in this paper combines antibodies specific for PAHs with enzyme labeled PAHs. The presence of PAHs in a sample is visualized through a colorimetric enzymatic reaction and results are obtained by comparing the color in sample tubes to those of calibrators.

MATERIALS AND METHODS

Amine terminated superparamagnetic particles of approximately 1 um diameter were obtained from Advanced Magnetics, Inc. (Cambridge, MA). Glutaraldehyde (Sigma Chemical, St. Louis, MO). Rabbit anti-PAHs serum and PAH-HRP conjugate (Ohmicron, Newtown, PA). Hydrogen peroxide and TMB (Kirkegaard & Perry Labs, Gaithersburg, MD). PAHs and related compounds, as well as non-related cross-reactants (Chem Service, West Chester, PA).

The anti-PAHs coupled magnetic particles were prepared by glutaraldehyde activation (Weston and Avrameas, 1971). The unbound glutaraldehyde was removed from the particles by magnetic separation and washing four times with 2-(N-morpholino) ethane sulfonic acid (MES) buffer. The PAHs antiserum and the activated particles were incubated overnight at room temperature with agitation. The unreacted glutaraldehyde

was quenched with glycine buffer and the covalently coupled anti-PAHs particles were washed and diluted with a Tris-saline/gel preserved buffer.

The various PAHs compounds used during cross-reactivity studies were diluted in DMF to obtain a stock concentration of 1 mg/mL. The stock was further diluted in PAH diluent to obtain concentrations of 10 , 1, 0.1, 0.01, 0.001, and 0.0001 ppm. The creosote sample was diluted in methanol to obtain a stock concentration of 1 mg/mL, the stock was further diluted as listed previously. After dilution, the diluted compounds were analyzed as samples in the assay.

When analyzing soil samples, a simple extraction is performed prior to analysis: 10 g of soil and 20 mL of a methanolic solution are added to a soil collector (Figure 1). The collector was shaken vigorously for 1 minute and the mixture allowed to sit at least five minutes. The cap of the soil collector was then replaced with a filter cap and the extract collected in a small glass vial. The filtered extract was then diluted 1:50 in PAH zero standard and assayed.

Diluted soil extract sample (250 uL) and horseradish peroxidase (HRP) labeled PAHs (250 uL) were incubated for 30 minutes with the antibody coupled solid-phase (500 uL) (step 1). A magnetic field was applied to the magnetic solid-phase to facilitate washing and removal of unbound PAHs-HRP and eliminate any potential interfering substances (step 2). The enzyme substrate (hydrogen peroxide) and TMB chromogen (3,3',5,5'-tetramethyl benzidine) were then added and incubated for 20 minutes (step 3). The reaction was stopped with the addition of acid and the final colored product was analyzed using the RPA-I RaPID Analyzer™ by determining the absorbance at 450 nm. The observed absorbance results were compared to a linear regression line using a log-logit standard curve prepared from calibrators containing 0, 2.0, 10.0, and 50.0 ppb of phenanthrene. If the assay is performed in the field (on-site), a battery powered photometer such as the RPA-III™ can be used.

RESULTS AND DISCUSSION

Figure 2 illustrates the mean standard curve for the PAHs calibrators collected over 30 runs; error bars represent two standard deviations (SD). This figure shows the typical response of the assay and the reproducibility of the standard curve from run-to-run. The displacement at the 2.0 ppb level is significant (81.3% B/Bo, where B/Bo is the absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard). The assay sensitivity in diluent based on 90% B/Bo (Midgley et al, 1969) is 0.70 ppb. When analyzing soils with PAH Sample Extraction Kit, the assay has a range of 0.20 ppm to 5 ppm as a result of sample dilution.

In a precision study conducted using diluent buffer fortified with phenanthrene at 4 concentrations, the samples were assayed 5 times in singlicate per assay on five different days. The results are shown in Table 1. Coefficients of variation (%CV) within and between day (Bookbinder and Panosian, 1986) were less than 10% and 15% respectively.

In another precision study, ten samples of two soils were weighed on a balance or measured by packed volume in the soil collector. The samples were then extracted and diluted (as described in the Methods Section), followed by assaying in duplicate in one assay. Results are shown in Table 2. The overall coefficient of variation for PAHs measurement using components of the Soil Collection and the PAHs Soil Extraction Kit with analysis by the PAHs RaPID Assay® was determined to be less than 18% in both cases.

Table 3 and Figure 3, summarize the cross-reactivity data of the PAHs RaPID Assay for various polynuclear aromatic hydrocarbons and petroleum products. The percent cross-reactivity was determined as the amount of analog required to achieve 50% B/Bo. The broad specificity of the antibody used, allows for the detection of a majority of the PAHs. Many non-structurally related organic compounds demonstrated no reactivity at concentrations up to 10,000 ppb (data not shown).

Table 4 summarize the accuracy of the PAHs RaPID Assay in soil samples. Thirteen different soil types were fortified with phenanthrene at 1 ppm. The samples were extracted and diluted as described above, followed by analysis in the immunoassay. The average recovery of phenanthrene in the samples was 108% with one sample (Alkali Lake) given higher recoveries; the reason for the higher recovery on that sample is currently under investigation. To demonstrate the detection of other PAHs in soil, anthracene, benzo[a]pyrene, chrysene, fluoranthene, and pyrene, were spiked into four soils at 1 ppm; recoveries of those PAHs (data not shown) agreed closely with the predicted response based on the previously reported cross-reactivity data for the assay.

Correlation of twenty five samples, including both field contaminated soils and analytically spiked soils analyzed by the ELISA method (y) and HPLC EPA Method 8310 (x) is illustrated in Figure 4. The regression analysis yields a correlation of 0.931 and a slope of 2.02 between methods.

SUMMARY

This work describes a magnetic particle-based ELISA for the detection of PAHs and its performance characteristics using soil samples. The assay compares favorably to HPLC determinations, is faster, and eliminates the need for expensive instrumentation and solvent disposal. The ELISA exhibits good precision and accuracy which can provide consistent monitoring of environmental samples. Using this ELISA, fifty (50) results from soil

monitoring of environmental samples. Using this ELISA, fifty (50) results from soil samples can be obtained in less than two hours without the variability encountered with antibody coated tubes and microtiter plates (e.g. coating variability, antibody leaching, etc.). This system is ideally suited for adaptation to on-site monitoring of PAHs in water, soil, and solid waste samples.

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Table 1

Precision of PAHs Measurement in Diluent

Pool Number	Pool 1	Pool 2	Pool 3	Pool 4
Replicates	5	5	5	5
Days	5	5	5	5
N	25	25	25	25
Mean (ppb)	5.48	8.67	21.98	42.08
% CV (within)	9.2	7.2	5.6	5.5
% CV (between)	12.5	14.5	13.7	10.9

Table 2

Precision of PAHs Measurement in Soil

Soil:	Wisconsin		Joshua Tree	
Sample Collection Method	weight	volume	weight	volume
Replicates	10	10	10	10
Mean (ppm)	1.57	1.18	1.43	1.26
% CV (total)	17.6	17.8	14.3	14.4

Table 4

Phenanthrene Recovery From Different Soil Types

Soil Sample	Neat (ppm)	Total (ppm)	Recovered (ppm)	Recovery (%)	Soil Type
Alkali Lake	0.50	2.19	1.69	169	loamy sand
Beardon	0.42	1.45	1.03	103	clay loam
Holland	2.30	3.22	0.92	92	silt loam
Joshua Tree	0.07	1.28	1.21	121	sand
Levittown	4.70	5.82	1.12	112	silt loam
Muck	2.90	3.94	1.04	104	organic potting
Munin	0.17	1.23	1.06	106	clay loam
Piscataway	2.69	3.67	0.98	98	sandy loam
Sagamore	4.40	5.56	1.16	116	silty clay loam
Sharkey	0.68	1.92	1.24	124	clay loam
Tennessee	0.30	1.29	0.99	99	sandy loam
Wiscosin	0.72	1.80	1.08	108	loam
Virginia	1.54	2.64	1.10	110	loamy sand
Mean			1.12	108	
SD			0.19		
%CV			17.1		

Table 3

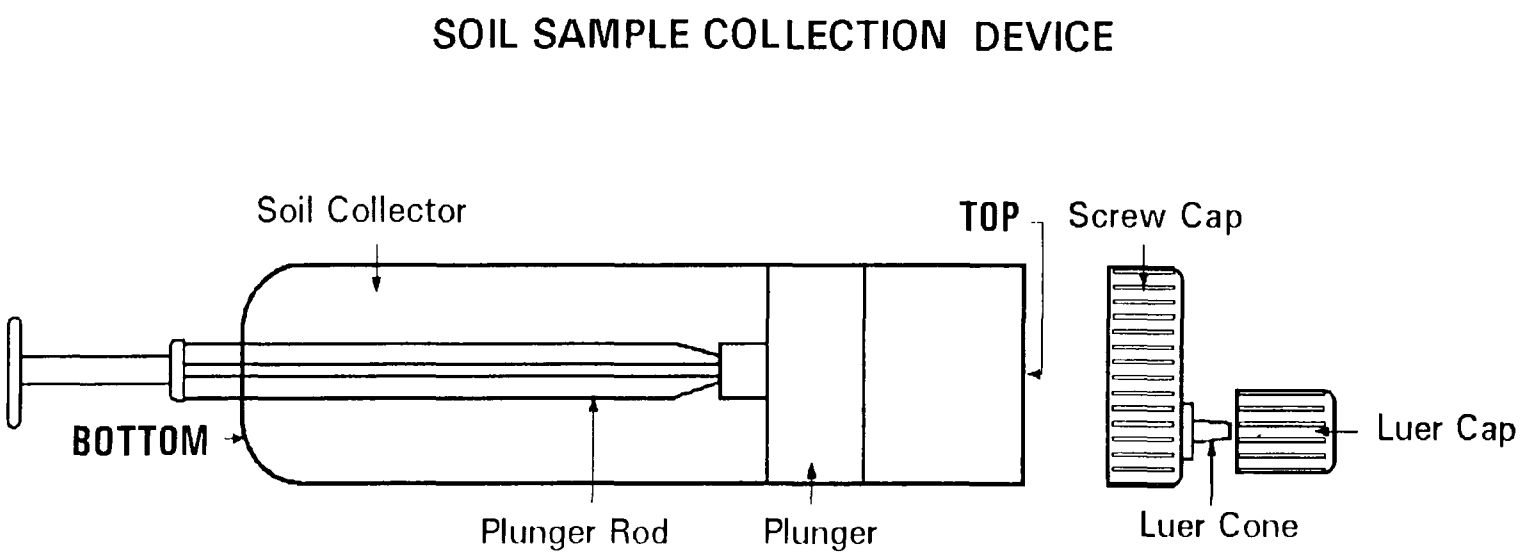
Specificity (Cross-Reactivity)

Compound	90% B/Bo LDD (ppb)	50% B/Bo ED50 (ppb)	% Cross Reactivity
Phenanthrene	0.70	16.5	100
Anthracene	0.54	12.5	132
Fluoranthene	0.32	4.7	351
Chrysene	0.40	7.8	212
Pyrene	0.70	15.1	214
Benzo(a)Pyrene	0.50	6.9	239
Fluorene	1.65	35.2	47
Benzo(b)fluoranthene	0.91	54.2	30
Benzo(k)fluoranthene	0.77	524	3
1,12 Benzoperylene	14.7	>1000	<2
1,2:5,6 Dibenzanthracene	25.7	>1000	<2
Indeno (1,2,3-c,d)pyrene	0.78	27.2	61
Naphthalene	65	>1000	<2
Acenaphthalene	12.9	688	2
Acenaphthylene	10	447	4
1.2 Benzanthracene	0.77	28.4	58
1-Methylnaphthalene	28.2	1330	1.2
2-Methylnaphthalene	28.2	802	2.1
Aroclor 1242	37.5	1450	1.8
Aroclor 1248	41.0	5330	0.4
Aroclor 1254	>10000	>10000	<0.2
Aroclor 1260	>10000	>10000	<0.2
Benzene	>10000	>10000	<0.2
Toluene	>10000	>10000	<0.2
Phthalate	>10000	>10000	<0.2
Pentachlorophenol	340	>10000	<0.2
Biphenyl	15.9	703	2.8
CCA	>10000	>10000	<0.2
Creosote	1.1	16.6	117
Fuel Oil #6	5	53.7	31
Gulf Diesel Fuel	19.6	497	3
Sunoco Home Heating Fuel	12.8	292	6
Kerosine	1250	>10000	<0.1
Jet A Fuel	>10000	>10000	<0.1
Regular Gasoline	1000	>10000	<0.1
Premium Gasoline	597	>10000	<0.1

Figure 1. Diagram of soil collector used to collect and extract soil samples.

Figure 2. PAHs RaPID Assay dose response curve. Each point represents the mean of 30 determinations. Vertical bars indicate +/- 2 SD about the mean.

Figure 3. Specificity of the PAHs RaPID Assay against selected polynuclear aromatic hydrocarbons and creosote.



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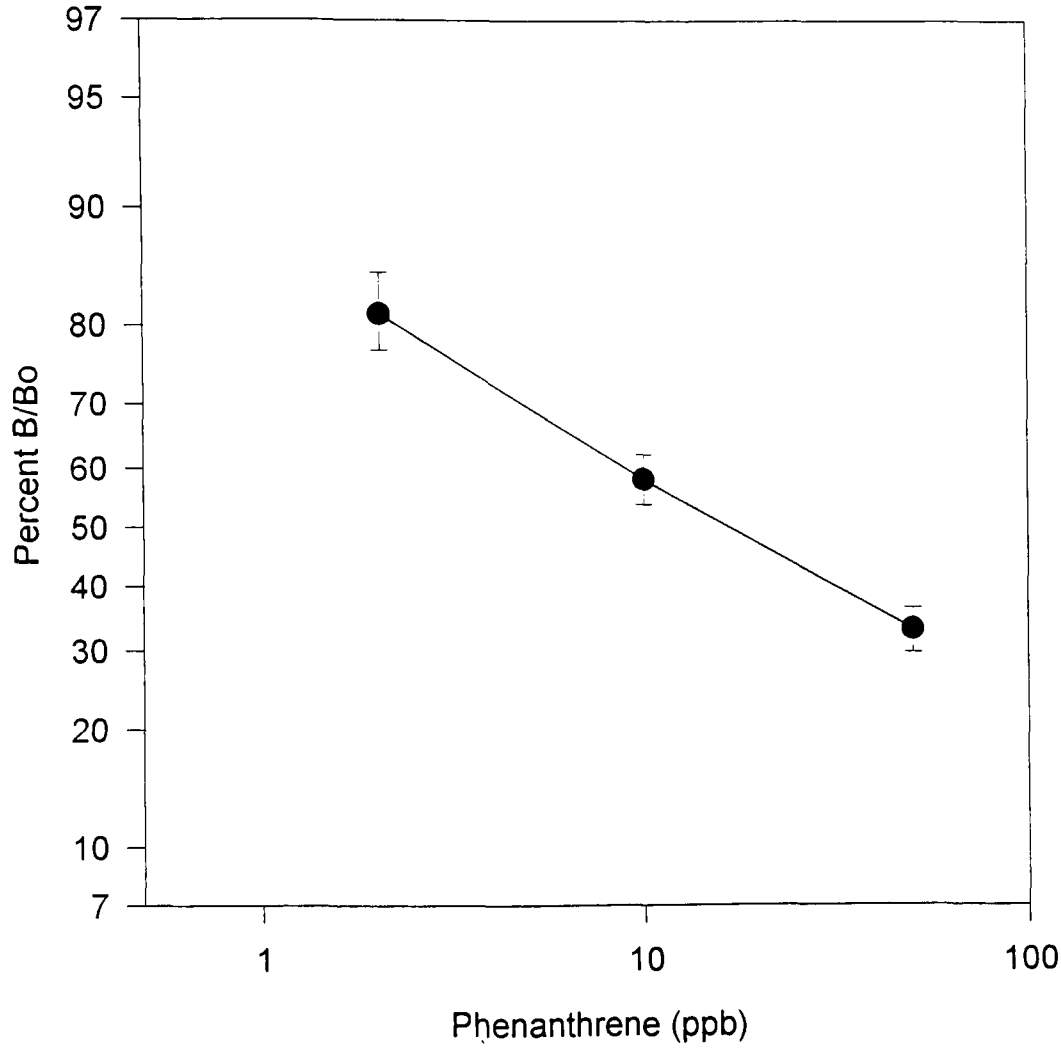

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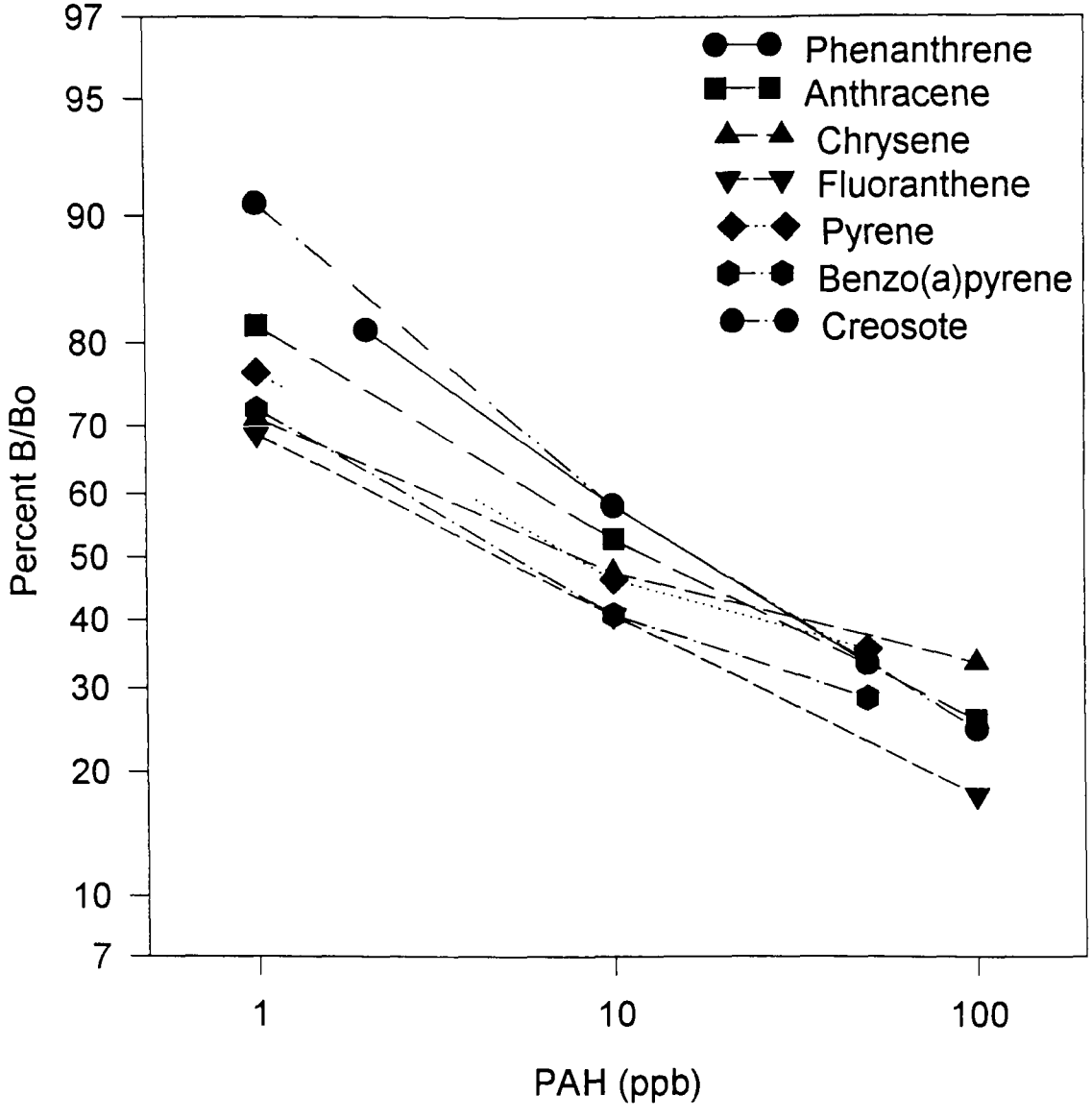

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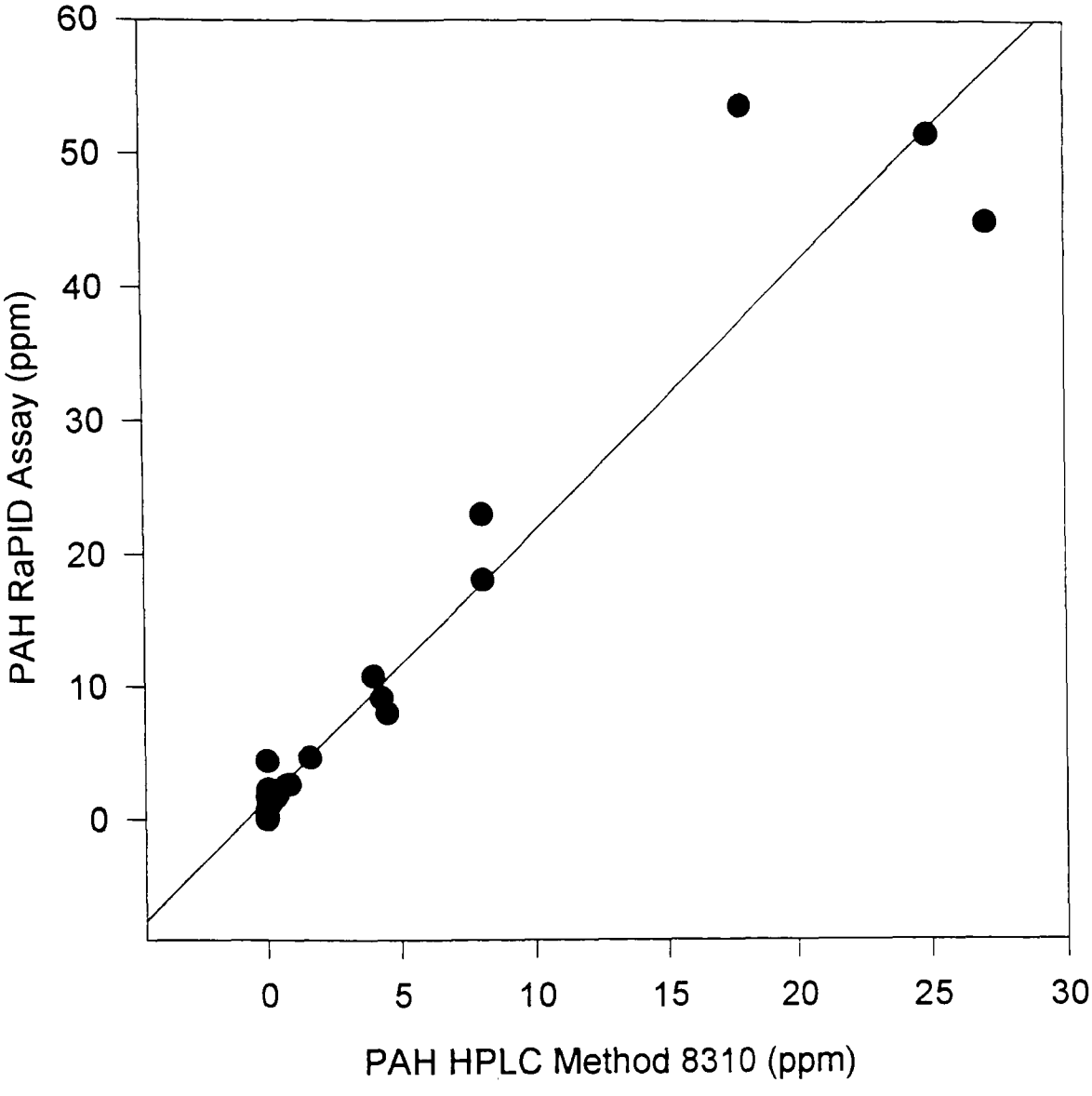

Figure 4. Correlation between PAH's concentrations as determined by the ELISA and HPLC Method 8310 in soil samples. n = 25, r = 0.931, y = 2.02x + 1.55.

LABORATORY EVALUATION OF IMMUNOASSAY PCB TESTS

Mark L. Bruce and Raymond M. Risden, Enseco, 4101 Shuffel Dr. NW, North Canton, OH 44720, Randolphe P. Swenson Jr., Enseco, 5251 DTC Pkwy Suite 415, Englewood, CO 80111, Kevin R. Carter, EnSys Environmental Products Inc., Box 14063, Research Triangle Park, NC 27709.

ABSTRACT

Immunoassay (IA) results were generally a factor of two higher than the GC-ECD results for the same PCB extract for the 41 samples studied. The manual assay procedure used for this study should be accurate enough to predict proper dilution levels for final GC-ECD analysis. The manual solvent exchange and assay requires less than 4 minutes of labor per sample. Equipment cost for the assay is minimal. The preliminary cost estimates indicate that immunoassay should be considered as a viable alternative to gas chromatography for internal PCB screening.

INTRODUCTION

Environmental concerns and economic forces are exerting pressure on the environmental analysis market to reduce turn-around times and costs. At the same time, some data users have realized that traditional QA/QC requirements are not necessary for all environmental decisions. One area ripe for streamlining time and cost is laboratory sample screening.

Several companies have adapted immunoassay (IA) to test environmental pollutants in order to bring IA's advantages to environmental analysis. IA has been widely used in the health sciences field where it has proven to be a low cost, fast turn-around, high capacity analysis technology.

These same characteristics make it very attractive for environmental testing. Immunoassay does not provide data that is identical to the traditional GC, LC and GC/MS tests. The specificity of IA should make it less susceptible to the interferences that limit chromatographic analyses. However, the biochemical nature of IA makes it sensitive to *new* interferences. The QA/QC data normally available from IA includes replicates and matrix spikes, but not internal standards or surrogates. This QA/QC reduction may not be acceptable to all data users. The IA response for multicomponent analytes such as PCBs, TPHs and PAHs changes as the composition of the mixture varies. Thus, the analytical accuracy for an unknown mixture will be reduced. The assay does not identify the components in the mixture. Some data users may view this reduced amount of information as lower quality data, but it should be more than adequate for many environmental decisions.

The current project focused on shortening sample turn-around time and reducing cost in the analysis of PCBs. We examined the IA PCB test as a replacement for GC in screening samples to determine the proper extract dilution for final analysis. This would be most useful to a lab that currently performs a high percentage of dilutions. This use for IA would be relatively fast to implement since no external approval would be required. IA could also be used for the final analysis under certain circumstances. In this case IA would replace a corresponding GC test. This use would produce the greatest time and cost savings. However, it would also require regulatory and client approval.

We examined the PCB results for about 10,000 samples analyzed at Enseco-North Canton. Most frequently no Aroclors were detected. About 16% of the time dilutions were required to bring the Aroclor concentration into the calibration range of the GC-ECD. Also, some samples reported as non-detect were diluted because of interferences. Other Enseco facilities estimate 20-30% dilution rates. GC instrument maintenance tends to increase if highly concentrated samples are injected. Thus quick, effective and inexpensive screening is needed to preserve the *health* of the GC used for final analysis.

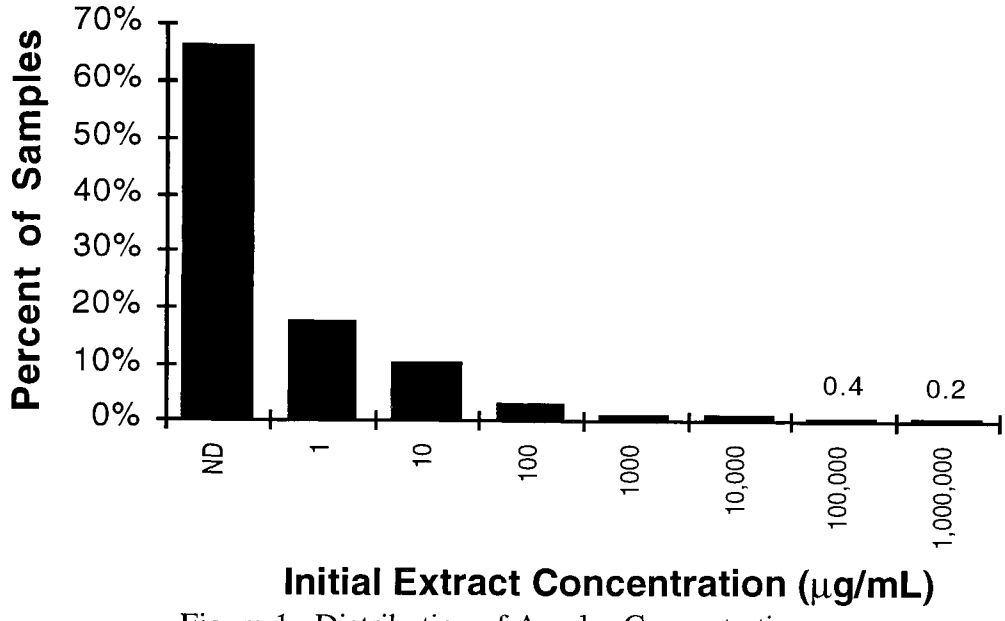

Figure 1. Distribution of Aroclor Concentrations.

The frequency of various Aroclor types and the IA sensitivity differences indicated that calibration with Aroclor 1248 was the best compromise. Samples analyzed in North Canton contained Aroclors 1242 and 1254 most frequently (Figure 2). According to EnSys, immunoassay response (sensitivity) with their kit varies as the Aroclor mixture changes. Table 1 has been normalized to 1248.

Table 1. Aroclor Response Differences

Aroclor	Relative Response†
1016	0.25
1232	0.25
1242	0.5
1248	1.0
1254	2.5
1260	2.5

† Higher number means more sensitive

EXPERIMENTAL

All samples were extracted with 3500 series SW-846 sample preparation techniques. The extracts were cleaned with 3600 series clean-up techniques prior to gas chromatographic analysis by method 8080 or 8081. These same extracts were then solvent exchanged from hexane to methanol and analyzed with immunoassay supplies developed by EnSys

for their field PCB kit. The EnSys PCB RIS$\underline{c}$® test is a chromogenic enzyme-linked immunosorbent assay (ELISA). The monoclonal antibody was produced to respond (i.e., bind) to a particular subset of the pentachlorobiphenyl congeners. As the pentachlorobiphenyl composition varies from one Aroclor mixture to the next, the sensitivity of the IA method changes. This is analogous to quantitating a PCB chromatogram using only the pentachlorobiphenyl peaks. Those Aroclors that have a high percentage of pentachlorobiphenyl have the best sensitivity.

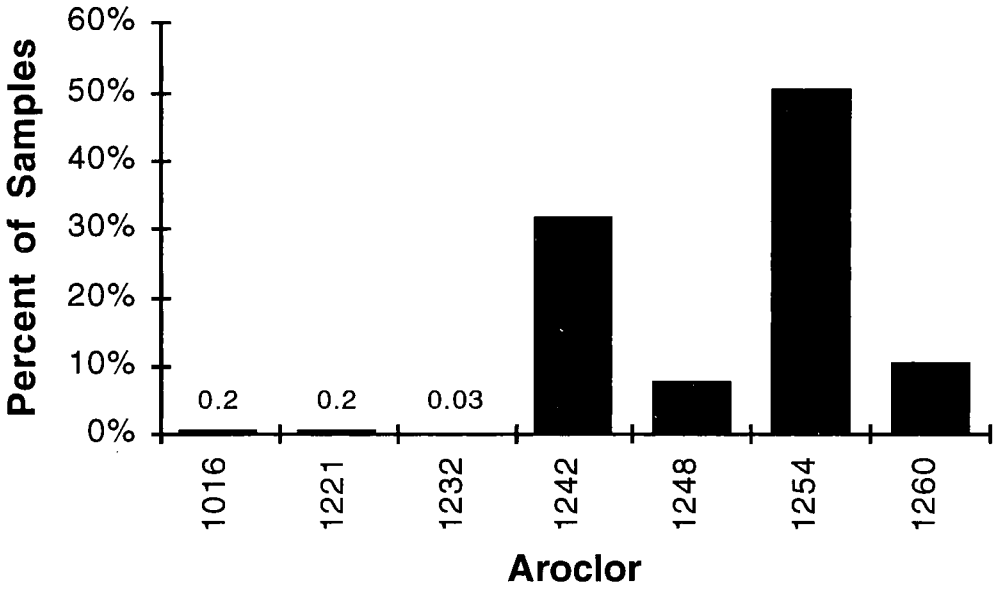

Figure 2. Frequency of Various Aroclors

The EnSys PCB kit uses an antibody immobilized on polystyrene tubes. This technique is a semicompetitive immunoassay where the antibodies are exposed to sample analytes. Later, enzyme conjugate is added to the same solution. This procedure summarized below was based on EnSys experience and chosen as starting point to determine the best compromise between analysis speed, accuracy, precision and cost. This process is completely manual using standard syringes and repeating single channel pipettes.

1) Set up buffer and antibody tubes in rows of 6. Do not exceed 5 rows.
2) Transfer 30 µL of standard, blank or sample extract into the buffer tube. Mix.
3) Transfer buffer tube contents to the antibody tubes. Mix and wait 10 minutes.
4) Dispense enzyme conjugate, mix and wait 5 minutes.
5) Wash antibody tubes thoroughly with dilute buffered detergent solution.
6) Add substrate A to antibody tubes.
7) Add substrate B to antibody tubes, mix and wait 2.5 minutes.
8) Add stop solution to antibody tubes.
9) Measure and record absorbance at 450 nm.

The sample extracts were exchanged to methanol (Fisher Optima grade or Burdick & Jackson Purge and Trap grade) by two different procedures. Early sample batches were exchanged from hexane to methanol using K-D concentration/exchange followed by nitrogen blowdown as described in SW-846 3500 series methods. Later extracts used a

simplified exchange procedure which was acceptable for high boiling analytes such as PCBs. Hexane extract (200 µL) was evaporated to dryness in a microvial using a gentle stream of nitrogen. The PCBs were then redissolved in 200 µL of methanol. Dilutions were prepared from this exchanged extract as needed. The samples were assayed singly in the same batch as replicate standards and blanks.

The standard SW-846 solvent exchange was time and labor consuming. The simplified exchange was adopted to reduce solvent requirements, accelerate the process and reduce labor. The evaporate to dryness exchange procedure showed no significant PCB losses when several 1248 standards were evaporated to dryness and redissolved in methanol.

RESULTS AND DISCUSSION

Calibration

The routine immunoassay calibration procedure consisted of replicate analyses of 3 Aroclor 1248 standards and a blank. Absorbance of the standard was plotted against the $\log_{10}$ of the standard concentration. This semilogarithmic calibration produced a straight line with a negative slope. Many traditional immunological calibration procedures plot % B/B_0 versus $\log_{10}$ (concentration). The absorbance of the standard (or sample) is divided by the absorbance of the blank and expressed as a percentage (% B/B_0). Since this scaling process does not affect the final calculated result, we decided to use the original absorbance readings, which are more familiar to environmental lab personnel.

A duplicate six point calibration from 20 to 400 ng/mL was constructed for Aroclor 1248. The semilog calibration was linear throughout the majority of the range with only a small amount of curvature at the extremes. The calibration *equation* was;

$$\text{absorbance} = 3.22 - 1.11 \bullet \log(\text{concentration})$$

The correlation coefficient (r) of the least squares line was 0.976. Subsequent calibrations consisted of duplicate measurements at three concentration levels (20, 70, 200 ng/mL). The calibration line equations were;

$$\text{absorbance} = 3.19 - 1.04 \bullet \log(\text{concentration}) \qquad r = 0.993$$

$$\text{absorbance} = 2.74 - 0.92 \bullet \log(\text{concentration}) \qquad r = 0.979$$

$$\text{absorbance} = 2.52 - 0.89 \bullet \log(\text{concentration}) \qquad r = 0.972$$

The average deviation between replicate assays of standards was 17%.

Samples

Soil sample extracts (41) were solvent exchanged as described above. Each extract was assayed once in conjunction with duplicate assays of three calibration standards and a blank. The results from the immunoassay are compared with the corresponding GC-ECD results in Table 2. Figure 4 graphs the same data in a log-log plot. The diagonal line represents 1 to 1 correspondence between the IA and GC results. The shaded region of the graph covers IA/GC ratios between 2:1 and 1:2. Typically the IA concentration estimate was about two times higher than that determined by GC-ECD. The high 1254 IA concentration was expected because of the sensitivity difference between the calibrant (1248) and sample analyte (1254). Refer to Table 1. The 1248 IA results were higher than expected in some extracts. This could have been caused by differences in the pentachlorobiphenyl composition of the calibrant and native Aroclor in the samples. Also, there may be interferences in the sample extracts which resulted in the occasional positive bias. Small errors in the extract solvent exchange process may account for part

of the difference, as well. Four extracts which had no PCBs detected by GC-ECD were analyzed by IA. These waste dilution extracts contained many chromatographic interferences. The IA results were all below the GC reporting limit. Thus, the IA showed no tendency toward false positives for these samples.

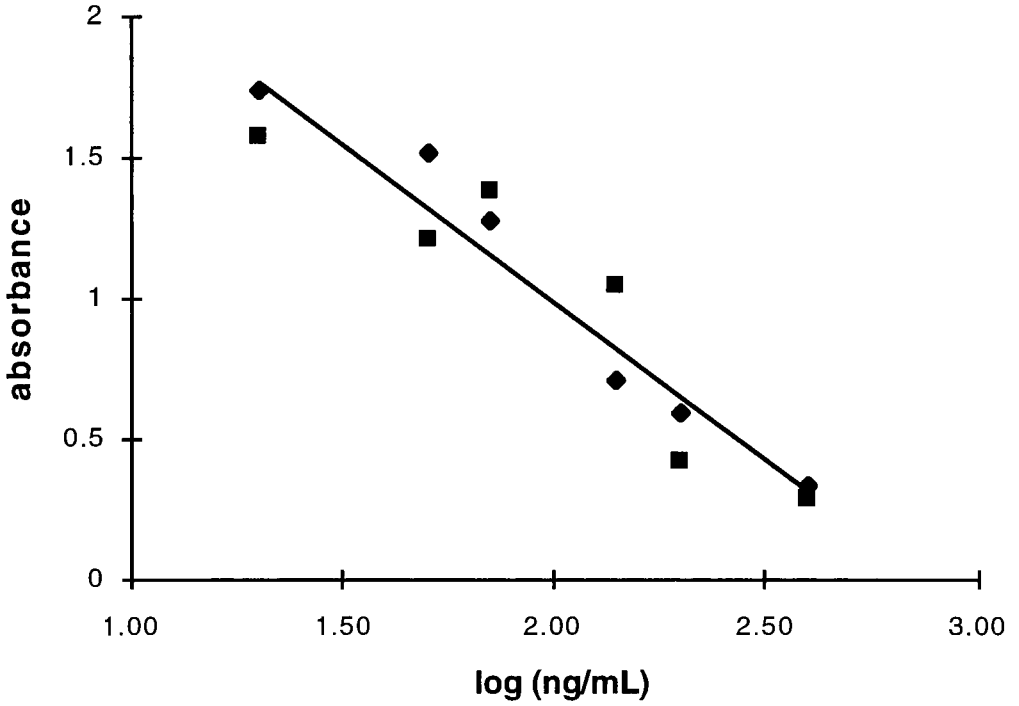

Figure 3. Aroclor 1248 Calibration.

Despite the differences between the GC-ECD and immunoassay results, the IA data were generally accurate enough to predict the proper dilution level for final GC-ECD analysis. Since the IA data were sometimes much higher than the GC data this would occasionally lead to over diluting the extract for final analysis. Sporadic over dilution is preferable to under dilution since GC reliability and maintenance should not be effected.

This manual immunoassay procedure was sensitive to analyst technique. Raw data often did not compare well from person to person. However, if the calibrants were prepared in the same batch as the samples by the same person then acceptable accuracy was achieved. Data reproducibility was very dependent on the consistency of the analyst. Partial or full automation should improve precision significantly.

Screening a batch of 16 samples by GC-ECD required about 8 hours including 45 minutes of labor to prepare the extracts, interpret the data and calculate the results. IA required about one hour to completely process a batch of 16 samples. Since this form of IA was completely manual the labor time was also one hour. The capital requirements were much lower for IA since the only instrument required was a small spectrophotometer. A detailed cost analysis has not been completed yet, but the initial estimates indicate that IA should be quicker and less costly than GC for extract screening.

Table 2. Comparison of GC-ECD and Immunoassay Data.

Extract #	Aroclor	GC conc (mg/kg or L)	IA conc (mg/kg or L)	IA/GC ratio
1	1248	34	80	2.4
2	1248	1.4	4.3	3.1
3	1248	14.0	30.2	2.2
4	1248	1.4	2.9	2.1
5	1248	2.3	2.6	1.1
6	1248	94.0	103.9	1.1
7	1248	3.0	7.9	2.6
8	1248	1400.0	1391.6	1.0
9	1248	2.3	1.9	0.8
10	1248	20.6	11.8	0.6
11	1248	29.7	31.2	1.1
12	1248	2.2	2.4	1.1
13	1248	7.0	12.1	1.7
14	1248	948.3	2905.1	3.1
15	1248	1.3	6.5	5.0
16	1248	0.4	1.3	3.0
17	1248	528.8	1777.8	3.4
18	1248	5.5	7.6	1.4
19	1248	27.7	66.6	2.4
20	1248	5.6	6.3	1.1
21	1248	3167.8	4181.4	1.3
22	1248	981.4	1483.6	1.5
23	1248	19.9	7.8	0.4
24	1254	20.0	60.0	3.0
25	1254	14.0	57.4	4.1
26	1254	7.7	22.6	2.9
27	1254	1.6	2.5	1.5
28	1254	15.0	20.2	1.3
29	1254	7.1	13.3	1.9
30	1254	8.1	13.0	1.6
31	1254	9.8	31.2	3.2
32	1254	1.0	0.9	0.9
33	1254	1.3	1.6	1.2
34	1254	3.9	6.3	1.6
35	1254	14.0	17.1	1.2
36	1254	0.00024	0.00065	2.7
37	1254	0.00022	0.00048	2.2
38	ND by GC	<0.5	0.4	
39	ND by GC	<0.5	0.1	
40	ND by GC	<0.5	0.1	
41	ND by GC	<0.5	0.1	
			Average Ratio =	2.0

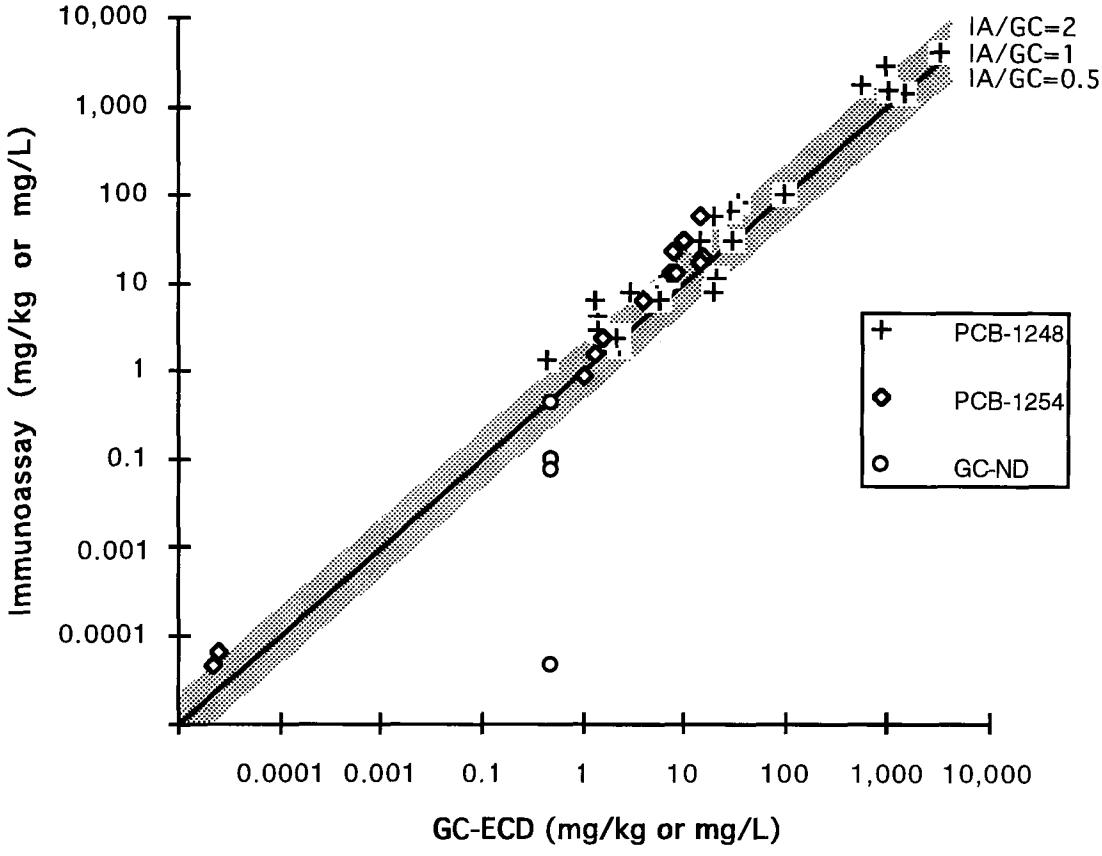

Figure 4 Comparison of Immunoassay Results to GC-ECD Results.

CONCLUSION

Immunoassay results were generally within a factor of two of the GC-ECD results for the same extract. This indicates that IA should be accurate enough to predict proper dilution levels for final GC-ECD analysis. The manual exchange and assay requires less than 4 minutes of labor per sample. Equipment cost for the assay is minimal. The preliminary cost estimates indicate that immunoassay should be considered as a viable alternative to gas chromatography for internal PCB screening.

ACKNOWLEDGMENT

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DETERMINATION OF TRICHLOROETHYLENE BY IMMUNOASSAY

Titan S. Fan, ImmunoSystems Inc, Millipore Corporation, Scarborough, ME 04074; Barbara Young, Millipore Corporation, Bedford, MA 01730; Robert E. Carlson, ECOCHEM Research Inc, Chaska, MN 55318-1043.

ABSTRACT

A competitive enzyme immunoassay (EIA) has been developed for the determination of trichloroethylene (TCE). TCE derivatives were attached to carrier proteins, and these immunogens were used to raise anti-TCE antisera in rabbits. The antisera were used in combination with enzyme labelled heterologous TCE derivatives to develop an EIA that is specific for TCE. Selected antisera and enzyme conjugates have been incorporated into an assay that is similar to our previous PCB, PAH, and Petroleum Fuels test kits for the field analysis of soil, water , and other matrices. Preliminary studies indicate good specificity for TCE. The assay has a working sensitivity range of ppb to ppm, which is suitable for the analysis of TCE in soil and water.

IMPORTANT FACTORS IN ENHANCING SUPERCRITICAL FLUID EXTRACTION EFFICIENCIES FOR ENVIRONMENTAL APPLICATIONS

Dr. Joseph M. Levy, Vice President of Technology and Customer Support; Lori A. Dolata, Technical Specialist; Robert M. Ravey, Application Chemist; Victor Danielson, Application Chemist; Anita Cardamone, Application Chemist; Suprex Corporation, 125 William Pitt Way, Pittsburgh, PA 15238

ABSTRACT

Supercritical fluid extraction (SFE) has a broad range of applicability, especially with regards to environmental matrices. SFE has achieved a significant amount of attention due to the benefits of eliminating toxic, liquid solvent usage, reduction in sample preparation time and an increase in the overall analytical reliability of determinations. SFE/GC-MS, GC-FID and IR are powerful techniques to accurately analyze and quantitate environmental analytes in soils and other solid wastes. The off-line transfer of SFE effluents to collection vials adds a considerable amount of flexibility in characterizing complex matrices since a full complement of analytical tools can be used (ie, GC, LC, IR, NMR and UV). Moreover, the advantages of SFE can be further augmented by the use of sequential automation for greater sample throughput for large volume sample preparation, statistical replicate analysis, and optimization of SFE operational parameters, which can be especially important for environmental applications.

Examples will be presented in this paper showing the use of SFE/GC-MS, GC-FID and IR methodologies for the quantitative determination of different target analytes in environmental matrices, such as polynuclear aromatic hydrocarbons (PAH), and total petroleum hydrocarbons (TPH) in soil.

INTRODUCTION

Before most chemical analyses can be performed, some type of extraction is usually required to remove suspected environmental contaminants from their particular environment matrix (ie, soil) and often this is a time-consuming and costly step. One of the most common extraction methods used in the US Environmental Protection Agency is SW 846 which often requires long extraction times (up to 24 hours for Soxhlet methods), large quantities of toxic organic solvents, (ie, Freon, methylene chloride) and lengthy solvent concentration or clean-up procedures. Historically, sample preparation involves as much as 75% of the total analysis time. Although much information has been published on SFE (1-15), little guidance is available for analysts who want to incorporate this powerful sample preparation technology into quantitative analytical methods. This includes all segments of the extraction process (ie, analyte removal, analyte transfer, and analyte collection). The fact that SFE with carbon dioxide (CO_2) has been touted as the solution to the organic solvent waste disposal problem, and that SFE is fast makes this methodology attractive for the analytical environmental laboratory of the 21st century. The successful collection of extracted analytes after SFE affords tremendous analytical flexibility in terms of the ability to collect into media that are suitable for subsequent

chromatographic or spectroscopic characterization. In some cases this can be done without any additional liquid solvent where the supercritical CO_2 vaporizes and only collected target analytes remain.

Supercritical fluids possess favorable physical properties that are intermediate between those of the gas and liquid states. These physical properties (high diffusion coefficients, low viscosities, high densities and zero surface tension) result in the rapid and efficient mass transfer of target analytes from the sample matrix into the extraction solvent. Liquids have higher surface tension, which often inhibit the timely penetration of liquid solvent molecules into the pores of a heterogeneous sample matrix (ie, soils). For this reason, Soxhlet extractions of soils for example, often need to be performed for many hours (8-24 hours) to allow for the physical penetration of a liquid solvent (ie, methylene chloride) into a typical porous matrix (ie, soil). Supercritical fluids, on the other hand, have no surface tension limitations which allow for a rapid penetration (minutes and not hours) of a sample matrix to achieve equal to or very often greater than the extraction efficiencies that a liquid solvent could achieve.

EXPERIMENTAL

A stand-alone manual supercritical fluid extraction system (PrepMaster®, Suprex; Pittsburgh, PA), which has been described earlier (15), and a sequentially automated supercritical fluid extraction system (AutoPrep-44™, Suprex; Pittsburgh, PA) were used for all of the extraction experiments. Extractions were accomplished with various sizes of extraction vessels (0.5 to 10 mL) using operating conditions that are listed in the text. An off-line collection module, (AccuTrap®, Suprex) was used to perform the cryogenic solid phase trap collection (6,7) for both the manual and automated systems. This collection module included the following components: a VariFlow™ (Suprex) automatically variable restrictor (kept at 50°C) which controlled the CO_2 flow rates (from 1 to 7 mL/minute compressed), a temperature-controlled solid phase trap packed with unibeads and C18 modified silica for analyte trapping, a liquid pump for delivering an appropriate wash solvent for analyte desorption, and a solenoid valve for delivering a stream of nitrogen to purge the adsorbent trap and connecting tubing after desorpton.

RESULTS AND DISCUSSIONS

SFE has been successfully applied for the extraction of environmental target analytes in soil, sand, silt, clay, fly ash, sludge, petroleum waster, river sediment, urban dust, diesel exhaust particulate, tar pitch, fish, grain and vegetable matrices. The target analytes that have been successfully extracted include the following general categories:

Polynuclear aromatic hydrocarbons (PAH)
Total petroleum hydrocarbons (TPH)
Pesticides
Polychlorinated biphenyls (PCBs)
Polychlorinated dibenzofurans (PCDFs)
Polychlorinated dibenzo-p-dioxins (PCDDs)

In order to perform successful extractions of these envrionmental categories from "wet" soils (>1% water), various approaches as shown in Table 1 have been employed to either remove or immobilize water.

Table 1: Approaches to Performing SFE of Wet Soils
• Adsorbent use • Pre-heating, freeze-drying, or air drying • Pre-extraction at low densities • Secondary effluent adsorbent filter

Many naturally incurred soils contain water which historically has been problematic in SFE due to the freezing of water in the restrictor tip after undergoing expansive cooling. This ultimately has resulted in plugging of the restrictor or have caused problems in maintaining extraction flow rates after vessel frits became blocked. Dehydration techniques have been time consuming and could promote the loss of volatile or semi-volatile analytes. Adsorbents have been used successfully to retain water such as hydro-matrix (diatomaceous earth), magnesium sulfate, sodium sulfate, calcium chloride, molecular sieve and silica inside the extraction vessel (16). Moreover, new developments in restrictor technology have further increased the likelihood of extracting wet soils. Specifically, utilizing the Variflow™ automatically variable restrictor with or without adsorbents (hydromatrix), soils with TPH (total petroleum hydrocarbons) and PAH (polynuclear aromatic hydrocarbons) contamination and 20 to 50% water content have been efficiently extracted using the sequentially automated SFE without flow inhibition problems. Historically, these sample types would cause restrictor plugging for conventional linear, fixed restrictors due to the freezing of the water at the point of decompression. Moreover, results were difficult to quantitatively replicate between lab sites since the restrictor operation was dependent on the operator's dexterity or level of experience. Analytical gas chromatographic results highlighting PAH and TPH contaminated native wet soil extractions are shown in Figures 1-3. Each of these results demonstrates the ability to load the sample as received in the extraction vessel without any sample pretreatment when utilizing the automatic variable restrictor. Thermally, both the restrictor and the solid phase trap were maintained at 100°C to keep the water as a vapor after decompression. The excess water was collected in an additional wash vial. Moreover, for each of these soils, analytical precision of < 5% RSD was demonstrated when performing replicate extractions on the automated SFE (16 replicates for the PAH contaminated soil and 24 replicates for the TPH contaminated clay).

Recent results have indicated that specific solid phases for off-line trapping can distinctly affect overall SFE efficiencies. Table 2, for example, shows the comparison between C18 modified silica and silanized glass bead solid phase traps used for the off-line SFE collection of extracted TPH from soils. When compared to the reference value after IR analysis, the C18 trap provided the closest agreement for the effective collection and desorption of the diesel range organics.

Table 2: Automated SFE/IR of TPH in Soils*
(C18 Modified Silica vs. Glass Beads Solid Phase Traps)

Replicates	Concentration (ppm) C18	Glass Beads
1	408	280
2	441	293
3	451	291
4	435	272
5	472	277
6	455	278
7	435	287
8	432	251
9	464	255
10	477	262
Average:	447	275
Standard Deviation:	19.9	13.8
% RSD:	4.45%	5.02%

*EPA Certified soil without fatty acids. Target value of 450 ppm (diesel range organics).

The SFE operating conditions (modified from EPA draft method 3560) that were used for this study, are summarized in Table 3.

Table 3: Operating Conditions for the Automated SFE of TPH in Soils

Extraction Conditions	
Pressure:	450 atm
Temperature:	120°C
Modes:	5 min static, 30 min Dynamic
Restrictor:	VariFlow at 50°C for <10% H_20, 100°C for >10% H_20
Restrictor Flow:	3.0 ml/min Compressed CO_2
Extraction Vessel:	3 ml vessel
Adsorbent/Dispersent:	Hydromatrix
Collection Conditions:	
Collection Temperature:	-10°C (<10% H_20), 100°C (>10% H_20)
Desorption Temperature:	40°C
Wash Solvent:	Freon, 3 mls

A further assessment of method precision using automated SFE with IR analysis was done with twenty four replicate extractions on an EPA certified soil. The results are listed in Table 4. Using IR analysis, relative standard deviations averaged at 13.3% with an average concentration of 228 ppm (compared to the 230 ppm target value).

Table 4: Automated SFE/IR of TPH in Soils*

Replicates	Conc. (ppm)	Replicates	Conc. (ppm)
1	293	13	225
2	256	14	211
3	208	15	195
4	255	16	183
5	256	17	203
6	266	18	182
7	241	19	211
8	245	20	201
9	276	21	202
10	246	22	205
11	248	23	197
12	248	24	207
		Average:	228
		Standard Deviation:	30.3
		% RSD:	13.3%

*EPA Certified soil without fatty acids. Target value of 230 ppm (diesel range organics).

CONCLUSION

Out of the numerous application areas for using SFE as a sample preparation technique, the extraction of environmental pollutants out of soils is perhaps one of the most straight-forward. This is partially due to the inherent porous nature and loose texture of soils and the fact that supercritical fluid technology has evolved to the extent that instrumental enhancements have provided increased capabilities for researchers to use in method development. SFE technology today provides environmental chemists with the opportunity to utilize new and automated sample preparation techniques to open up virtually new frontiers. This includes the use of environmentally friendly, politically acceptable solvents (ie, CO_2), the decrease of sample turnaround times, the elimination of toxic chemical exposure, and the elimination of solvent disposal costs. Moreover, SFE can improve the overall reliability of analytical results and establish new standards for efficient monitoring of the environment. With the key development of variable restriction and with automation, SFE has reached a new pinnacle for economic application of this technique.

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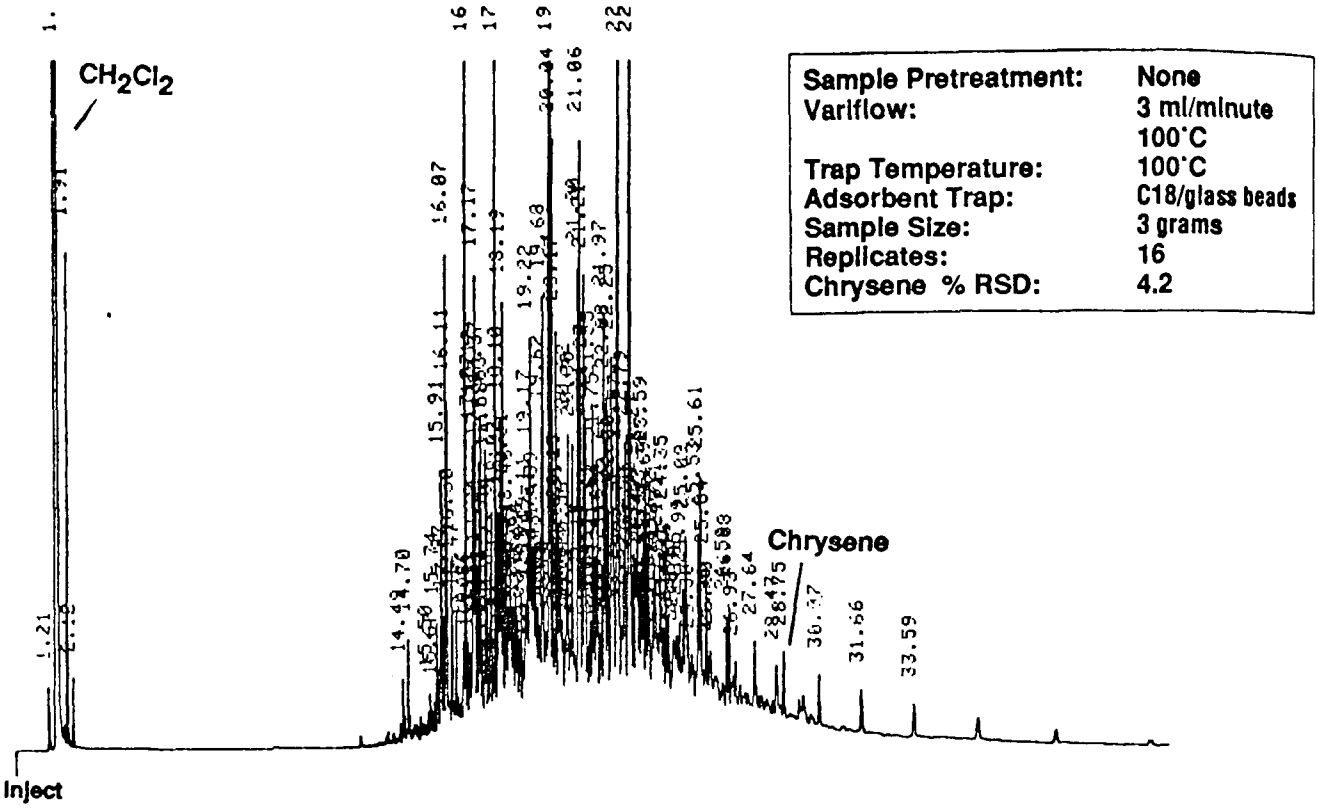


Figure 1: Automated Off-Line SFE/GC-FID Characterization of PAH Contaminated Soil (20% water)

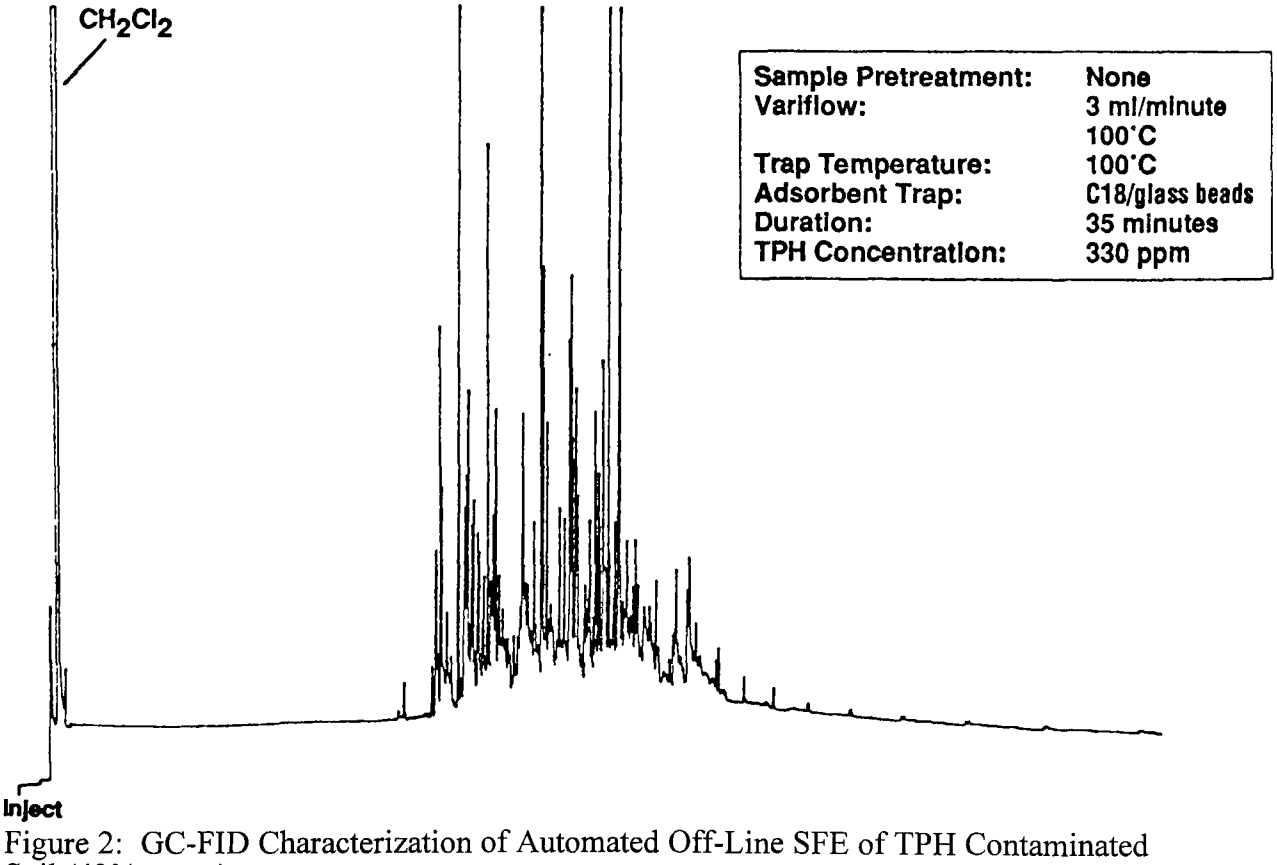
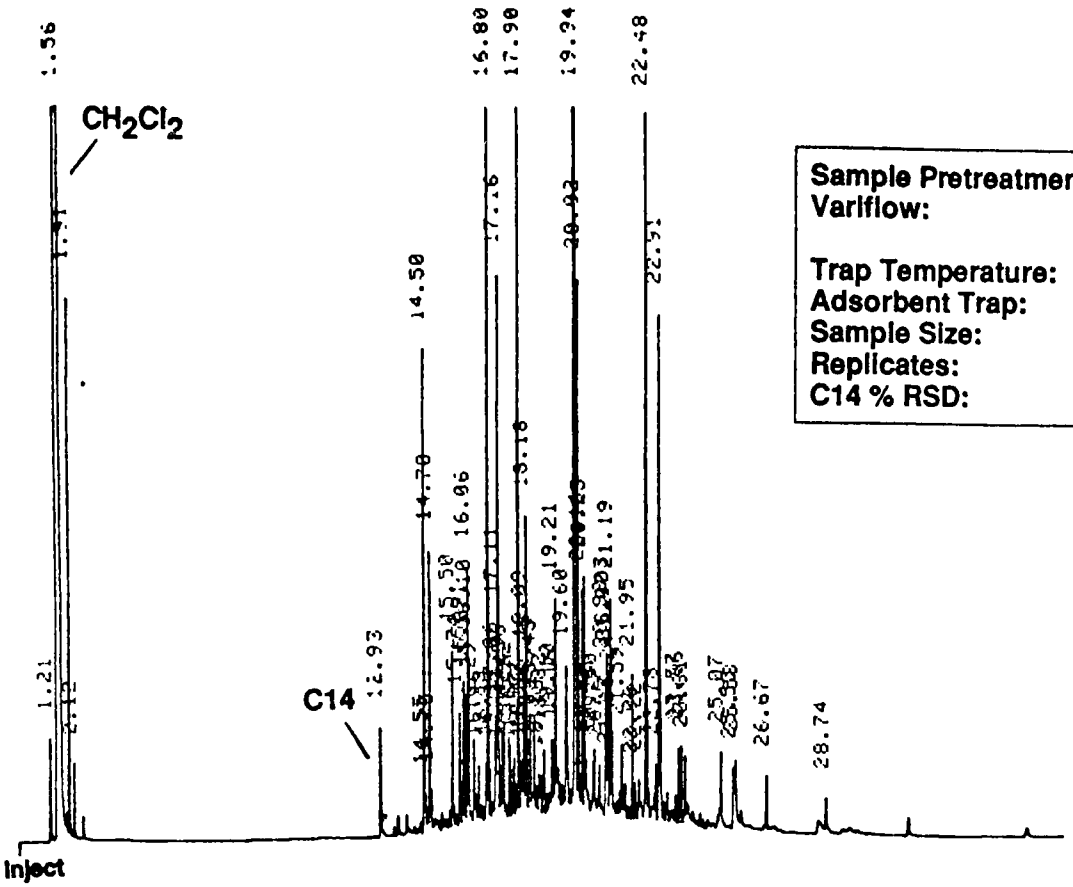


Figure 2: GC-FID Characterization of Automated Off-Line SFE of TPH Contaminated Soil (43% water).



Sample Pretreatment:	None
Variflow:	3 ml/minute
	100°C
Trap Temperature:	100°C
Adsorbent Trap:	C18/glass beads
Sample Size:	1 gram
Replicates:	24
C14 % RSD:	3.9

Figure 3: Automated Off-Line SFE/GC-FID Characterization of TPH Contaminated Clay (36% water).

Applications And Performance Of The D TECH™ TNT Environmental Testing System

George B. Teaney, James M. Melby, and James W. Stave
Strategic Diagnostics Incorporated
128 Sandy Dr.
Newark, DE 19713

ABSTRACT

Field screening technologies have gained increased attention in recent years. Immunoassay based field screening systems, designed to detect small molecular weight priority pollutants, are relatively new to the environmental market, however their core technology has been proven in the medical diagnostics industry since the early 1950's. In order to be effective, field screening systems should be quick, easy to use, reliable, and inexpensive. Immunoassay based field screening systems can provide all of these qualities as well as a high degree of sensitivity and specificity towards the analyte of interest.

The D TECH TNT Environmental Testing System is an immunoassay based, self contained, field screening system which employs a competitive enzyme immunoassay format. Free TNT in a water or soil sample competes with an enzyme linked TNT analog for binding sites on Anti-TNT antibody coated latex particles. Unbound materials are separated from the latex by filtration and wash step, and an enzyme substrate is added to the particles. The color that develops is inversely proportional to the concentration of TNT in the assay. This color is determined using either the color card provided with the kit, or the DETECHTOR™ reflectometer. This test has demonstrated 5 ppb and 0.2 ppm sensitivity in waters and soils, respectively. All EPA SW-846 Method 8330 analytes were tested for cross-reactivity in this assay. Four (4) of these compounds were found to be marginally (3%) to moderately (30%) cross-reactive. The assay shows little interference from non-explosive organic pollutants as well as nitrates and nitrites. Furthermore, the assay's performance has been unaltered when tested in a wide range of soil and water matrices. Field trial data show a low occurrence of false positives and false negatives, and good correlation to Method 8330. The cost effectiveness of this system was demonstrated during a 334 sample field trial in the western U.S.

INTRODUCTION

Field screening technologies have gained increased attention in recent years. Immunoassay based field screening systems, designed to detect small molecular weight priority pollutants, are relatively new to the environmental market, however their core technology has been proven in the medical diagnostics industry since the early 1950's. In order to be effective, field screening systems should be quick, easy to use, reliable, and inexpensive. Immunoassay based field screening systems can provide all of these qualities as well as a high degree of sensitivity and specificity towards the analyte of interest.

The D TECH TNT Environmental Testing System is an immunoassay based, self contained, field screening system. This portable assay has been designed to quickly and effectively identify TNT contaminated soils and waters during site characterization studies and throughout the remediation process.

This paper describes many of the performance characteristics of the D TECH TNT assay and details some of its applications in the field.

METHODS

The D TECH TNT Environmental Testing System employs a competitive enzyme immunoassay format (Figure 1). Free TNT in a water or soil sample competes with an enzyme linked TNT analog for binding sites on Anti-TNT antibody coated latex particles. A reference reaction is run simultaneously to the test reaction in which a known amount of TNT reference material competes with the enzyme conjugate for antibody binding sites. This reference reaction sets the minimum detection limit (MDL) of the assay and helps to control for environmental influences on the assay. Unbound materials are separated from the latex in the 2 reactions by a filtration and wash step, and an enzyme substrate is added to the particles. The color that develops from the bound enzyme is inversely proportional to the concentration of TNT in the assay. This color is determined using either the color card provided with the kit, or the DETECHTOR™ reflectometer.

Water samples are simply diluted into an assay buffer and filtered into the assay. Sample preparation for soil analysis involves pulling a 4.5 g sample using a volumetric coring device. The soil sample is extracted in 100 % acetone for 3 minutes and the soil extract is diluted into assay buffer. This diluted soil extract is then treated as if it were a water sample.

RESULTS AND DISCUSSION

The assay can detect TNT concentrations as low as 5 ppb in water samples and 0.2 ppm in soils. The assay dose response curve indicates an assay range of 5 ppb to 60 ppb in water samples (Figure 2) and 0.2 ppm to 2.0 ppm in soils (data not shown). The test has been evaluated for cross-reactivity with all 13 of the compounds listed in EPA SW-846 Method 8330[1] (Table 1). A compound is considered cross-reactive if it can be detected at a concentration 100 times the MDL of the target analyte. The four compounds, Tetryl, 1,3,5-trinitrobenzene, 2-amino-4,6-dinitrotoluene, and 2,4-dinitrotoluene, have been defined as cross-reactants in the TNT kit. The degrees of cross-reactivity for these compounds are 30%, 25%,17%, and 4% respectively (Figure 3). Because these cross-reactants are common to sites contaminated with TNT, D TECH sample results are reported as TNT equivalents.

Twenty three potential co-contaminants were screened as possible interfering substances in the TNT assay (Table 2). All of the compounds listed were tested at a level equivalent to 100 ppm in soil (1 ppm in water samples). None of the 23 compounds tested yielded a positive result in the assay at the concentration tested.

Sample matrix effects on assay sensitivity were assessed at the false positive (FP) and false negative (FN) thresholds. As defined by the EPA[2], a FP is a positive result from a sample containing less than one half of the method detection limit (2.5 ppb in water). Similarly, a FN is a negative result from a sample containing greater than twice the method detection limit (10 ppb in water). Thirty chemically diverse soil and water types were spiked with TNT at one half and twice the assay detection limit and were run in the assay (Figures 4 and 5). Samples yielding a % relative reflectance (%RR) greater than zero are determined to be greater than the assay detection limit. Likewise, samples yielding a %RR less than one are determined as less than the assay detection limit. None of the water and soil

samples spiked at the FN threshold were determined to be negative, where as 2 of the water samples and 2 of the soil samples spiked at the FP threshold were seen as positive (6.6%).

The application of these tests in the field has been demonstrated at several sites across the United States. Results from a TNT field trial at Joliet Army Ammunition Plant reported good agreement between the D TECH method and Method 8330 (Table 3). During this study, 42 soil samples were screened on site by the D TECH method and shipped to an independent laboratory for Method 8330 confirmation. Results from this study reported no false negatives and 1 false positive (2 %). When confirmed by Method 8330, 98% of the samples showed the same trends as Method 8330 with 74 % of the sample results in direct agreement between methods.

Results from a larger scale TNT study (334 samples) has shown these tests to be accurate as well as cost and time effective (Figure 6). During this study, the D TECH TNT kit was used to screen 334 samples on site at a cost of approximately $30 per test. Approximately 50 samples were tested by a person on a given day. Four tests could be executed in approximately 20 minutes. The total number of samples run in a day was limited by the speed with which they were collected from the field. All soil samples were submitted for Method 8330 confirmation at a cost of $300 per test. Ninety one percent of the 334 samples screened on site by the D TECH method were in agreement with Method 8330 results. Ten samples were reported as false positive (3%) the D TECH method reported 108 of the samples contained TNT concentrations greater than the project action limit (2 ppm). If the D TECH results had been used to determine which samples were greater than the project action limit, and only those samples were submitted for Method 8330 confirmation, a net savings of $57,000 would have resulted.

CONCLUSIONS

This environmental EIA has demonstrated a high degree of sensitivity and specificity for the analyte of interest. False positive and false negative rates are well within acceptable limits in soil and water matrices. This assay is field tested and shows good correlation with EPA SW-846 Method 8330 while demonstrating the time and cost effective attributes required for field screening systems.

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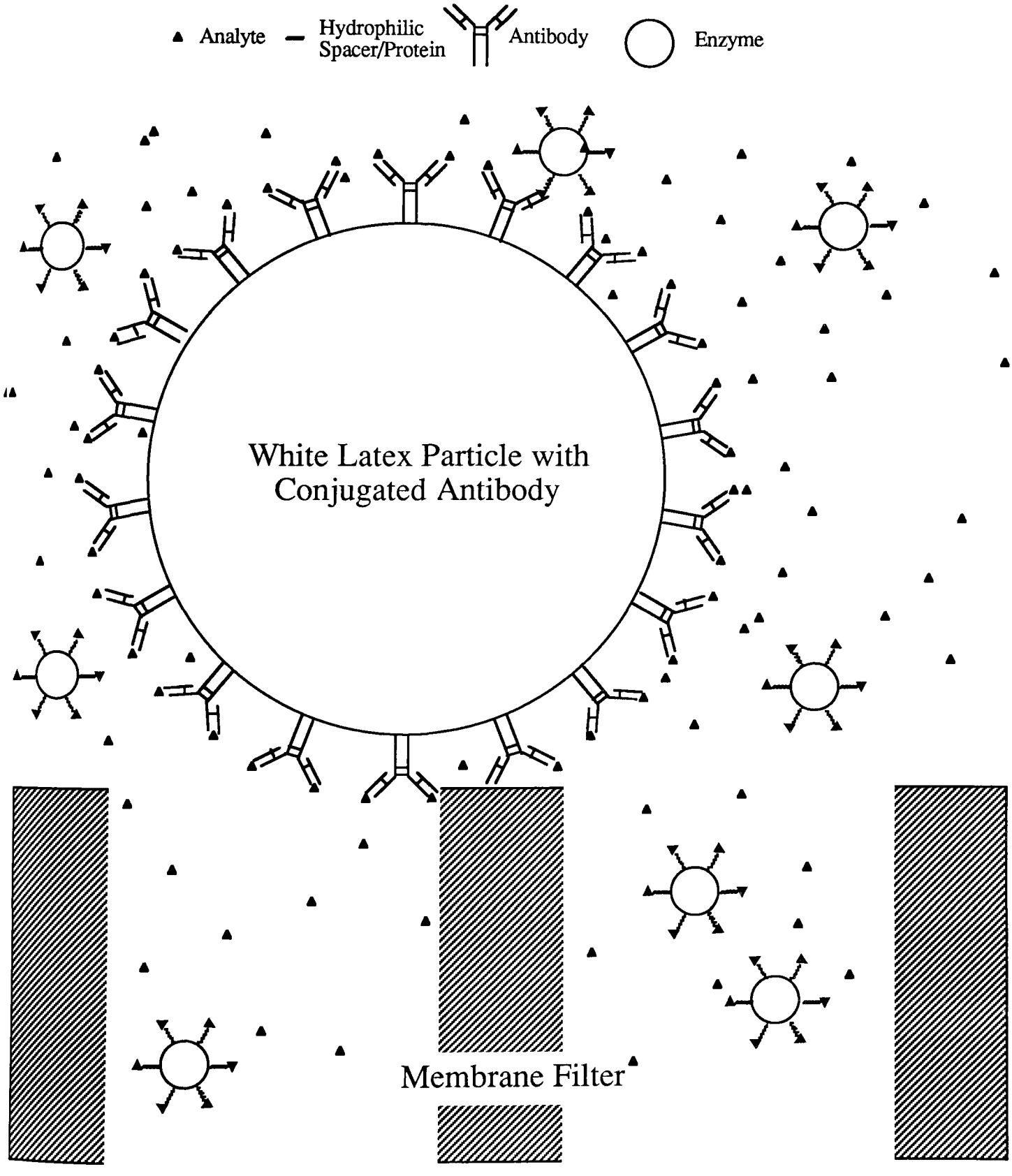
Figure 1. Competitive Enzyme Immunoassay



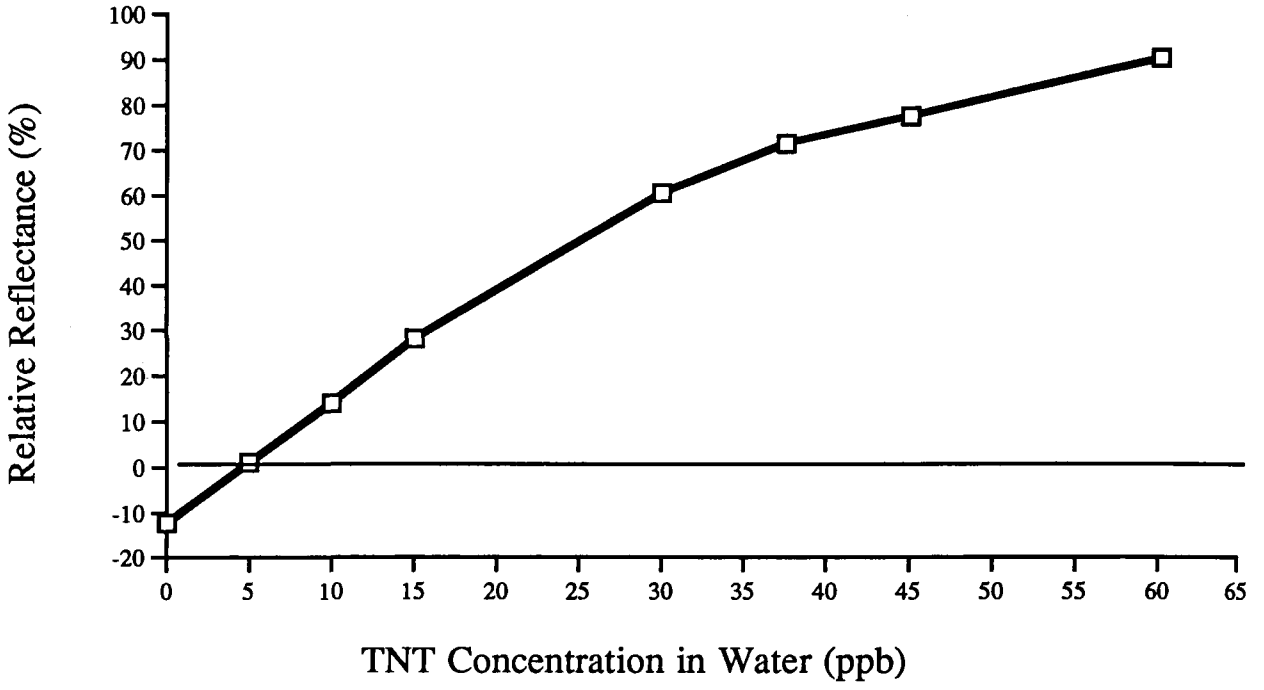


Figure 2. The D TECH TNT water kit standard curve

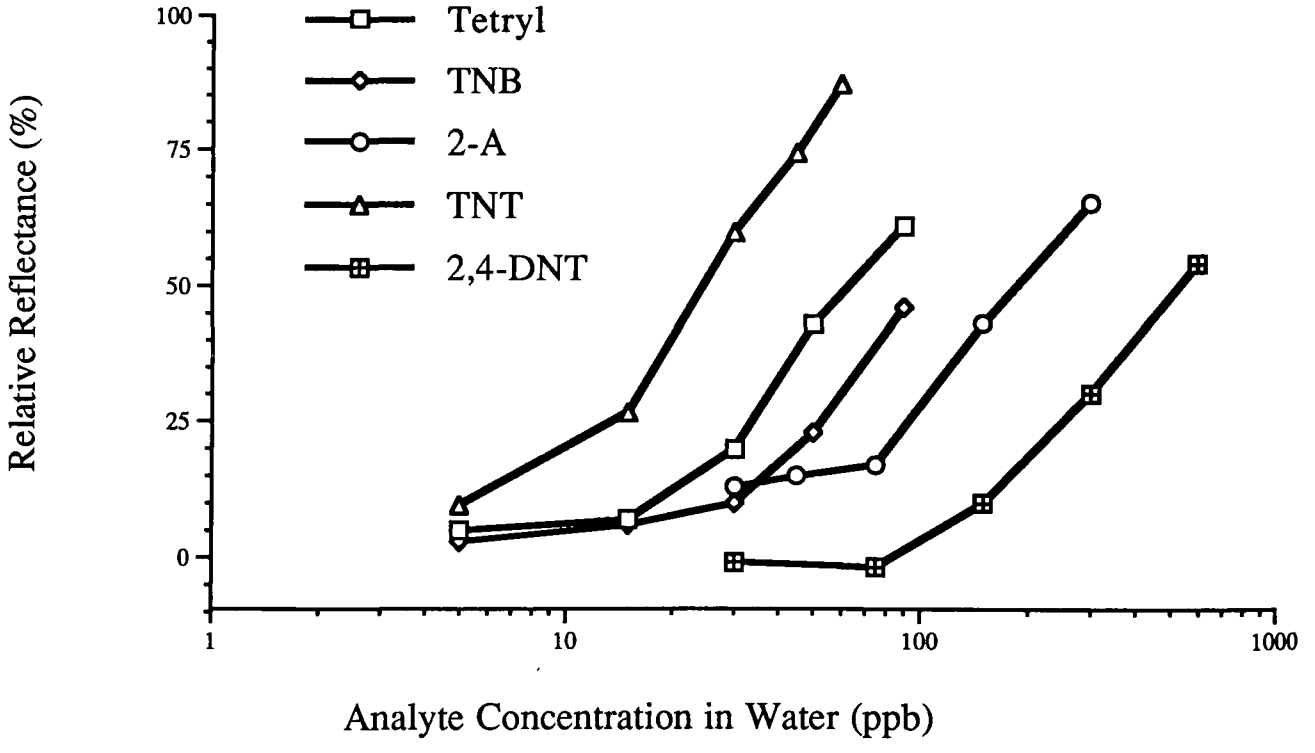


Figure 3. The TNT assay sensitivity to cross-reactive analogs

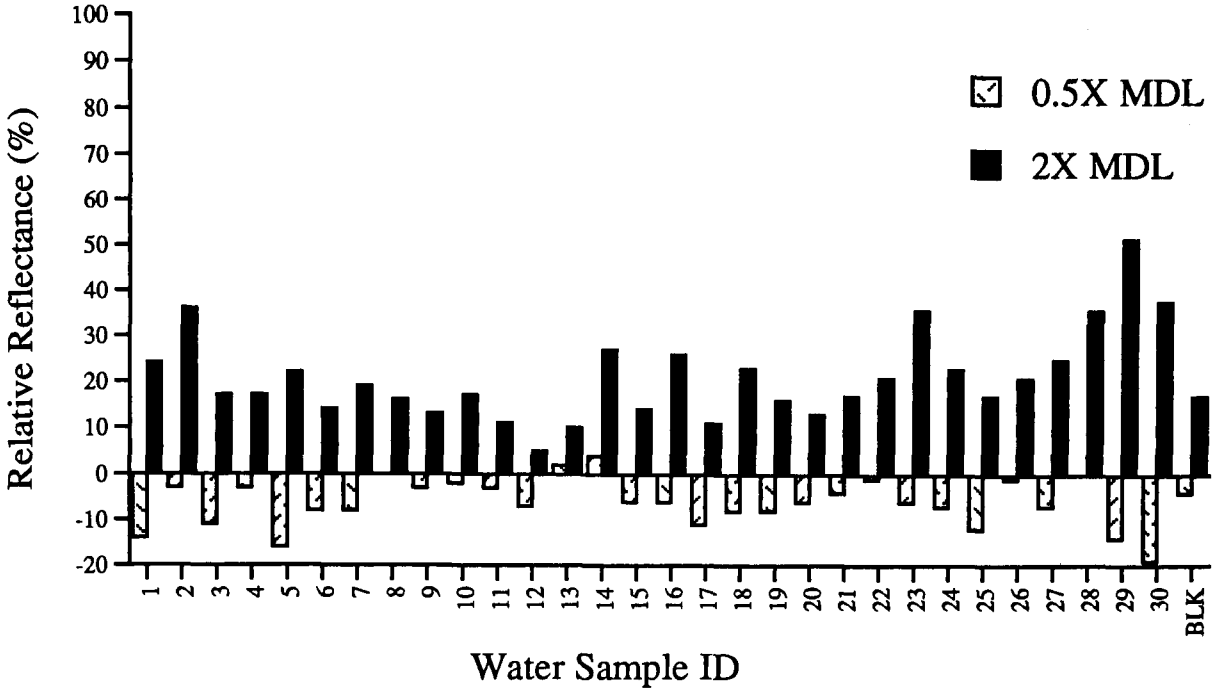


Figure 4. Water sample matrix effects on the TNT assay sensitivity

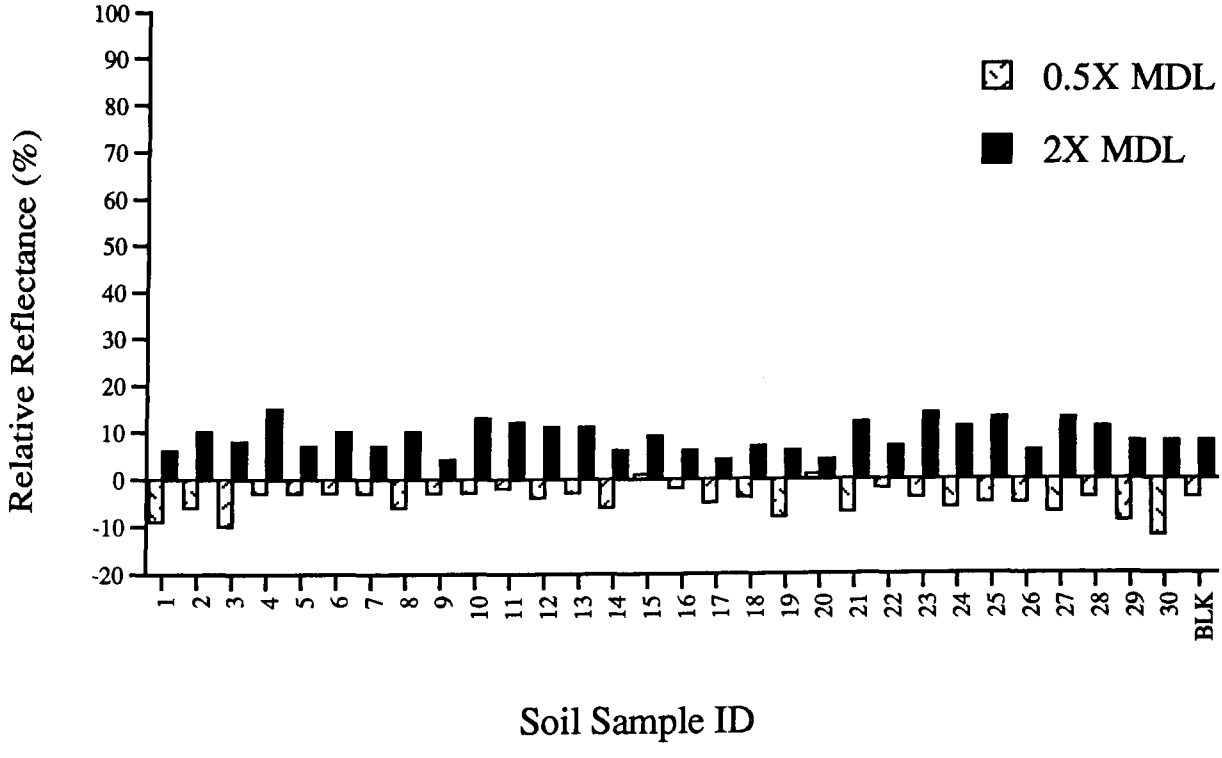


Figure 5. Soil sample matrix effects on the TNT assay sensitivity

Figure 6. TNT field study cost analysis

- **Analytical Costs without Field Screening:**

334 Samples @ $300 per HPLC Sample = $100,020

- **Analytical Costs with Field Screening:**

334 Samples @ $30 per D TECH Sample = $10,020

108 Samples @ $300 per HPLC Sample = $32,400

Total Costs = $42,420

Savings = $57,600

Table 1. Compounds tested for cross-reactivity in the D TECH TNT assay. If detected at 500 ppb or less, the compound was determined to be cross-reactive.

Analytes of Interest	Detected
M8330 Compounds	
1,3-Dinitrobenzene	No
2,4-Dinitrotoluene	Yes
2,6-Dinitrotoluene	No
HMX (octahydro-1,3,5,7-tetranitro-1,3,5-triazine)	No
RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	No
Nitrobenzene	No
2-Nitrotoluene	No
3-Nitrotoluene	No
4-Nitrotoluene	No
Tetryl (Methyl-2,4,6-trinitrophenylnitramine)	Yes
2,4,6-Trinitrotoluene	Yes
1,3,5-Trinitrobenzene	Yes
2-Amino-4,6-dinitrotoluene	Yes
4-Amino-2,6-dinitrotoluene	No
Others	
Nitrate	No
Nitrite	No

Table 2. Potential interfering organic co-contaminants tested in the TNT assay

Compound	Concentration of analyte in a water sample required to yield a positive test result (ppm)
Atrazine	> 100
Aroclor 1254	> 100
Acetone	> 100
Toluene	> 100
Ethylbenzene	> 100
Xylene	> 100
Benzene	> 100
Methanol	> 100
Benzo(a)pyrene	> 100
Acenaphthene	> 100
Acenaphthalene	> 100
1,2-Benzanthracene	> 100
Benzo(k)fluoranthene	> 100
Benzo(ghi)perylene	> 100
Benzo(b)fluoranthene	> 100
Chrysene	> 100
Dibenz(ah)anthracene	> 100
Fluoranthene	> 100
Fluorene	> 100
Indeno(123-cd)pyrene	> 100
Naphthalene	> 100
Pyrene	> 100
Phenanthrene	> 100

Table 3. TNT field trial results from Joliet Army Ammunition Plant

Sample ID	D TECH Result (ppm)	Method 8330 Result (ppm)	Correlation Between Methods
61-1	< 0.2	< 0.09	YES
61-10	< 0.2	< 0.09	YES
61-11	< 0.2	< 0.09	YES
61-12	< 0.2	< 0.09	YES
61-13	< 0.2	< 0.09	YES
61-14	< 0.2	< 0.09	YES
61-15	< 0.2	< 0.09	YES
61-16	< 0.2	< 0.09	YES
61-17	< 0.2	< 0.09	YES
61-18	< 0.2	< 0.09	YES
61-19	< 0.2	< 0.09	YES
61-2	> 1.5	> 3.0	YES
61-20	< 0.2	< 0.09	YES
61-21	0.5-1.0	2.44	UE
61-22	< 0.2	< 0.09	YES
61-23	< 0.2	< 0.09	YES
61-24	1.0-1.5	1.4	YES
61-25	< 0.2	< 0.09	YES
61-26	< 0.2	< 0.09	YES
61-27	0.2-0.5	0.27	YES
61-28	< 0.2	< 0.09	YES
61-29	< 0.2	< 0.09	YES
61-3	1.0-1.5	1.3	YES
61-30	< 0.2	< 0.09	YES
61-4	> 1.5	1.1	OE
61-5	0.5-1.0	1.0	YES
61-6	> 1.5	> 3.0	YES
61-7	< 0.2	< 0.09	YES
61-8	0.5-1.0	1.0	YES
61-9	0.2-0.5	0.54	YES
TET-1	0.5-1.0	< 0.09	FP
TET-2	< 0.2	< 0.09	YES
TET-3	< 0.2	< 0.09	YES
TL-1	0.2-0.5	0.99	UE
TL-2	> 1.5	1.2	OE
TL-3	> 1.5	> 3.0	YES
TL-4	0.2-0.5	0.66	UE
TL-5	> 1.5	> 3.0	YES
TL-6	0.2-0.5	0.66	UE
TL-7	0.2-0.5	0.71	UE
TL-8	0.5-1.0	1.46	UE
TL-9	0.2-0.5	0.92	UE

OE = Over Estimate
UE = Under Estimate
FP = False Positive

SCREENING WASTE BY FT-IR

David L. Bumgarner, Director, Analytical Services, Leslie S. Bucina, Laboratory Manager, Kemron Environmental Services, 109 Starlite Park, Marietta, Ohio, 45750.

ABSTRACT

Infrared (IR) spectrophotometry has been widely used in industrial and academic laboratories as a powerful tool in the identification of unknown compounds, especially in combination with nuclear magnetic resonance (NMR), mass spectrometry, and physical properties such as melting and boiling points. In recent years its utility for qualitative and quantitative determinations has been enhanced significantly with the introduction of Fourier Transform Infrared (FT-IR) Spectrophotometry . However, its implementation in environmental analysis has been limited to a few special applications, specifically EPA Method 418.1 for the determination of petroleum hydrocarbons in water and soil in support of NPDES permit monitoring and investigations of leaking underground storage tanks. For the past three years we have used IR for identification of major components in unknown waste samples. Our results, which will be summarized in this paper, indicate the technique is useful as both a screening tool and, in some cases, the primary analytical procedure. Our paper will provide details for sample preparation, analysis, example spectra, and the use of commercial and user compiled libraries for both organic and inorganic liquids and solids. Our examples will illustrate specific laboratory analyses in which FT-IR was the primary tool used to identify such products and wastes as high purity industrial solvents, paint wastes, antifreeze, aqueous wastes, and inorganic cyanide compounds. It is also a useful screening procedure for identification of hydrocarbon mixtures such as gasoline, diesel and jet fuels, lubricating oils, and solvent mixtures. IR spectra of these samples will be included along with discussion to document the analytical conclusions of such projects. The data will demonstrate the utility of FT-IR as a quick and cost-effective method for identification of major constituents in an unknown, often limiting the need for subsequent lengthy and expensive analyses.

INTRODUCTION

Background

More and more, environmental laboratories are being required to provide fast, cost-effective methods for analytical screening of samples of unknown composition. These unknowns may originate from various regulatory compliance and site investigation activities, and typically consist of bulk liquids and solids collected from unlabeled drums, tanks, or pits with little or no history to verify the contents. Without a systematic approach to the screening of such waste, the laboratory will often embark on a costly analytical project which might include comprehensive analyses for inorganics, metals, volatile and semivolatile organics, pesticides, and herbicides. A screening technique which can narrow the list of possible components is necessary to minimize both cost of analysis and turnaround time. Many clients request extensive waste analyses including full TCLP on unknowns that are later found to be solvents or other organic liquids. Matrix interference on these samples can result in detection limits higher than regulatory limits which are either interpreted as useless, or potentially may cause the waste to be designated RCRA hazardous by default. A screening analysis can be used to quickly categorize the waste as a pure product, or common commercial mixture, often ruling out TCLP. In this context we would like to discuss the use of IR, and FT-IR in particular, in the determination of unknown waste profiles (major constituent analysis). The techniques and some actual laboratory examples will be presented in this paper.

Equipment and Supplies

Hardware:
- Infrared Spectrophotometer: Perkin Elmer Model 1600 FT-IR
- Hewlett-Packard Color Pro Plotter
- Potassium Bromide Windows (KBr plates) (38.5 x 19.5 x 4 mm)
- Demountable Cell Mount
- Potassium Bromide Mini-Press
- Beta Gas Cell (10 cm)
- Precision Scientific Convection Oven Model EG

Reagents:
- Acetone Resi-analyzed reagent for residue analysis
- Water - Ionpure Type I or equivalent
- Hexane Resi-analyzed reagent for residue analysis
- Potassium Bromide - Infrared quality

Sample Preparation

Sample preparation for liquid samples is extremely simple requiring only disposable pipets and two potassium bromide (KBr) plates which serve as a cell. A small drop of the sample is placed on one of the plates and a thin film is formed by pressing the two plates together. The plates are placed in the cell holder and the spectrum determined by FT-IR. The complete sample preparation/analysis process takes less than one minute. Cleaning of the KBr plates consists of rinsing with resi-analyzed acetone. Etching from water and other liquids is inevitable, however, this is eliminated by rubbing of the plates on fine grit sandpaper. Solids are prepared by the KBr mini-press pellet procedure. Highly concentrated solvents are analyzed utilizing their vapor phase by gas cell methodology in which the gas cell contents is evacuated and replenished with the vapor phase of the sample through the transfer of sample headspace using a gastight syringe.

FT-IR Analysis - Method Overview

Both commercial and user prepared spectral reference libraries are necessary to maximize the information obtained from the IR spectrum of an unknown material. Some general conclusions can usually be drawn very quickly regarding the general composition for certain classes of liquid wastes. It is often readily apparent that the waste is either of aqueous or petroleum origin based the characteristic simple spectra for water and hydrocarbons. Further investigation will often suggest the presence of ketones, alcohols, glycols, or chlorinated solvents. An instrument with library search capabilities can be very helpful in identification of specific liquid unknowns when the purity is high, although the information provided by the spectra on complex mixtures must be verified by additional analytical techniques.

RESULTS AND DISCUSSION

Sample 1

This transparent, colorless, liquid was miscible in water and acetone but immiscible in hexane. The FT-IR spectrum was determined using the dual KBr plate thin-film technique, and is presented in Figure 1A. The library spectrum for deionized water is presented in Figure 1B and it is obviously a close match. The liquid was presumed to be an aqueous waste, with no major organic constituents probable at one per cent or greater. The water content was later confirmed by the Karl Fischer titration method to be greater than 99 %. Based on the clients knowledge of the waste profiles at the base, the laboratory was instructed to limit additional testing to the eight TCLP metals on a total basis.

Sample 2

A state regulatory agency collected this white, unidentified solid while conducting an investigation at an abandoned site. Although unlabeled, history and other evidence at the site suggested the possibility the material could be cyanide salts. The agency requested that the sample be tested for total cyanide by SW-846 Method 9010. Due to concern for analyst safety and apparatus contamination, a screening analysis by FT-IR was proposed to determine if the solid contained high levels of cyanide. The KBr pellet technique was employed in this case and the spectrum presented in Figure 2A was generated. The absorption band at 2079 cm^{-1} is characteristic of cyanide salts attributed to the C-N bond. The laboratory used solid potassium cyanide and a KBr pellet to produce the spectrum labeled as Figure 2B. Due to the excellent match, we presumed the white powder to be a cyanide salt and the cyanide analyst was able to proceed on that assumption. A known mass of the sample was prepared in the manner of a cyanide standard stock solution and serially diluted into the expected linear range of the calibration curve. The analysis by Method 9010 confirmed the IR data, giving a result of 440,000 mg/kg CN (44% cyanide).

Sample 3

This transparent liquid with solvent-like odor was miscible in acetone and hexane but immiscible in water. The FT-IR spectrum (Figure 3A) was very similar to the library spectrum for methyl ethyl ketone (Figure 3B). Client had requested analysis by EPA Method 8240 to check for solvents. The preliminary FT-IR analysis provided the GC/MS analyst with enough information about the sample to prepare the proper dilution of the waste and confirm the screening data. Although the KBr plate method (thin film) was employed for this sample, the gas/vapor cells are often used in similar situations to identify solvents of relatively high purity.

Sample 4

This transparent liquid with familiar odor was received as an unknown from the airforce base. The sample was hexane and acetone miscible but water immiscible. A thin film was prepared between two KBr plates and the FT-IR spectrum presented in Figure 4A was generated. A library search gave several possibilities with the best match being unleaded gasoline presented in Figure 4B. Confirmation by direct injection into a GC/FID produced a fingerprint with a carbon range of C_4 C_{10}, which was indicative of gasoline range organics. No additional testing was indicated or required.

Sample 5

This was an amber, clear liquid with solvent like odor which was miscible in hexane but immiscible in water or acetone. The thin film KBr plate technique yielded the FT-IR spectrum shown in Figure 5A. This spectrum is typical of many petroleum distillate unknowns received at our laboratory for identification, classification, or possible candidates for fuels blending. Note the similarity of the spectrum to that of Figure 5B- a laboratory specific entry in our library for a "brush cleaner", a product similar to an oil-base paint stripper. Confirmation by GC/FID produced a fingerprint and carbon range not unlike that of our standard brush cleaner. Although, the FT-IR spectrum is typical of many petroleum distillates, the absorption band at approximately 1700 cm^{-1} is typical of carbonyl compounds. Because of this additional data, it was determined that analysis by GC/MS Method 8240 might be needed to identify and quantify any other major components. GC/MS analysis confirmed the presence of 4-methyl-2-pentanone, 2-butanane, toluene, and total xylenes all at percent levels.

Sample 6

A clear, colorless liquid, this sample was miscible in both water and acetone, but immiscible in hexane. The thin-film KBr plate technique yielded the spectrum labeled as Figure 6A. The spectrum shows characteristics of -0H from water and alcohols (3400 cm^{-1}) and the absorption band at 2900 3000 cm^{-1} is typical of the C-H stretch. The IR spectrum was similar to that of short chain alcohols and glycols including methanol and ethylene glycol. It was determined that further analysis by SW-846 Method 8015 (GC/FID) would be necessary to identify and quantitate the major constituents. Based on retention time data for a series of alcohols, it was determined that the sample was high purity methanol. The IR spectrum for methanol is presented as Figure 6B, however; note the similarity to ethylene glycol (Figure 7B).

Sample 7

Another typical waste originating from an airforce base, this green liquid was miscible in water and acetone but immiscible in hexane. The thin film KBr plate technique was used to produce the FT-IR spectrum presented in Figure 7A. The bands at 3345, 2944, and 2832 cm^{-1} are typical of neat alcohols and glycols, or aqueous solutions of the same. In this particular sample the particular fluorescent green color is often indicative that we are dealing with an ethylene glycol based antifreeze mixture. Although confirmation may not have been necessary based on the color, sample origin, and the similarity to the spectrum for ethylene glycol (Figure 7B), the composition was confirmed both qualitatively and quantitatively by GC/FID analysis to be ethylene glycol.

Sample 8

A transparent liquid sample with a solvent-like odor was collected from an unknown waste drum for characterization. Solubility tests were performed which revealed the miscibility of the sample in both hexane and acetone as well as the immiscibility of the sample in water. A FT-IR spectrum was obtained using the thin film dual KBr plate technique, presented in Figure 8A. The IR spectrum when library searched closely resembled the laboratory Freon 113 standard which contains characteristic bands within the fingerprint region (Figure 8B). The confirmation for the halogenated solvent was performed by use of a volatile GC/MS analysis. The Freon 113 was qualified by a positive spectral identification and quantified at a concentration of greater than 99%.

Sample 9

This sample which was a yellow liquid which was soluble in hexane and insoluble in water and acetone was submitted from a vehicle maintenance facility. The FT-IR spectrum was achieved using the thin film KBr plate technique (Refer to Figure 9A). The resulting spectrum which was characteristic of a hydrocarbon was library searched with a tentative identification of a lubricating oil (See Figure 9B). The hydrocarbon sample was then fingerprinted by GC using a modified SW-846 Method 8015. The hydrocarbon fingerprint in the chromatogram had a carbon range of C_{14}-C_{32} which is similar to a lube oil carbon range.

Sample 10

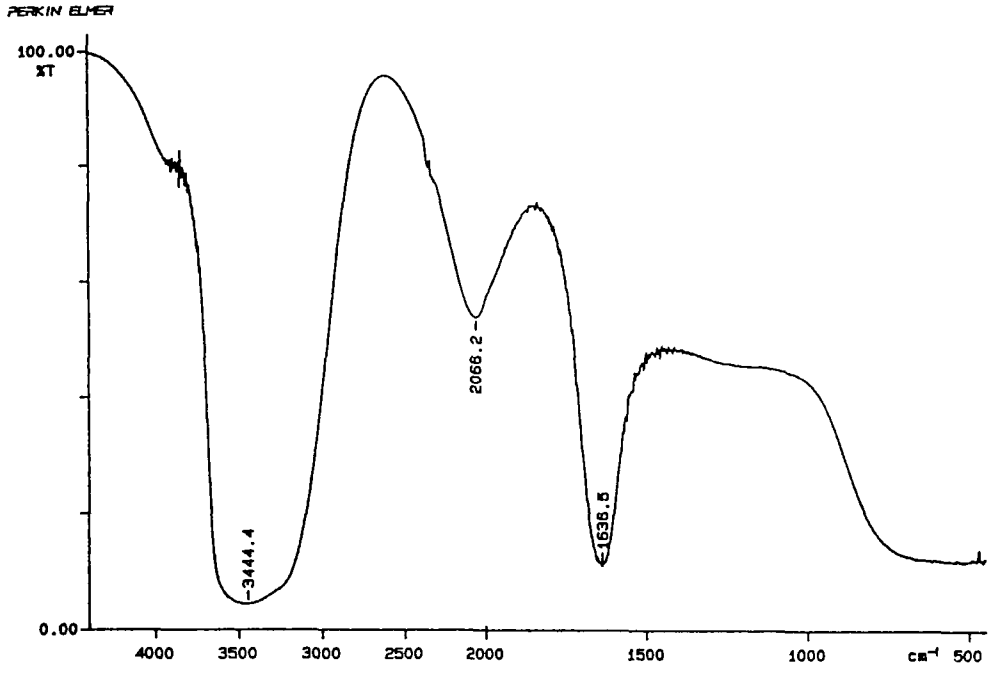
This unknown was a transparent liquid sample which exhibited a distinct fuel odor. The FT-IR analysis using the thin film KBr plate technique gave a characteristic hydrocarbon spectrum as shown in Figure 10A. The fuel library when searched gave a tentative match of diesel fuel (Figure 10B). The sample was then analyzed for diesel range organics by a modified SW-846 Method 8015 to confirm the carbon range and to provide a quantitation. The diesel pattern had a carbon range of C_9-C_{28} and a total area quantitation of approximately 67%.

SUMMARY

From the examples discussed in this paper, we have shown that FT-IR can be a fast and effective tool in the identification of unknown wastes. Basic infrared sample preparation techniques which employ the thin film plate technique, KBr pellets, mulls, disposable porous cells, and the gas cell are used to prepare the sample for the FT/IR screening. This preparation and screening with resultant spectra, which provide enough information to characterize wastes as aqueous, petroleum distillates, pure solvents, solvent mixtures, and common commercial products, can be performed in just a few minutes. Although some samples can be positively identified by FT-IR alone, the main utility of the spectra is to guide the laboratory in the in the selection of subsequent confirmatory techniques. Armed with the information from the FT-IR analysis and with, or without, knowledge of waste, several costly and time consuming analytical methods (i.e. TCLP) can be reduced or eliminated entirely.

ACKNOWLEDGMENTS

The authors would like to thank the management and technical staff at the Occupational and Environmental Health (OEHL) Laboratory and Brooks Airforce Base, San Antonio, for their technical assistance in implementing these procedures. Most of the original work with the IR screening procedures presented were developed at OEHL's Armstrong Laboratory. We would also like to thank KEMRON employees Chad Barnes, Rodney Campbell, and Cheryl Koelsch for their help in preparing this paper.



94/04/29 14:56
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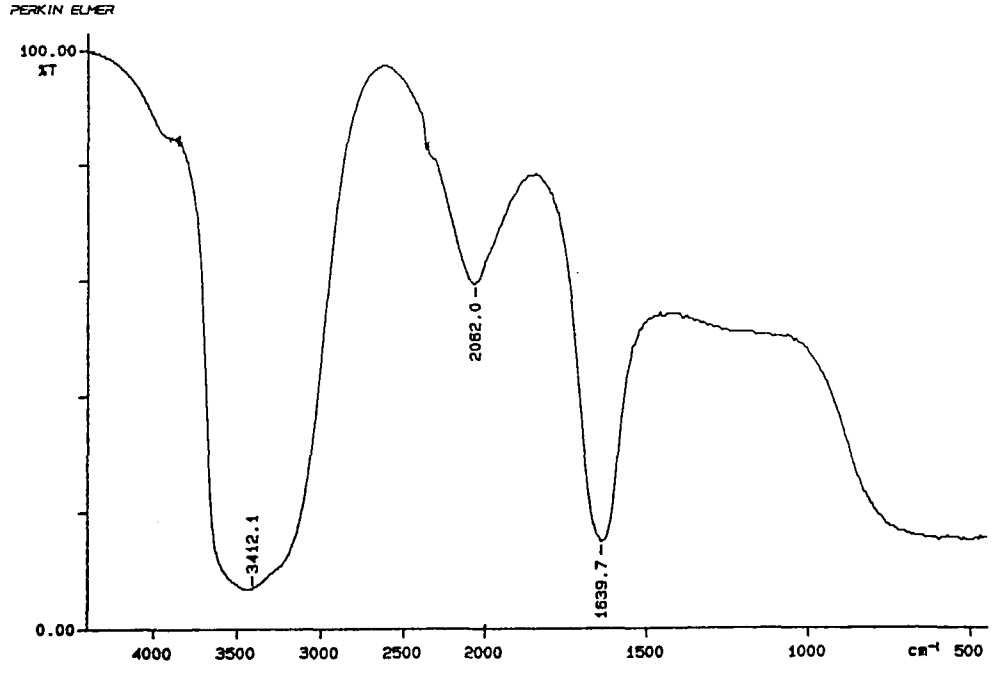
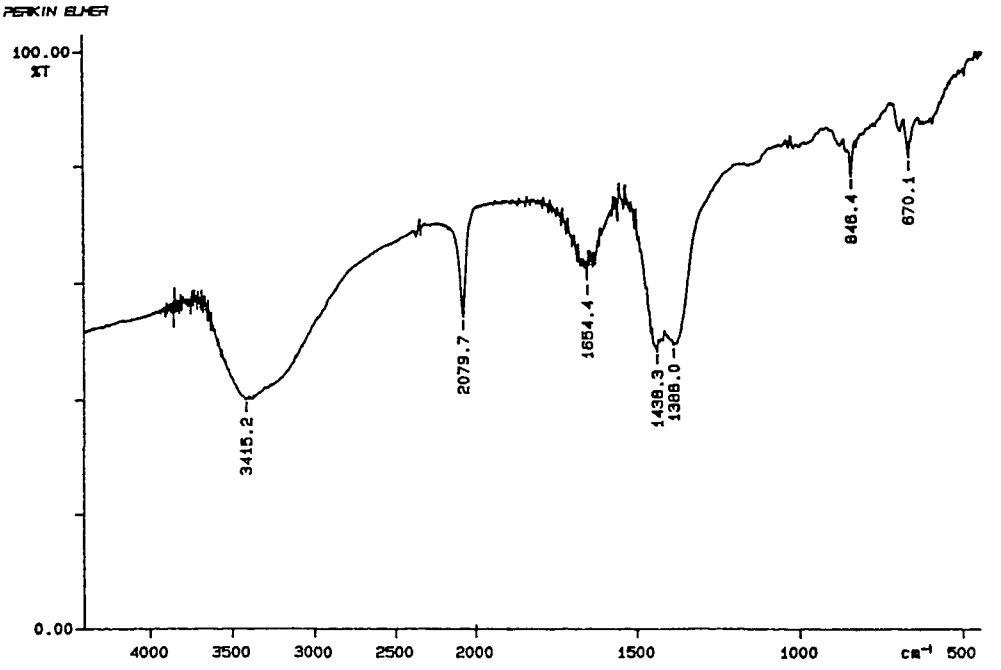
Sample 1

FIGURE 1A



BU0007: 0 scans, 0.0cm-1, apod none, not 1600
DI Water

FIGURE 1B



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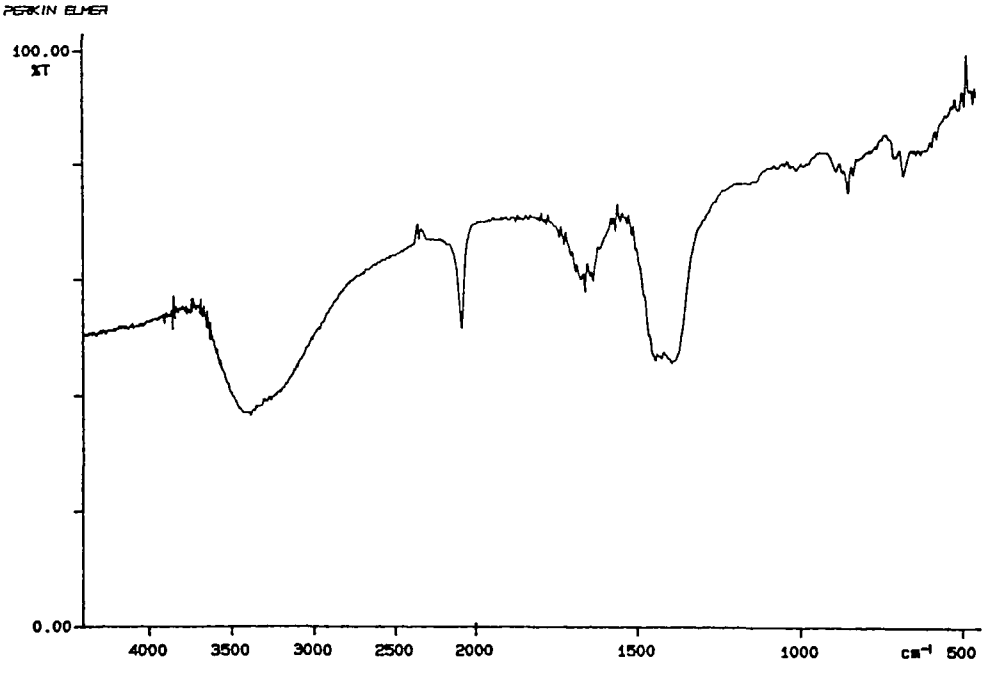
X: 4 scans, 4.0cm-1, abex
Sample 2

FIGURE 2A



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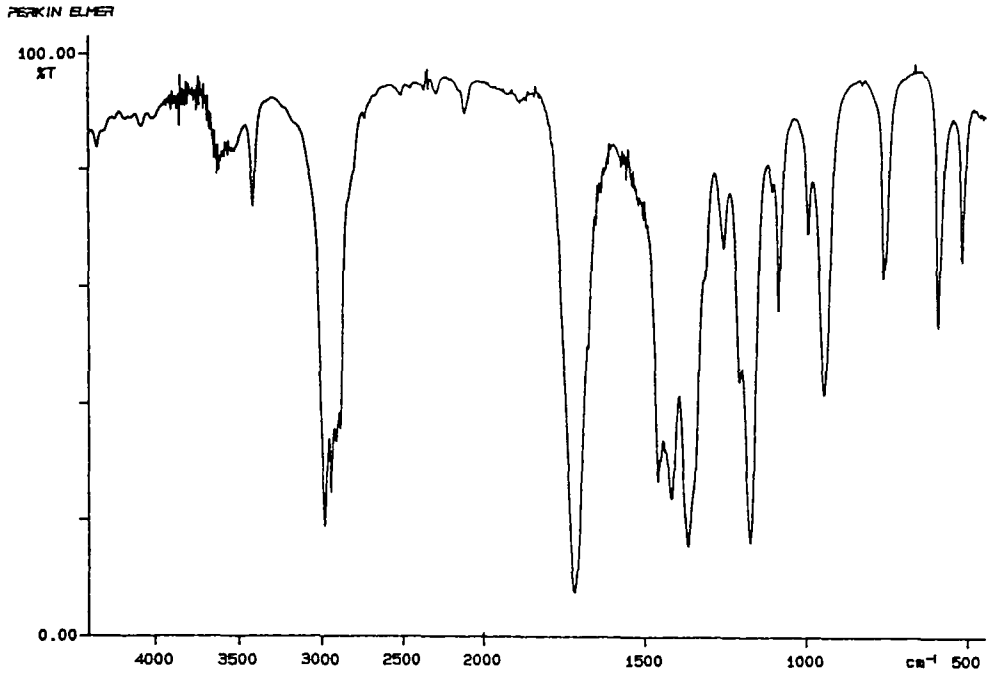
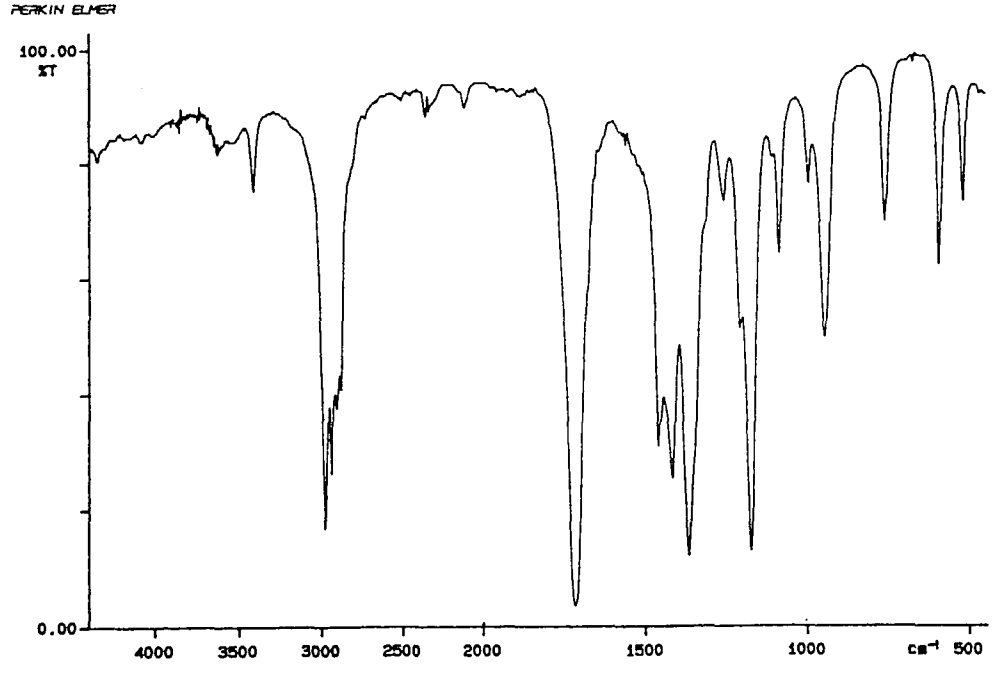
CYANIDE KBr

FIGURE 2B



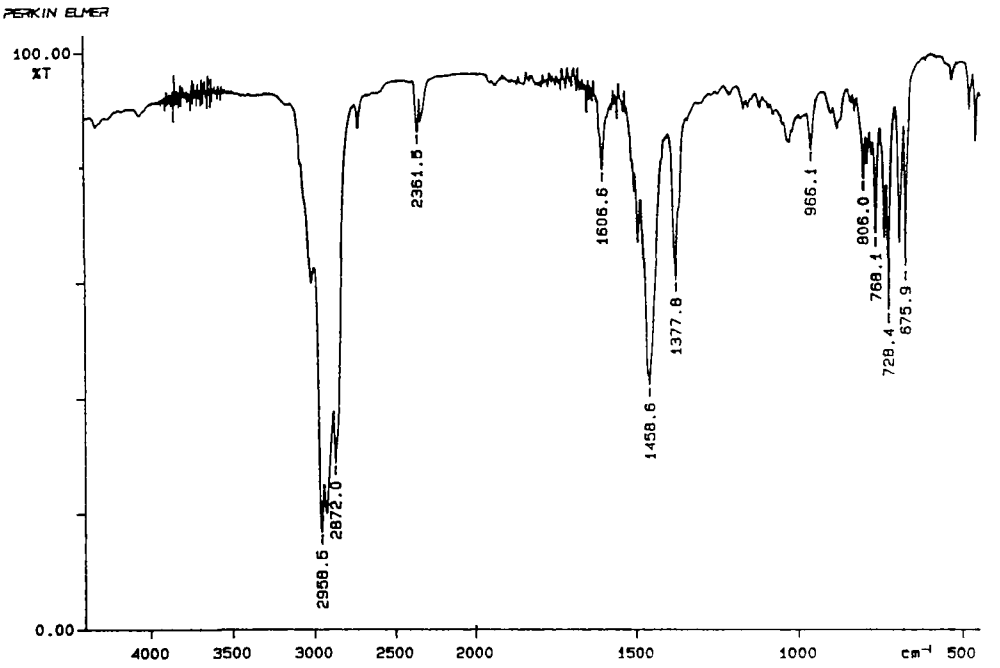
94/05/04 10:01
X: 4 scans, 4.0cm-1, abex
sample 3

FIGURE 3A



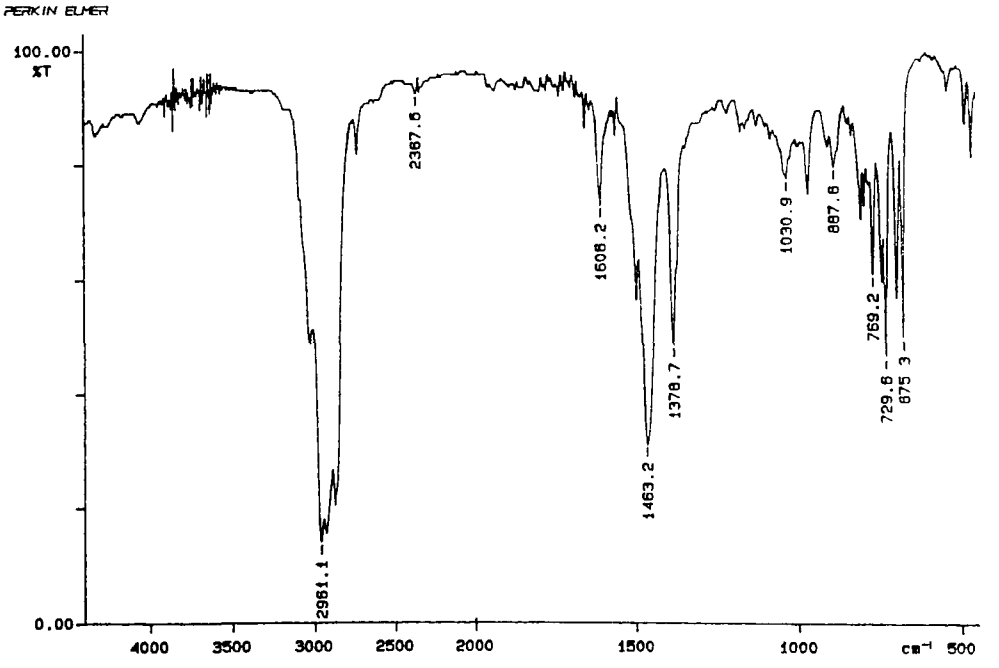
BU0074: 0 scans, 0.0cm-1, apod none, not 1600
MEK (BRKS)

FIGURE 3B



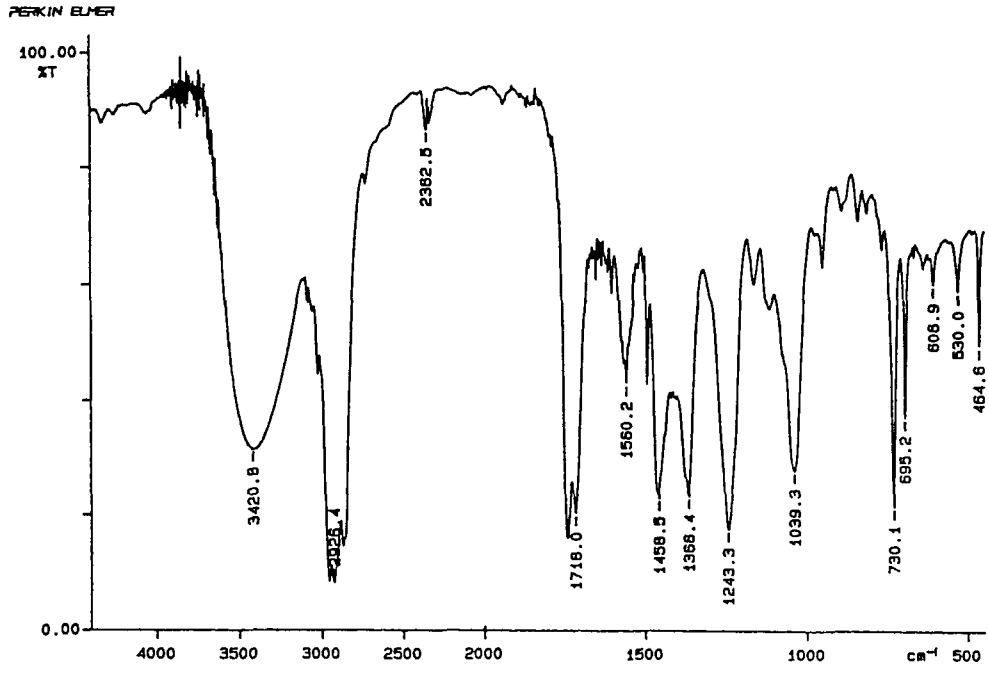
94/04/29 15:31
X: 4 scans, 4.0cm-1, abex
Sample 4

FIGURE 4A



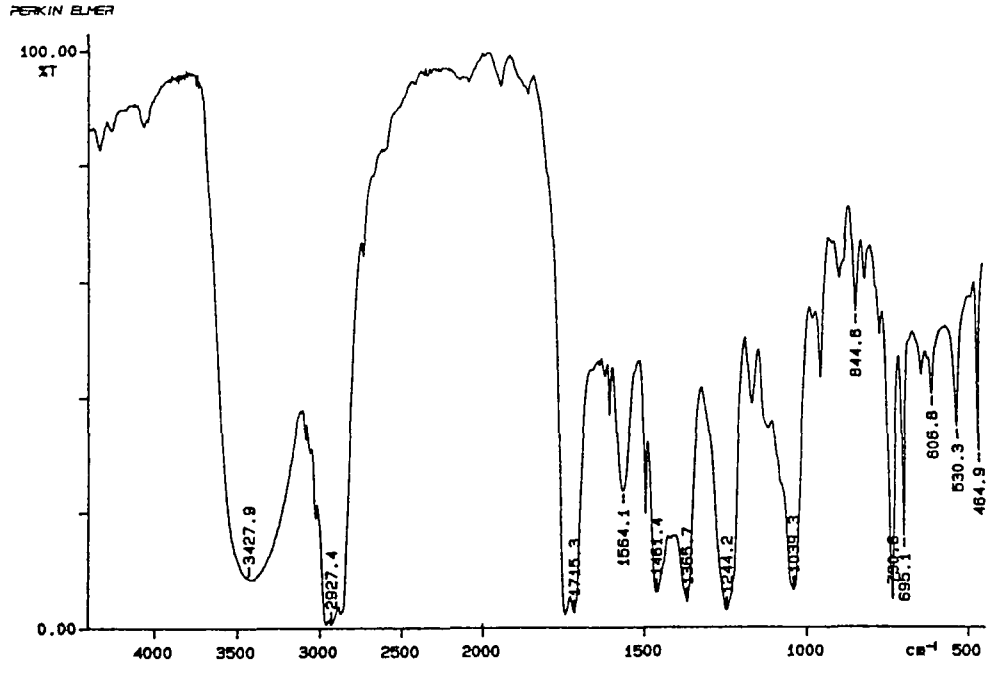
94/04/29 15:34
Y: 0 scans, 0.0cm-1, apod none, abex, not 1600
GASOLINE

FIGURE 4B



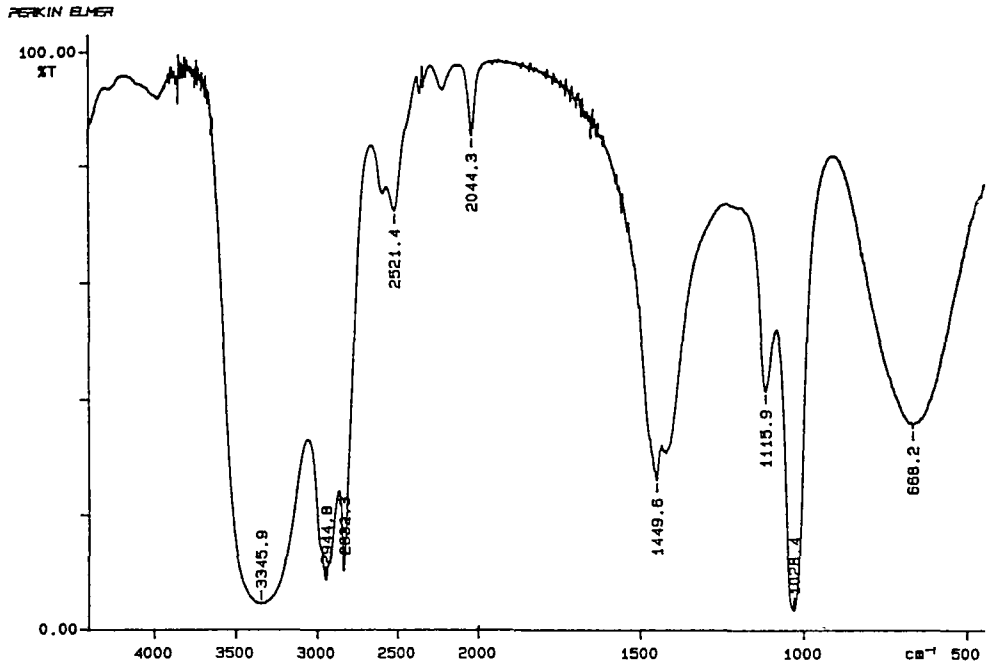
94/04/29 15: 12
X: 4 scans, 4.0cm-1, abex
Sample 5

FIGURE 5A



BU0063: 0 scans, 0.0cm-1, apod none, not 1600
Brush Cleaner

FIGURE 5B



94/04/11 09: 49
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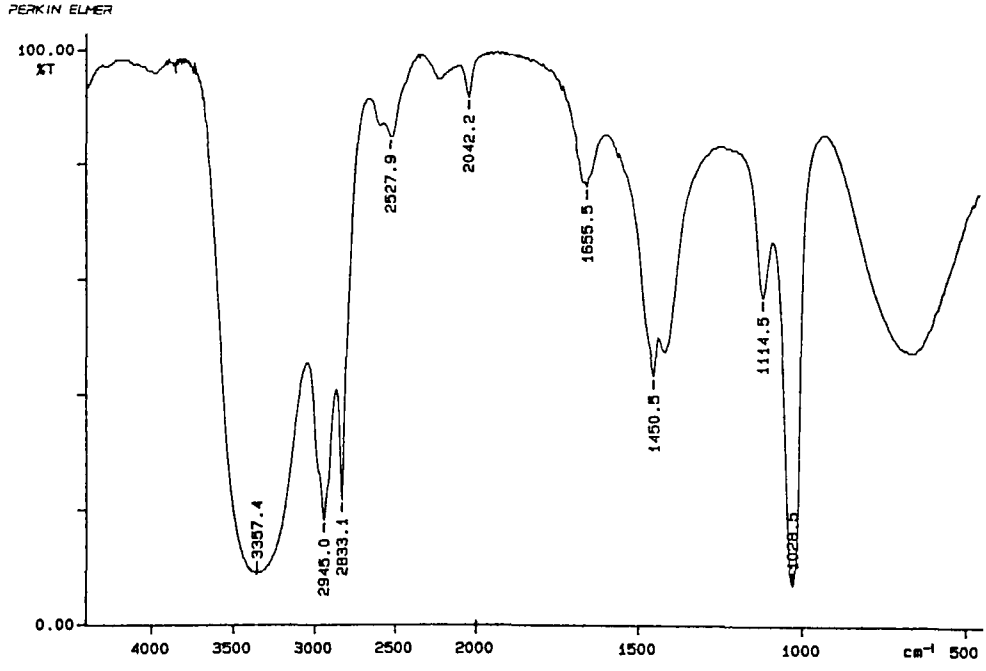
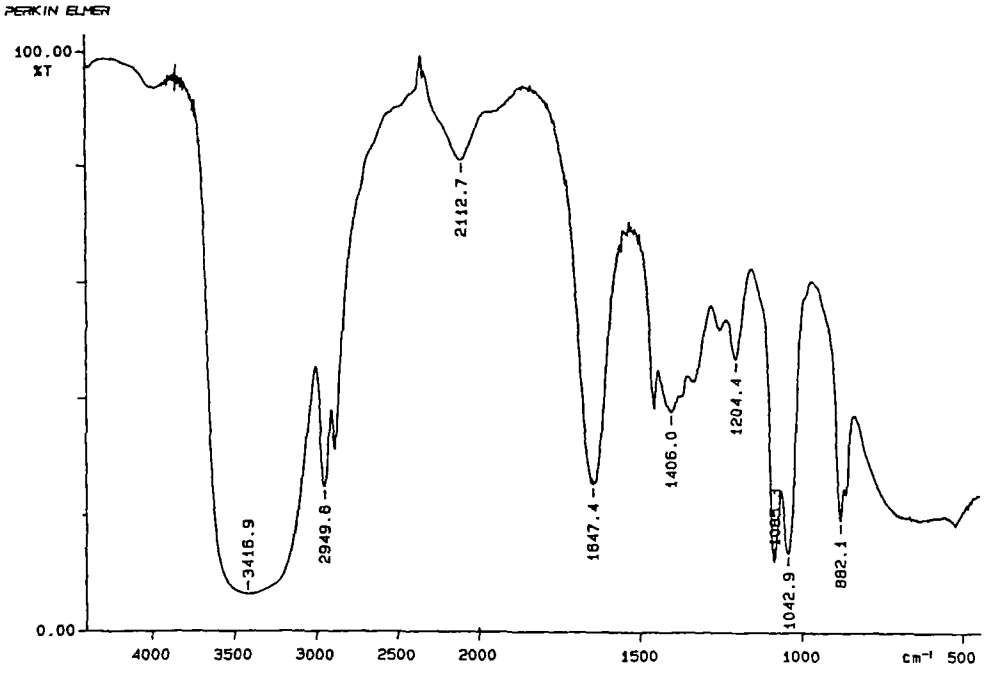
Sample 6

FIGURE 6A



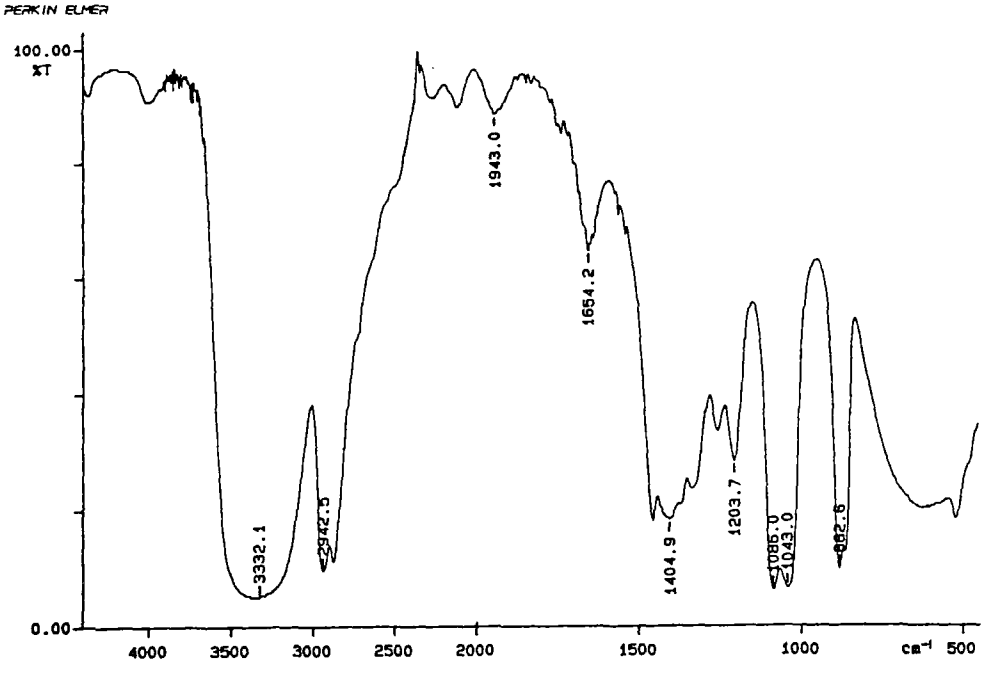
BU0005: 0 scans, 0.0cm-1, apod none, not 1600
Methanol

FIGURE 6B



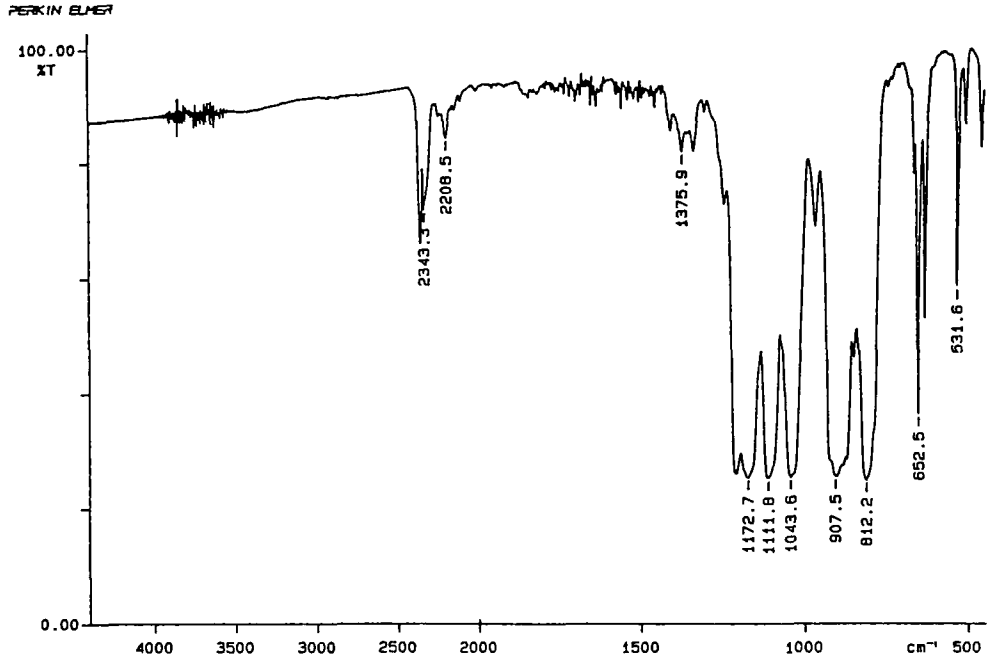
94/04/28 13:30
0441601: 4 scans, 4.0cm-1, abex
Sample 7

FIGURE 7A



BU0051: 0 scans, 0.0cm-1, apod none, not 1600
Ethylene Glycol

FIGURE 7B



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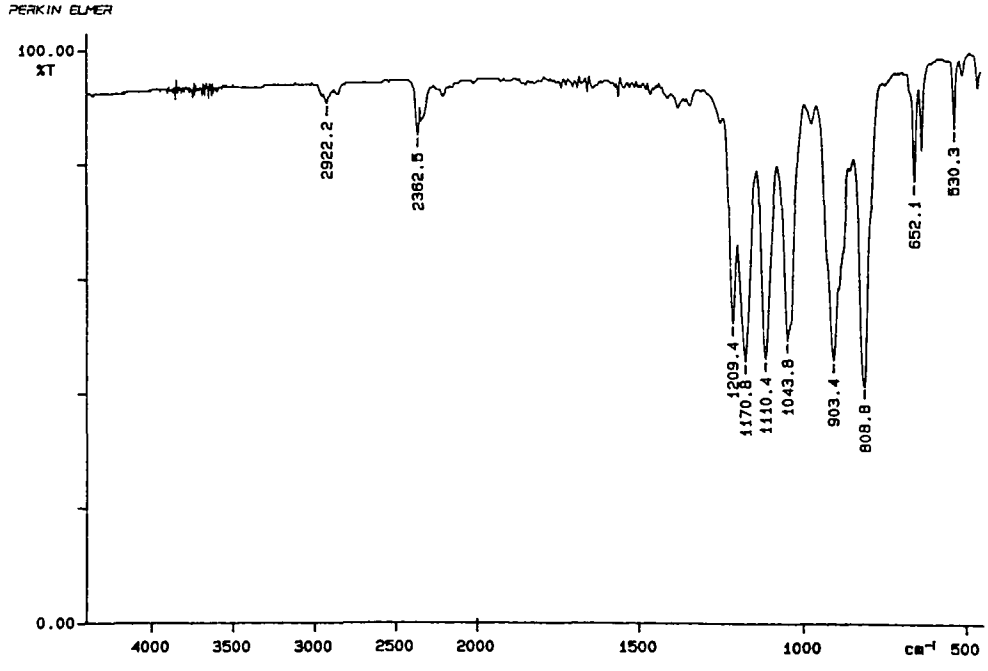
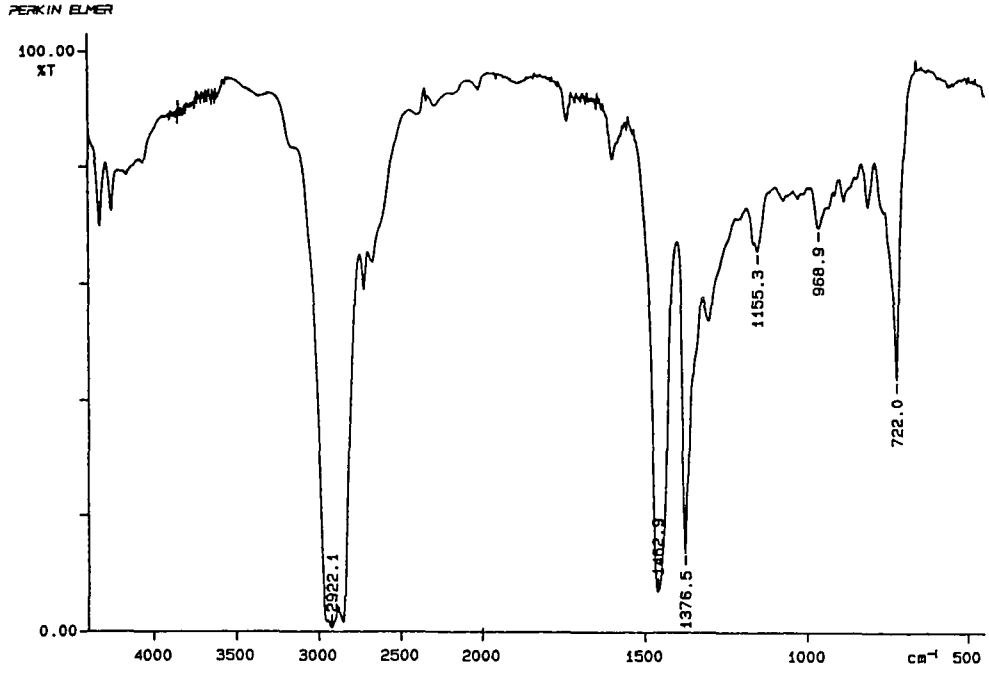
0224201: 4 scans, 4.0cm-1, abex
Sample 8

FIGURE 8A



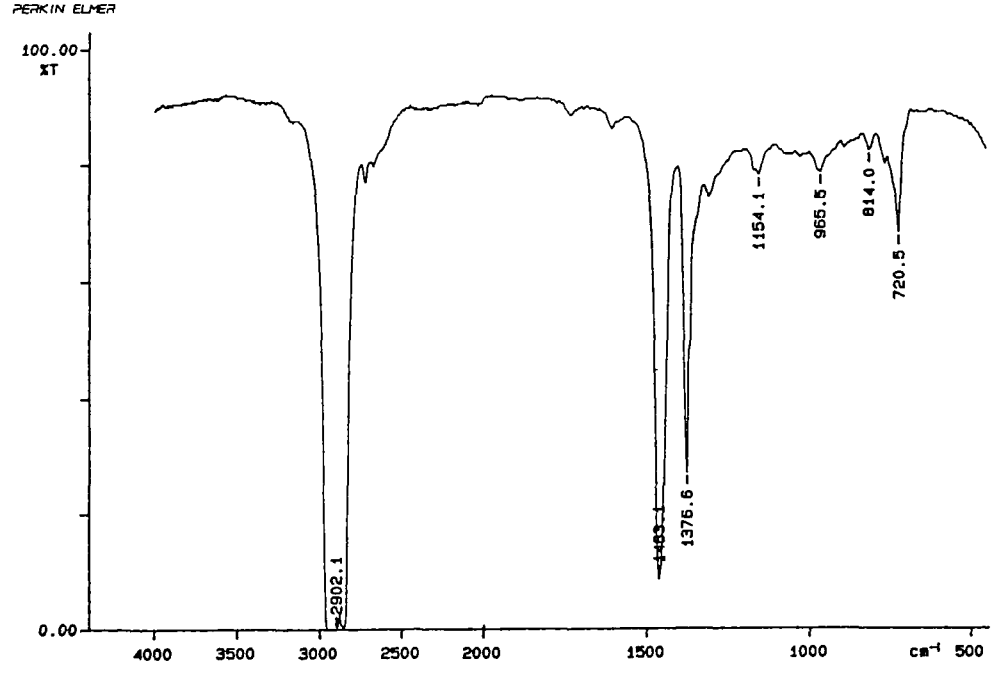
BU0038: 0 scans, 0.0cm-1, apod none, not 1600
Freon-113

FIGURE 8B



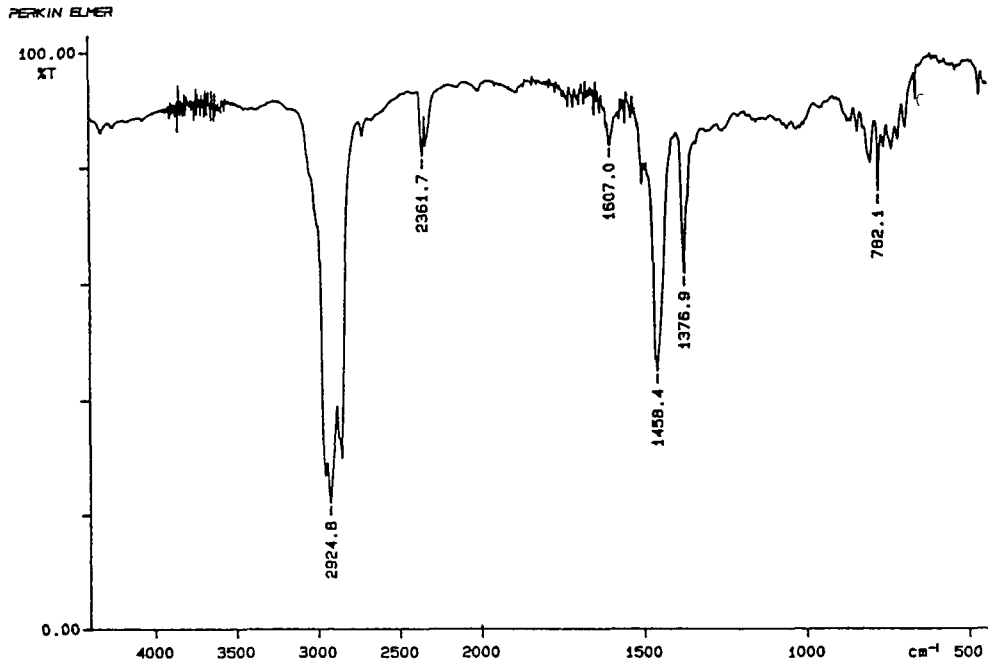
94/03/04 13: 13
0308101: 1 scan, 4.0cm-1, abex
Sample 9

FIGURE 9A



LU255A: 0 scans, 0.0cm-1, apod none, not 1600
SHELL TELLUS LUBRICANT

FIGURE 9B



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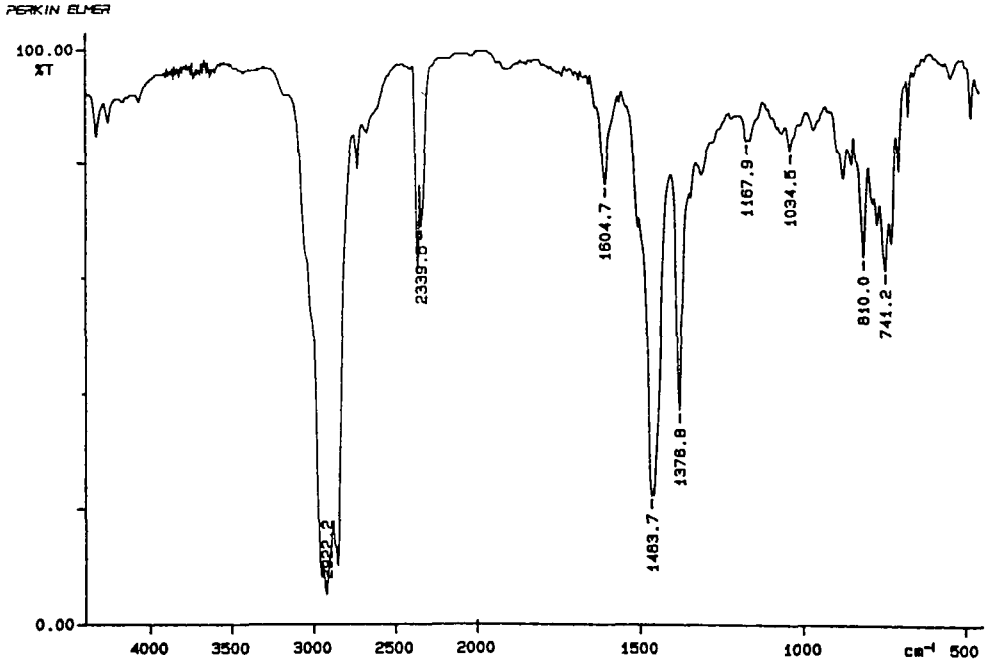
0412601: 1 scan, 4.0cm-1, abex
Sample 10

FIGURE 10A



BU0082: 0 scans, 0.0cm-1, apod none, not 1600
diesel fuel

FIGURE 10B

An Immunoassay for the Detection of Benzene in Water

S. Friedman, T. Stewart, and R. Allen

EnSys Environmental Products, Inc.
Research Triangle Park, NC 27709

Benzene is a toxic component of gasoline and other refined petroleum products. It is classified as both a carcinogen and a mutagen and presents a serious health risk to the general population. The contamination of groundwater is facilitated by its water solubility and occurs during the transport, processing, and storage of refined petroleum products. Total benzene usage in the United States has been estimated to be approximately 11 billion gallons per year, and 238,000 people are believed to be occupationally exposed to its toxic effects. Benzene testing is usually performed with a laboratory by GC using EPA Method 8020 or 8021A.

The antigen-antibody binding reaction of an immunoassay is a function of conformational complimentary of the reactants (i.e. lock and key). The equilibrium constant of the complex limits the sensitivity attainable by the assay, and is a function of cooperative, non-covalent, interactions that exist between the ligand and side chain chemistry of the antibody binding pocket. Larger ligands, having numerous sites of interaction with the antibody, produce the most sensitive immunoassay methods.

Benzene is, from an immunochemical perspective, a small and unremarkable molecule. Its aromatic ring configuration is a common constituent of many other compounds found in the environment. An antibody and immunoassay that recognizes benzene will often recognize other irrelevant compounds found in the same sample. The molecule's small size and chemistry also limits the potential association constant and assay sensitivity that can reasonably be expected. Current regulatory statutes for drinking water in most states, however, necessitates a method that can reliably detect benzene at approximately 10^{-9}M.

We have developed an immunoassay that can detect benzene at 5 ppb in a water sample. The test can be completed on location within approximately thirty minutes. The method includes a sample processing component that is used to collect, concentrate, and modify benzene in the sample. Extracted samples are subsequently analyzed using a monoclonal antibody-based ELISA that provides a chromogenic indication of contamination. The cross-reactivity of the test to a variety of associated aliphatic and aromatic compounds was found to be <1% for the majority of compounds tested. Analysis of BTEX compounds indicated approximately 10% cross reactivity for toluene, <1% for xylene isomers, and <1% for ethylbenzene. The technical strategy, protocol, and performance characteristics of the Benzene-RIS$^{c®}$ immunoassay method will be presented.

CHARACTERIZATION OF MULTIPHASE PARTITIONING

H. M. Liljestrand, Y. Shimizu, I. Lo, Y. D. Lee, and *J. K. Koo*, Civil Engineering ECJ 8.6, The University of Texas, Austin, Texas 78712.

ABSTRACT
The characterization of partitioning of pollutants among the various phases in complex mixtures is a common and challenging question. For neutral hydrophobic pollutants at low concentrations, the batch equilibrium partitioning between gas, aqueous, oily, and solid natural organic carbon phases is linear and depends upon the relative amounts of each phase as well as the partition coefficients between phases. By varying the total mass of mixture while holding total mass of tracer species and total volume constant in a headspace analysis for chemical species of a range of octanol-water coefficients, one can determine the product of the linear partitioning coefficient to a phase and the mass fraction of that phase, analogous to Kp = (%OC) Koc in aqueous-solid natural organic carbon systems. Ideally for n different phases, n different tracer species are used, with one species preferentially partitioning into each different phase. In practice, the number of species introduced is at least 3X the number of phases. For samples with a high content of oily phase, the headspace partial pressure of a homologous series of perfluorocarbons is used with the mass balance to determine the oil content and partitioning. A comparison of this process of introducing tracers and measuring the headspace fugacity after sorption equilibrium with the alternative approach of quantifying the amount of each phase and determining the desorption equilibrium by sequential extraction measurements indicates the former is more rapid both in terms of the time to reach equilibrium and the number of tests.

Validation of an Enzyme Immunoassay Based Field Screening System for the Detection of RDX in Soil and Water Samples

George B. Teaney and Robert T. Hudak
Strategic Diagnostics Incorporated
128 Sandy Dr.
Newark, DE 19713

ABSTRACT

RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine, is a secondary military explosive commonly found in soils and ground water at munitions demilitarization sites. This compound is very mobile in soils, and is often used to indicate the leading edge of the explosives plume in soils and ground water. The development of a field screening method specific to RDX would greatly benefit the explosives remediation effort. The use of inexpensive field screening methods can reduce the total cost and improve the efficiency of site surveys and remediation projects. Field screening techniques can also circumvent the long turnaround time of laboratory analysis by providing reliable on site results.

The portable RDX enzyme immunoassay (EIA) is a quick, cost effective, highly specific, and user friendly field screen option. The components of this EIA include RDX specific antibodies (Ab) covalently linked to small latex particles, an RDX analog which is covalently linked to alkaline phosphatase, and the free RDX in the water sample. The free RDX competes with the enzyme linked analog for the Ab binding sites. The latex particles are then collected on a filter device, washed, and an enzyme substrate is added. The amount of color produced is inversely proportional to the concentration of free RDX in the water or soil sample, and can be determined using a hand held reflectometer, or a color card.

This paper presents much of the work undertaken to validate this field screening method. This assay has demonstrated 5 ppb and 0.5 ppm sensitivity in water and soil samples respectively, with minimal cross-reactivity to EPA SW-846 Method 8330 analytes and other common organic pollutants. This assay has displayed minimal false negative and false positive rates in soil and water matrices, and incorporates a 3 minute soil extraction step with average recoveries of 90%. The RDX assay has been proven effective and reliable as field trials report 90% and 96% correlation to Method 8330. False positive rates during field trials have been reported as approximately 4 %, where as no false negative results have been reported.

INTRODUCTION

RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine, is a secondary military explosive commonly found in soils and ground water at munitions demilitarization sites. This compound is very mobile in soils, and is often used to indicate the leading edge of the explosives plume in soil and ground water. As such, characterization and remediation of these sites are essential to insure ground water quality in the surrounding region.

Initial efforts in any remediation project will generally focus on site characterization. The most commonly used analytical method for explosives determination is EPA SW-846 Method 8330[1]. This laboratory method is very robust, however it is also time consuming, and costly. When surveying the boundaries of the contaminant plume, a large percentage of the samples analyzed

are free of contamination. These sample can be more efficiently identified using field screening techniques, sending only known positive samples to be confirmed by the laboratory procedure. The development of a field screening method specific to RDX would greatly benefit the explosives remediation effort providing the method is accurate, reliable, cost effective and user friendly. The use of inexpensive field screening methods can reduce the total cost and improve the efficiency of site surveys and remediation projects. Field screening techniques can also circumvent the long turnaround time of laboratory analysis by providing reliable on site results.

Immunoassay based field screening techniques have gained increased popularity in recent years. Immuno-technology is rooted in medical diagnostics industry and has been used since the late 1950's. This technology is based on the specificity and sensitivity of the antibody-antigen interaction. Antibodies are proteins produced in response to a foreign substance (antigen) in the body. These proteins recognize 3-dimensional molecular structure and physically bind the compound which elicited their response.

This paper discusses the development of an immunoassay based field screening system for the detection of RDX.

METHODS

The assay format of this test is a competitive enzyme immunoassay (EIA). Briefly, the components of this EIA include RDX specific antibodies (Ab) covalently linked to small latex particles, an RDX analog which is covalently coupled to alkaline phosphatase, RDX reference material, and the free RDX in the water sample. The water sample is added to a test vial containing lyophilized Ab-Latex and enzyme conjugate. At the same time a rehydration buffer is added to the reference vial, suspending the lyophilized Ab-Latex, enzyme conjugate and reference material within. The free RDX in the water sample or the reference material competes with the enzyme linked analog for the Ab binding sites. The latex particles from the test and reference vials are then collected in a duel well filter device, and washed to remove any unbound material. An enzyme substrate is added, and the reference color allowed to develop. The amount of color produced in the test well is inversely proportional to the concentration of free RDX in the water or soil sample, and can be determined relative to the reference well using a hand held reflectometer, or a color card. The reflectometer measures the reflectance in each well and displays its results in units of percent relative reflectance (%RR), the reflectance of the test relative to that of the reference. The %RR can be used with the translation table supplied in the D TECH™ kit to estimate RDX concentration.

Sample preparation of soil or water matrices is minimal. Soil samples must go through a quick and simple extraction in 100 % acetone followed by a 2 step dilution and filtration step prior to testing. A water sample requires a quick 1 step dilution and filtration prior to testing. Unless noted below, all extraction, dilution and filtration steps were carried out as described in the D TECH product literature.

Using the test as described above, we investigated the sensitivity, and specificity of the assay. Attributes of the test such as the false positive / false negative rates were determined both theoretically and using spiked and real world samples. Organic co-contaminants were evaluated as possible interfering substances. Soil extraction efficiencies were evaluated as was performance under field conditions.

RESULTS AND DISCUSSION

Assay sensitivity was determined for water and soil systems by developing standard curves (Figure 1) while assessing the error associated with one half and twice the minimum detection limit (MDL) (Table 1). The assay sensitivity has consistently been demonstrated at 5 ppb in water and 0.5 ppm in soil samples with an over all assay range of 5 ppb to 60 ppb and 0.5 ppm to 6.0 ppm respectively. As described by the EPA a false positive is a sample which yields a positive test result but contains less than half of the method detection limit [2]. Similarly, a false negative is a sample which yields a negative test result but contains more than twice the method detection limit. Using these criteria, and a 96% confidence interval (2 standard deviations), 5 ppb is clearly discernible from zero, the false positive (2.5 ppb) and the false negative (10 ppb) thresholds in water. The false positive threshold (2.5 ppb) is clearly discernible from the MDL by 2 standard deviations(SD) while the false negative threshold (10 ppb) is discernible by 3 SD (99 %).

Assay specificity was evaluated by testing a host of explosives commonly associated with RDX remediation sites. All compounds described in Method 8330 as well as others were tested for cross-reactivity in the assay (Table 2). These compounds were initially tested at a concentration 100 times the method detection limit (5 ppb) in the assay. One analyte, octahydro-1,3,5,7-tetranitro-1,3,5-triazine (HMX), was found to be marginally cross-reactive (≈2% relative to RDX), while all other compounds tested were undetected (Figure 2). The MDL of HMX in a water sample is approximately 150 ppb and the IC_{50} (concentration yielding 50 % inhibition in the assay) approximates 900 ppb. In the real world, sites containing RDX contamination are also likely to have HMX. Due to this likelihood, the results of the field screen are expressed as RDX equivalents.

Twenty three potential organic co-contaminants were evaluated in the RDX assay at a concentration of 500 ppb (100 times the MDL of the assay). These compounds represent a cross section of herbicides, organic solvents and polyaromatic hydrocarbons likely to be found at explosives sites (Table 3). When tested at 500 ppb, none of these compounds tested positive in the assay.

Water and soil matrix effects were evaluated by testing 22 different RDX-free water and soil samples collected from across the country (Table 4). The water samples encompass a wide range of ground and surface water chemistries. Likewise, the soils tested reflect a wide range of soil types, textures, and chemistries. Water and soil extracts were spiked at 0.5X and 2X the assay detection limit to determine the effect of sample matrix on the assay. All treatments were run in triplicate including non-matrix controls (Figures 3 and 4). All water samples spiked at 10 ppb were reported to contain RDX at levels greater than 5ppb (%RR > 0). Similarly, with the exception of sample 8, all of the waters spiked at 2.5 ppb were reported as < 5ppb (%RR < 0). The water type in question (sample 8) was collected from the Pacific Ocean, where all other samples were collected from fresh surface water or ground water sources. As a result, the use of a salt water matrix in this system is not recommended. Soil matrix results show similar trends (Figure 4). In all 22 soil treatments, the assay false negative threshold (1.0 ppm) were reported as > 0.5 ppm, while samples containing the false negative threshold (0.25 ppm) were reported as < 0.5 ppm (no false negative or false positive samples reported).

Soil spike and recovery studies were conducted using 10 chemically and physically diverse soils (Table 5). Soil samples were spiked with RDX concentrations of 1 ppm and 6 ppm and each treatment was replicated 6 times. All samples were run as described in the product users guide and the relative reflectance data was converted to discrete RDX concentrations using the assay standard curve. Extraction efficiencies across all treatments ranged from 53 % to 114 % recovery (Table 6). Recoveries of the 6 ppm spike appears to be highly efficient where as

recoveries of the lower concentration averaged 86 %. There was no apparent correlation between the soil characteristics in table 5 and the poor recovery in soil 101 spiked at 1 ppm. Considering most of the analytical laboratories accept a matrix spike recovery of ± 30 %, the field screen extraction procedure is effective across the soils tested.

Thirty one (31) real world soil samples were collected from proprietary sites in the north western United States. The field moist samples were mixed thoroughly and split into 2 sub-samples. One sub-sample from each of the 31 soils was sent to Data Chem Laboratories, Salt Lake City, Utah, for Method 8330 analysis. The second set of sub-samples were tested using the D TECH RDX immunoassay. The samples were extracted using the standard D TECH procedure with the following exception; in order to lower the sensitivity of the assay, the soil extract dilution step was modified. This lowered the working range of the kit from 0.5 - 6.0 ppm to 0.4 - 4.0 ppm. The results from the D TECH assay were compared with the results of Method 8330 to assess the correlation between methods (Figure 5). No false positive or false negative samples were reported by D TECH. In order to obtain a more accurate assessment of the correlation in the quantitative range of the kit, samples reported as less than 0.4 ppm by both methods were omitted from the analysis. Similarly, samples greater than 4.0 ppm by both methods were omitted from the analysis. Regression analysis of this modified data indicate a slope of 1.02 with a coefficient of correlation reported as 90% (Figure 5). When all of the data were included in the analysis the coefficient of correlation increased to 94% and the y-intercept was reported as 0.03 (data not shown). In either case there is good agreement between the laboratory based method and the field screening method.

The results of a recent field trial report exceptional agreement between D TECH and Method 8330. Sixty six samples were extracted and tested in duplicate by D TECH and were then sent to Hercules Environmental Testing Laboratories, Magna, Utah, for Method 8330 confirmation. No false negatives were reported by D TECH during this trial. However, 3 samples (4%) were reported as false positive. Linear regression analysis of the D TECH and Method 8330 data was performed as described above. Samples less than 0.5 ppm by both methods and greater than 6.0 ppm by both methods were omitted from the data set. The results from this analysis report a slope of 1.1 and a 96% coefficient of correlation (Figure 6).

A collaborative field trial was conducted with the Roy F. Weston Company in Lionville, PA. During this study 30 soil samples from random explosives sites were pulled from the Weston archives. Using the historical analytical data, samples were selected so that 10 were below a concentration of 1.3 ppm and the remaining 20 were greater than 1.3 ppm. In cases where the historical data yielded RDX concentrations greater than 6 ppm, the sample extract was diluted in an appropriate volume of acetone to bring the sample within the working range of the assay. The samples were tested using the immunoassay and results confirmed by SW-846 Method 8330. All assays were run by Weston personnel. No false positive or false negative samples were reported in this study. Using the assay standard curve, the relative reflectance data and the additional dilution factor were transformed into discrete RDX concentrations. These data were regressed against Method 8330 results omitting the samples below the detectable limit of both methods. The regression analysis reported a slope of 0.92 and a correlation coefficient of 91 % (Figure 7)

In the field, soil samples were tested in less than 20 minutes (15 minutes for a water sample). and several tests can be run simultaneously. Previous experience with this system has shown that 1 person can run, on average, 50 tests per day. The water test requires the user to follow 7 easy steps and all components required to run a test are included in the kit. The cost of this system is approximately one fifth to one tenth the cost of more rigorous analytical procedures.

CONCLUSIONS

The D TECH RDX field screen system has demonstrated a high degree of sensitivity and specificity while demonstrating a low false positive (≤ 4 %) and false negative (< 1%) potential. The assay has been designed to minimize sample matrix effects in water and soil. The low cost per test coupled with the ease of use and quick results facilitate a much wiser use of the analytical dollar. Using such a system greatly reduces the number of negative samples sent to the laboratory for analytical confirmation.

The D TECH method has shown greater than 90 % correlation with EPA SW-846 Method 8330, while exhibiting the ease, time and cost effective attributes required for field screening systems.

ACKNOWLEDGMENTS

The authors would like to thank Robin Dolan for her outstanding effort at the bench, Dr. Larry Motyka and Dr . James Stave for their work in developing the RDX antibody, and Dr. James Melby for his guidance throughout the project.

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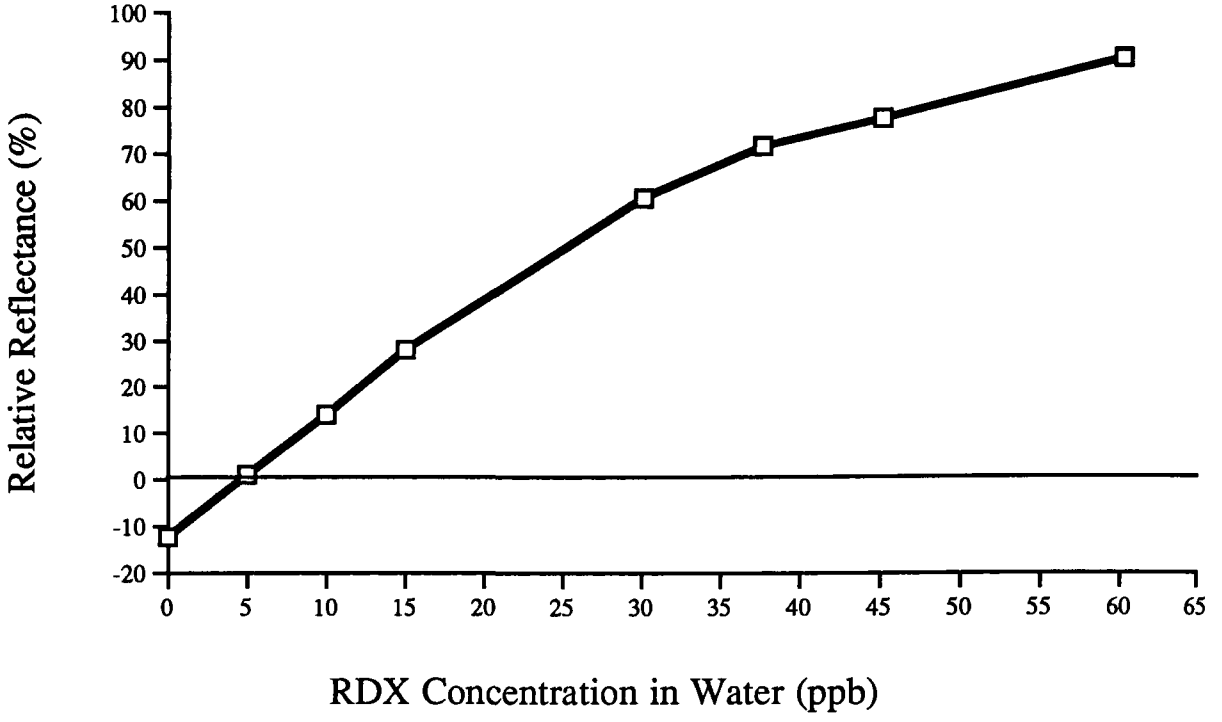


Figure 1. The D TECH RDX water kit standard curve

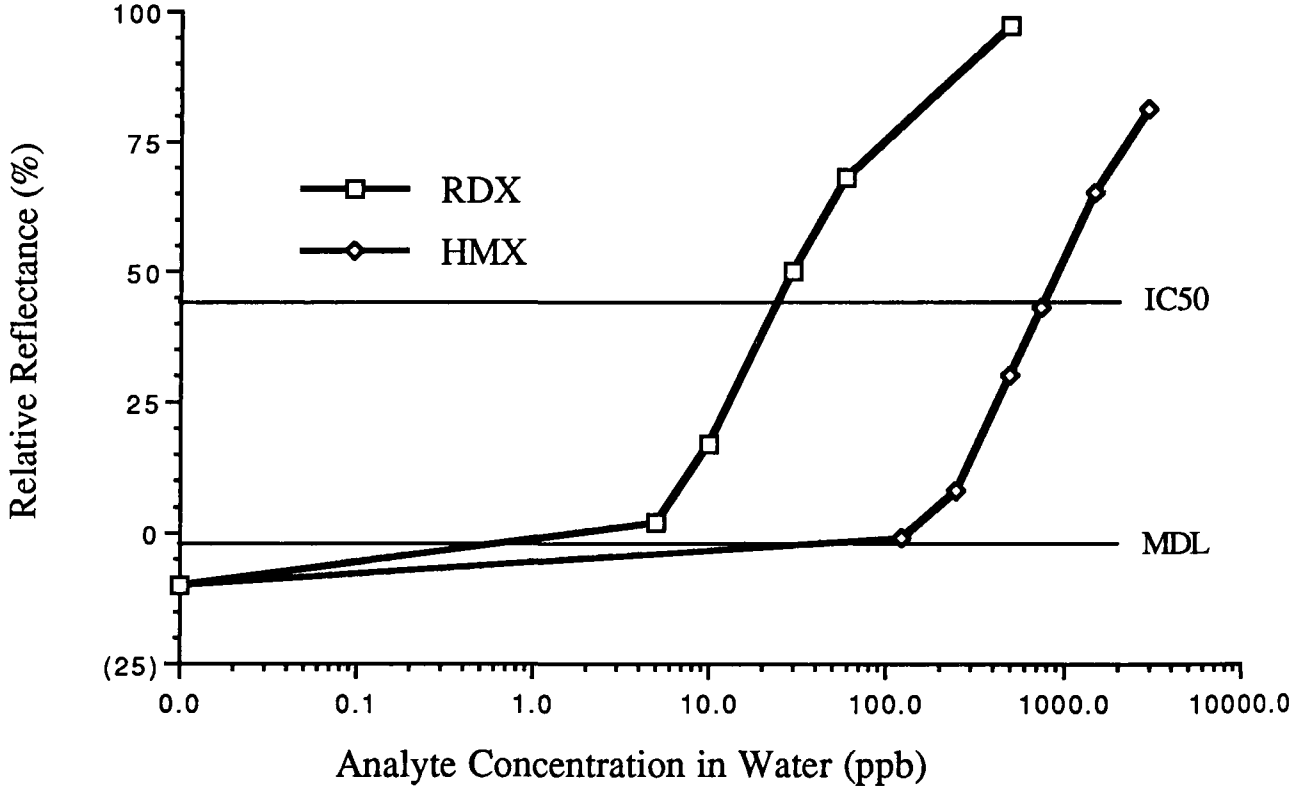


Figure 2. Cross-reactivity characteristics of HMX in the D TECH RDX assay

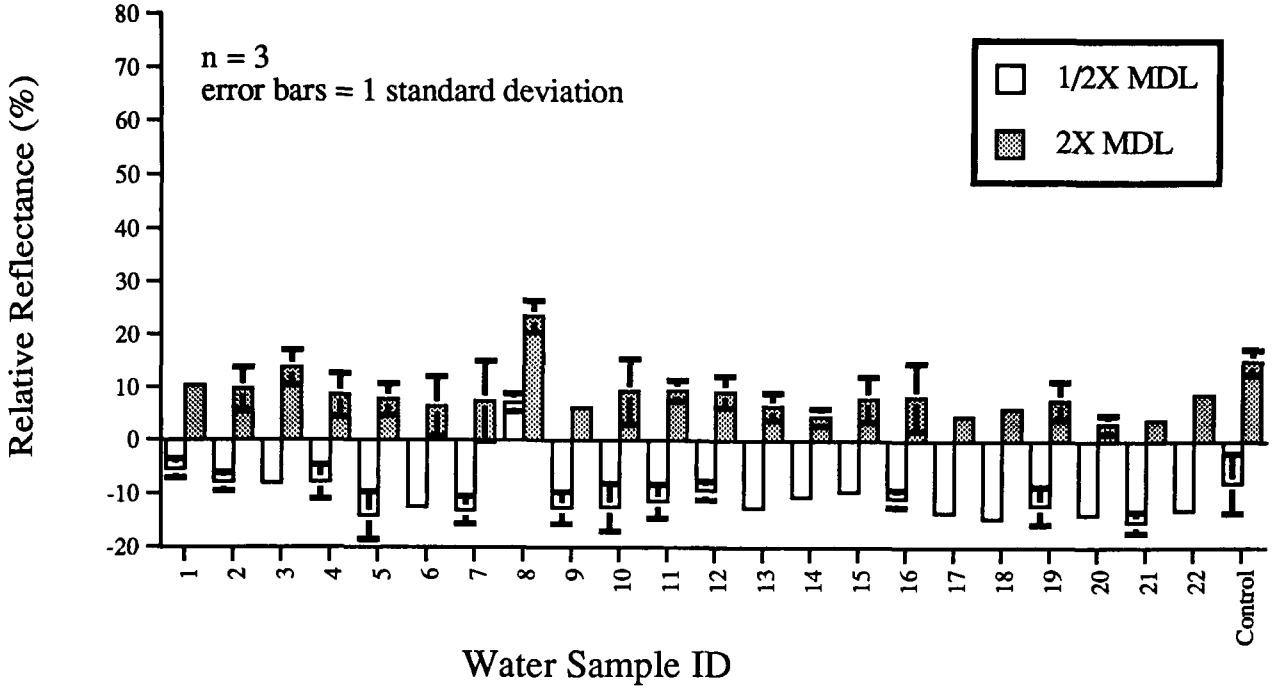


Figure 3. The effect of different water types on the sensitivity of the D TECH RDX assay.

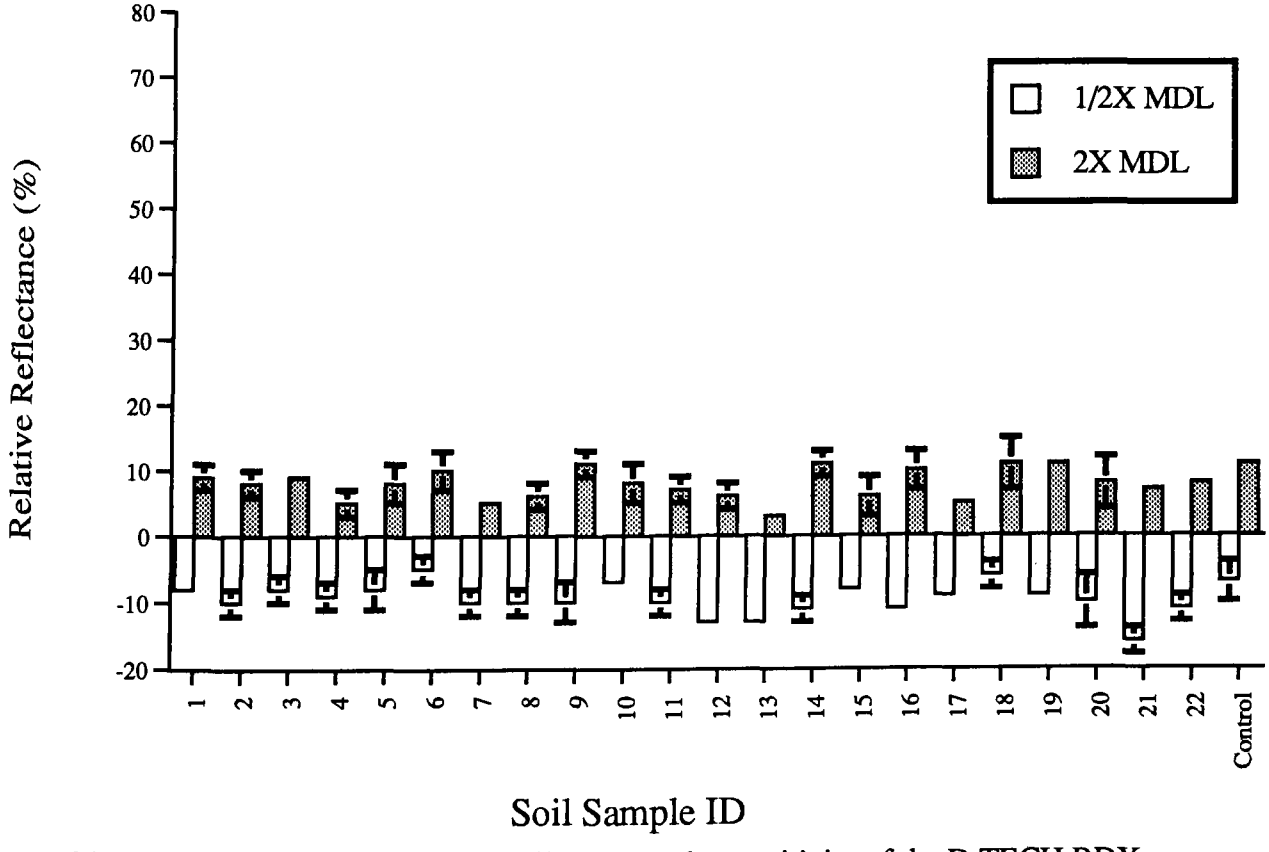


Figure 4. The effect of different soil types on the sensitivity of the D TECH RDX assay.

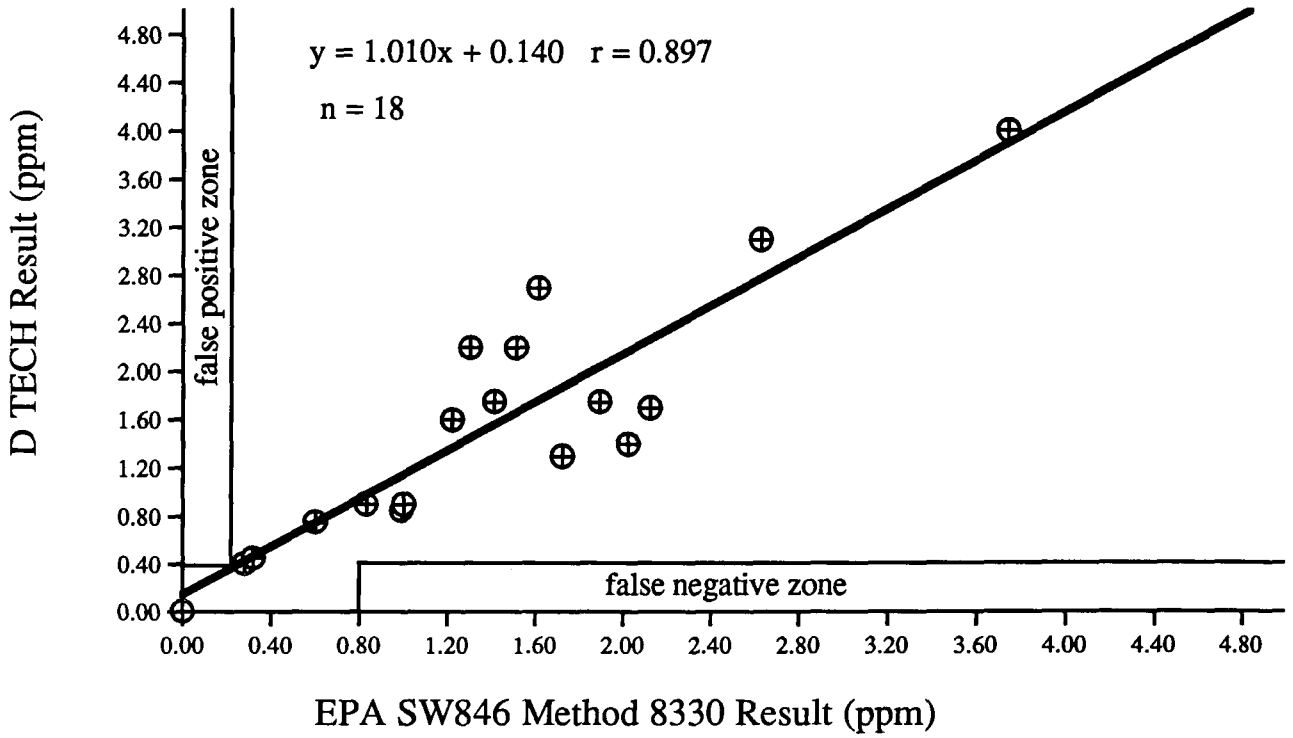
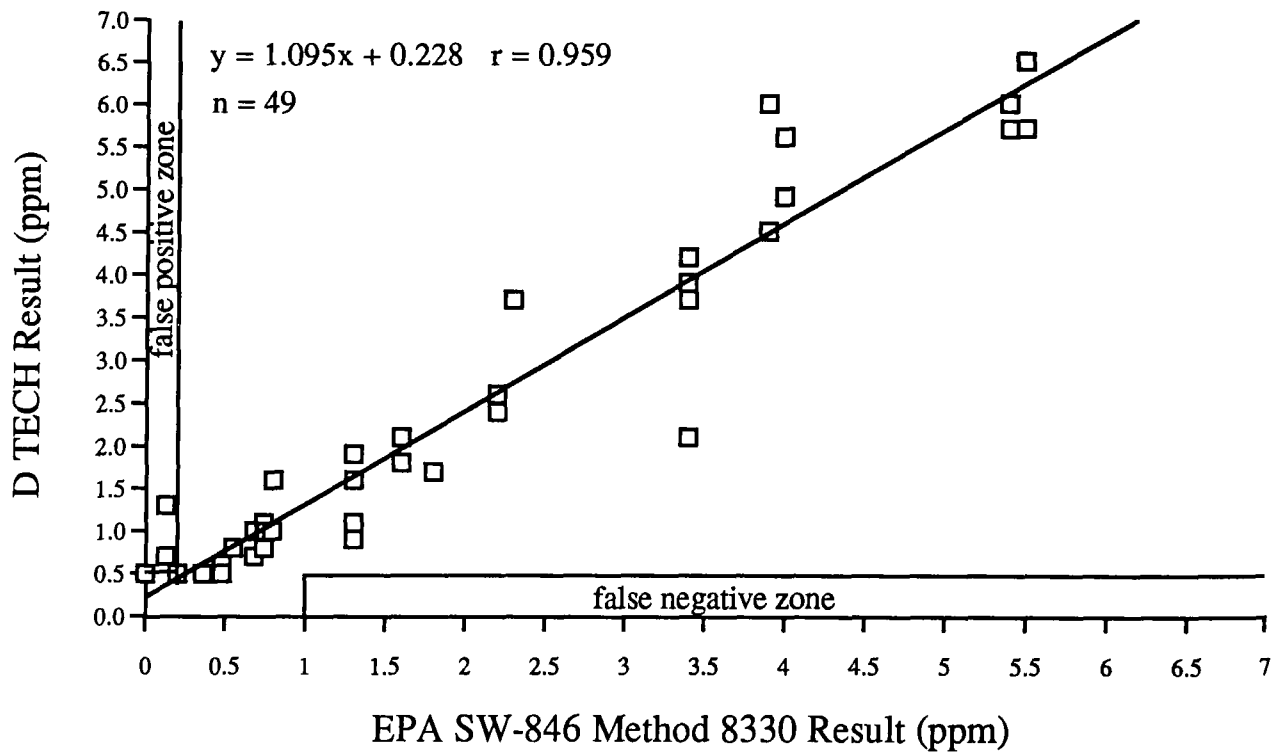


Figure 5. Method correlation from an analysis of 18 real world RDX soil samples



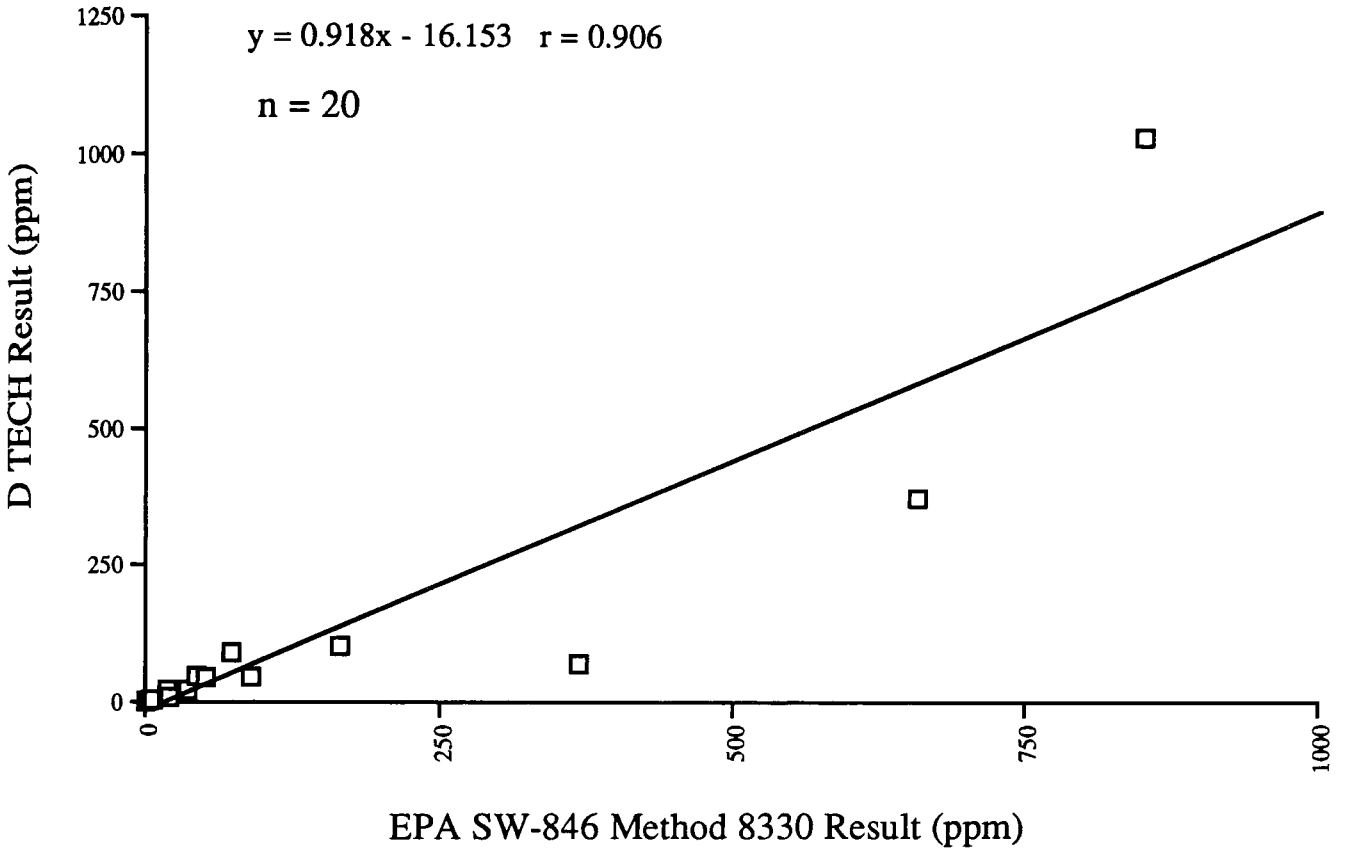


Figure 7. Method correlation from an analysis of 20 RDX contaminated soils conducted by Roy F. Weston Company

Table 1. RDX Assay sensitivity and range in deionized water

RDX Concentration (ppb)	Concentration Significance	Mean RR (%)	Standard Deviation
0	True Negative	-10	3
2.5	FP Threshold	-4	2
5	MDL	4	4
10	FN Threshold	18	3
30	Mid-Range	56	4
60	High-Range	77	5

n = 10
FP = false positive
FN = false negative
RR = relative reflectance

Table 2. Compounds tested for cross-reactivity in the D TECH RDX assay. If detected at 500 ppb or less, the compound was determined to be cross-reactive.

Analytes of Interest	Detected
M8330 Compounds	
1,3-Dinitrobenzene	No
2,4-Dinitrotoluene	No
2,6-Dinitrotoluene	No
HMX (octahydro-1,3,5,7-tetranitro-1,3,5-triazine)	Yes
RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	Yes
Nitrobenzene	No
2-Nitrotoluene	No
3-Nitrotoluene	No
4-Nitrotoluene	No
Tetryl (Methyl-2,4,6-trinitrophenylnitramine)	No
2,4,6-Trinitrotoluene	No
1,3,5-Trinitrobenzene	No
2-Amino-4,6-dinitrotoluene	No
4-Amino-2,6-dinitrotoluene	No
Others	
NG (Nitroglycerine)	No
PETN (Pentaerythritoltetranitrate)	No

Table 3. Potential interfering organic co-contaminants tested in the RDX assay

Compound	Concentration of analyte in a water sample required to yield a positive test result (ppb)
Atrazine	> 500
Aroclor 1254	> 500
Acetone	> 500
Toluene	> 500
Ethylbenzene	> 500
Xylene	> 500
Benzene	> 500
Methanol	> 500
Benzo(a)pyrene	> 500
Acenaphthene	> 500
Acenaphthalene	> 500
1,2-Benzanthracene	> 500
Benzo(k)fluoranthene	> 500
Benzo(ghi)perylene	> 500
Benzo(b)fluoranthene	> 500
Chrysene	> 500
Dibenz(ah)anthracene	> 500
Fluoranthene	> 500
Fluorene	> 500
Indeno(123-cd)pyrene	> 500
Naphthalene	> 500
Pyrene	> 500
Phenanthrene	> 500

Table 4. Soil and water types used in D TECH RDX assay matrix studies

Soil / Water ID	Soil Type	Water type
1	Low organic clay loam	Adamsville, RI
2	Sassafras sandy loam	Buttermilk Falls, PA
3	Cecil soil sandy clay loam	Hudson River, PA
4	Davidson clay loam	Germantown, PA
5	Shontik-Casa Grande clay loam	Houston, TX
6	Trix sandy clay loam	Houston, TX
7	Trix-Casa Grande clay loam	Ontario, CA
8	Yolo loam	Pacific Ocean
9	Capay silty clay	Dartmouth, MA
10	Sycamore silt loam	Newark, DE
11	Dennis silt loam	# 641
12	Luray silty clay loam	# 643
13	Wooster silt loam	# 645
14	Vienna loam	# 654
15	Opal clay	# 659
16	Raub silt loam	# 843
17	Rockfield silt loam	# 848
18	Cisne	# 850
19	Muscatine	Georgetown, DE
20	Avonberg	Georgetown, DE
21	Matapeake silt loam	Smith Island, MD
22	Evesboro low OM samd	Newark, DE
23	Non-Soil Control	DI Water Control

Table 5. Chemical and physical charicteristics of soils used in the RDX spike and recovery studies

Soil ID	Sand (%)	Silt (%)	Clay (%)	pH	OM[a] (%)	Soluable Salts (mmho/cm)	Fe-Oxide (mg/kg)	Al-Oxide (mg/kg)	CEC[b] (meq/100g)
101	34	46	20	6.0	1.5	0.12	5170	1129	9.1
106	93	4	3	5.5	0.1	0.34	740	334	2.0
108	31	15	54	6.6	2.2	0.09	27875	3265	8.3
109	37	12	51	5.4	2.3	0.12	25250	1724	13.5
110	88	6	6	4.9	12.1	0.33	252	1086	24.8
116	14	35	51	6.8	2.2	0.02	6870	595	34.1
117	52	30	18	7.6	2.8	0.37	5605	332	23.8
123	11	27	62	6.7	3.6	0.45	9010	725	36.0
126	15	46	39	5.2	5.2	0.38	4711	939	41.2
128	22	68	10	6.2	4.4	0.75	4286	593	29.5

[a] OM = Organic Matter content as derived by loss on ignition
[b] CEC = Total Cation Exchange Capacity at pH 7.0

Table 6. RDX soil spike and recovery study

Soil ID	RDX Spike (ppm)	Mean RDX Concentration (ppm)	Standard Deviation	Coefficient of Variation (%)	Recovery (%)
101	1	0.53	0.19	35	53
106	1	0.88	0.13	15	88
108	1	0.86	0.23	26	86
109	1	0.66	0.22	34	66
110	1	0.70	0.14	19	70
116	1	0.96	0.12	13	96
117	1	0.92	0.42	46	92
123	1	1.00	0.45	45	100
126	1	1.03	0.25	24	103
128	1	1.02	0.18	18	102
Non-Soil Control	1	1.05	0.13	12	105
Average	1	0.86	0.23	27	86
101	6	4.92	0.54	11	82
106	6	6.15	0.84	14	103
108	6	5.67	1.09	19	95
109	6	6.11	0.93	15	102
110	6	6.12	0.46	8	102
116	6	6.26	1.21	19	104
117	6	5.71	0.72	13	95
123	6	6.05	0.80	13	101
126	6	6.82	0.33	5	114
128	6	6.02	0.62	10	100
Non-Soil Control	6	6.02	0.83	4	100
Average	6	5.98	0.75	13	100

DIRECT ANALYSIS BY RAMAN SCATTERING: AN EMERGING TECHNOLOGY FOR WASTE REMEDIATION

Charles K. Mann, Thomas J. Vickers, Department of Chemistry, Florida State University, Tallahassee, FL 32306-3006

Abstract

The property of Raman spectroscopy of producing distinctive vibrational spectra by measuring light scattered from a sample make it an attractive basis for direct analysis of complex mixtures. Accordingly, an extensive study has been made with the aim of understanding the requirements for its routine application in chemical analysis. After examination of both dispersive and interferometer-based spectrometers, it became apparent that, for chemical analysis, dispersive instruments using charge coupled device (CCD) detectors and operating in the visible or near-infrared offer significant advantages in sensitivity.

We describe developments aimed at reducing Raman scattering measurements to automated routine practice. These involve several types of corrections of systematic errors that occur. Detector sensitivity variation, wavelength dependence, read pattern signal and dark signal must be compensated. In addition, corrections are made for wavelength calibration error and for day-to-day variations in the sensitivity of system response. Procedures have been worked out to support automated implementation of these corrections. There are two stages. The first is a calibration of spectrometer wavelength response which is performed on installation of a system. The second consists of several measurements that are made at each measurement session to monitor and compensate for day-to-day changes in performance.

Limits of detection for quantitative analysis range from 0.005 to 5 percent, depending upon the identity of the analyte. Limits for qualitative analysis are usually about an order of magnitude higher than the quantitative limits. Examples are shown.

Raman measurements applied to several types of samples are illustrated. One group consists of examples of measurements that were made on material that was removed from the disposal tanks at the Hanford Site in Richland, WA. Another is a sequence of quantitative measurements that were made on slurries of organics and inorganics. Another class is taken from a study of analysis of paint films. A fourth type demonstrates the wide dynamic range of the technique with a series of measurements in which a minor component is extracted from the signal produced by a major component that is present in 1000-fold excess.

Introduction

Raman spectroscopy is capable of dealing with certain types of samples that are difficult to handle by most other techniques available to the analytical chemist. It works well with solids, mixtures of solids and liquids and with nonvolatile solutes in solutions. Water does not interfere with analyses, but it can be determined down to about the five-percent level.

Raman scattering produces a form of vibrational spectra. Accordingly, only substances with some degree of covalent structure show Raman activity The selection rules differ from those for infrared, however in compounds with more than a few atoms, both forms generally produce bands at the same position, with differing intensities. From the perspective of chemical analysis, both types of spectra produce similar information. The spectra are very distinctive. A molecular structure change as subtle as variation in the geometry around a single carbon atom in an 800-Dalton molecule produces obvious changes in the spectrum.

In a mixture, it will ordinarily be true that any component that is present in excess of one percent of the sample will make a visible contribution to the shape of the mixture spectrum. The Raman effect is linear and it is possible to measure spectra under conditions that preserve that linearity. Accordingly, the distinctive features of a one-percent constituent can usually be made the basis for a direct quantitative determination, *irrespective of the global composition of the sample*. This works because the true limit of detection (LOD) is ordinarily one to two orders of magnitude below one percent. With current technology it varies from 0.005 to 5 percent, depending upon the analyte. In the usual case it is around 0.1 percent., with high LOD values being found for disordered polymeric materials, such as water, the hydrous oxides and ammonium ion.

Unlike absorption spectra, Raman signals of both solids and liquids follow the same relationships governing peak position and intensity. In general the peaks produced by materials in the solid state are slightly more narrow than those for the same substance in solution. Often they are slightly displaced along the abscissa. Therefore it is possible to determine the solution and solid phase of a substance in a single sample.

The exact position and shape of peaks is a function of the chemical environment of the sample, particularly the dielectric constant of a solvent or the counter ion of a solid salt. Preparation of reference spectra should be done with that restriction in mind, but this does make it possible to discriminate between different forms of salts. For example sodium, potassium, barium and ammonium sulfates can be distinguished from each other and from dissolved sulfate in a mixture. With attention to chemical environment, references prepared in the laboratory can be used in subsequent field measurements.

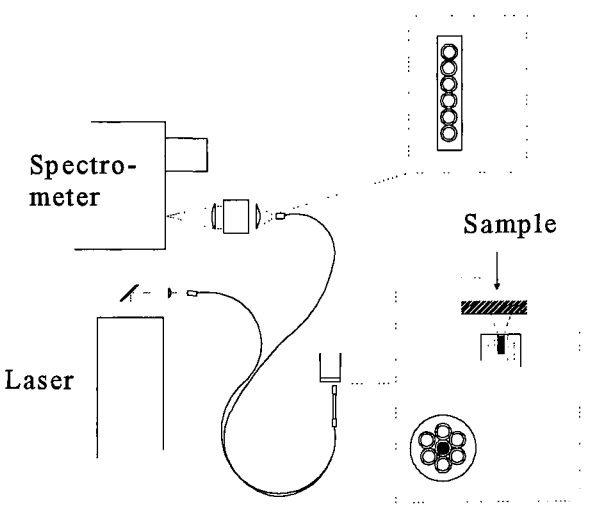


Figure 1 Spectrometer block diagram.

The shape of spectral features of solids is not a function of particle size. The intensity of those features is affected because particle size variations can alter the average depth of penetration of the exciting beam into the sample. However, a substance in a strongly scattering sample produces the same spectrum that would be found in a weakly scattering sample, providing that the chemical environment remains the same.

Sample morphology affects the calibration of an analysis. Relevant factors are particle size, color and dielectric constant. Observations on paints has demonstrated that dielectric constant is considerably more important than the other factors.

Description of the Instrument

The components of a typical system are illustrated in Fig. 1. The sample is illuminated by a laser beam, usually brought in through an optical fiber. The laser is usually either green light around 520 nm or near-infrared around 800 nm. The most commonly used one is the argon-ion laser which has a convenient line at 514.5 nm. For field operation, the diode-pumped doubled Nd:YAG laser offers a 532-nm line. It has the advantage of providing

higher efficiency and smaller size than an argon-ion laser. Near infrared operation is available by using stabilized external cavity diode lasers.

Light scattered by the sample is collected by a second fiber, in this case actually a group of six symmetrically arranged around the excitation fiber to enhance collection efficiency. The collected radiation is taken to the spectrometer for analysis.

For analytical applications, single stage spectrographs with 0.25...0.64-m focal lengths are used. When these are fitted with 1000-element CCD detectors, the spectral window will vary from around 1000...3000 cm^{-1}. Spectral resolution of 8...10 cm^{-1} is appropriate for this type of application. To achieve the stability that is required for routine mixture analysis, it is necessary to control the temperature of the spectrograph to ±2°, so the use of a temperature controlled enclosure is required for field operation. Remote control can be arranged by using a telephone line to connect the host and remote computers.

Instrument Calibration

Emission spectroscopy, of which Raman scattering is an example, is not readily implemented through two-channel design. A consequence is that operation of emission spectrometers has ordinarily been less convenient than absorption spectrophotometers. We undertake to sidestep this disadvantage by computer control of the measurement, rather as is done in FT spectrometry which is also inherently single channel.

The are several factors. Raman spectrometer outputs have conventionally had abscissa measurements in wavelength. Conversion to wavenumber shifts by a process that is invisible to the operator is desirable. This is accomplished by a one-time calibration of a system at the time of installation.[1] Some dispersive instruments do not record the entire fundamental vibrational region in one spectral window. This is rarely much of a disadvantage because one generally doesn't use the entire region in a single measurement. However, there is ordinarily no convenient method for relating signal intensity in one window to that in another. This is overcome by the calibration procedure.

Current technology has developed sufficiently to make short term fluctuations in laser intensity, detector sensitivity and amplifier response small enough to be ignored in most applications. Once conditions are established in a measurement session, they will normally not show appreciable change. However, that is not true of day-to-day fluctuations and single channel instruments do not provide the compensation that is achieved by ratioing in two-channel design. This is overcome by the calibration procedure, based on a chemical reference standard. CCD detectors exhibit both wavelength dependence and pixel-to-pixel sensitivity variations. These are overcome by daily measurement of the response of a standard lamp.

Vibrational spectra are highly distinctive, making it possible to do qualitative and quantitative analysis for a minor component of a mixture without having to be concerned for spectral interference, so long as LOD criteria are met. However, this assumes that measurements are not corrupted by abscissa error or by ordinate nonlinearity. In practice the most important abscissa errors originate from calibration errors, rather than from nonlinear abscissa response. Accordingly, each-session calibration that is keyed to neon emission line references can hold abscissa errors to less than 0.1 cm^{-1}, which is good enough to support mixture analysis.[2]

Several calibration measurements are therefore required at each measurement session. The calibration process has been automated by designing calibration signals that can be used on a day-to-day basis without requiring operator attention other than to observe a warning signal generated by the host computer. To do this it is necessary to measure the calibration

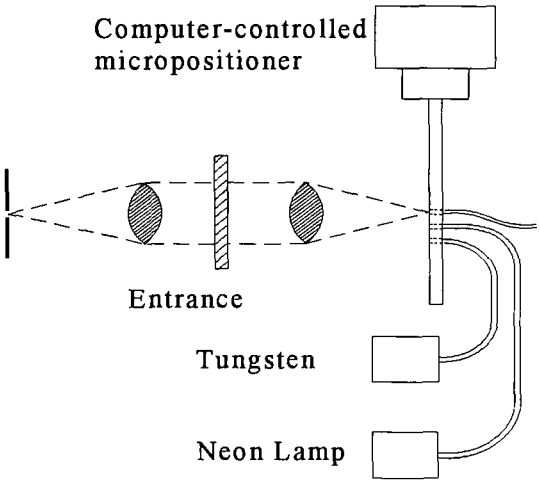


Figure 2 Fiber optic signal switching.

signals, under the control of the controlling computer. The apparatus currently in use is illustrated in Fig. 2.

Direct Analysis of Solid Waste Samples

As an illustration of the ability of Raman measurements do deal with the kinds of complex samples that are encountered in waste remediation work, we present some spectra that have been recorded on waste material that was recovered from the disposal tanks on the Hanford Site in Richland, WA.

This material is housed in tanks with capacities of as much as one million gallons. It consists of residues from plutonium and uranium recovery processes that have been in use since the 1940's. The actual waste took the form of acidic solutions, with organic phases at certain times. These were neutralized with NaOH and concentrated by precipitation and evaporation to leave material which is a basic mixture of solids and liquids. Although the amount and identities of the original tank charges are known, the contents have been mixed during operation of the tank farms with the result that the composition of material in any particular tank can not be obtained from records.

As a part of the waste remediation process, the contents of some of the tanks are being sampled by taking cores. These are brought to a laboratory and examined by chemical analysis. The spectra that we present were obtained by direct measurements on some of these cores by remote controlled fiber optic Raman sampling in a hot cell.[3] Measurements were made with one-minute to ten-minute integration times.

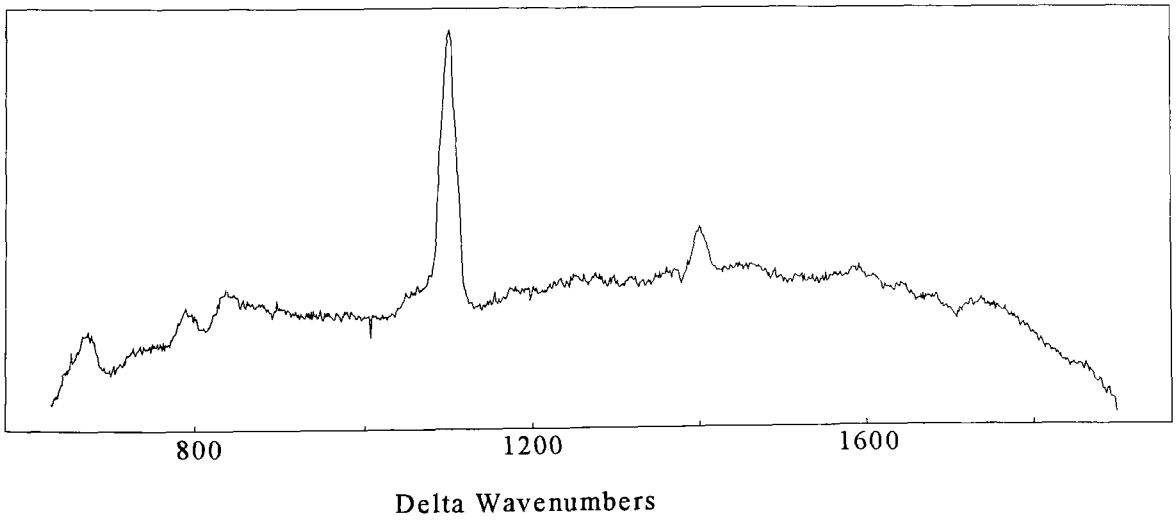


Figure 3 Nitrate region for waste tank material. The prominent peak is nitrate. No correction for fluorescence.

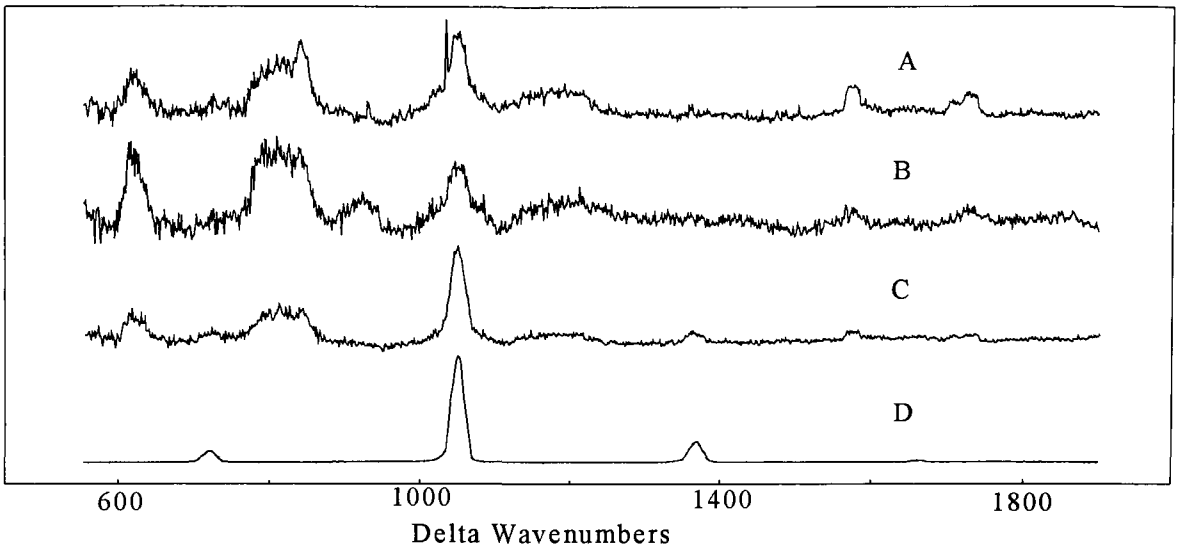


Figure 4 Nitrate region. **A...C**, three locations on the same core, showing variations in composition. Curve **D** is a solid $NaNO_3$ reference spectrum. Ten minute exposures.

These are preliminary results, made to determine whether it is possible to observe signals from individual compounds from this type of sample. No attempt has been made to identify the peaks, other than those of nitrate, which is the major component.

An example is shown in Fig. 3. This is the spectral region that contains the nitrate response. It was made with a two-minute integration. The silica response is strong in this region and that signal component has been subtracted from the data. The curved background is mainly caused by fluorescence. Several peaks are evident, of which the strongest is the 1067-cm^{-1} nitrate response.

In Fig. 4 we show measurements in the same spectral window, but at three locations on a core from a different tank. These are 10-minute exposures. A reference spectrum of $NaNO_3$

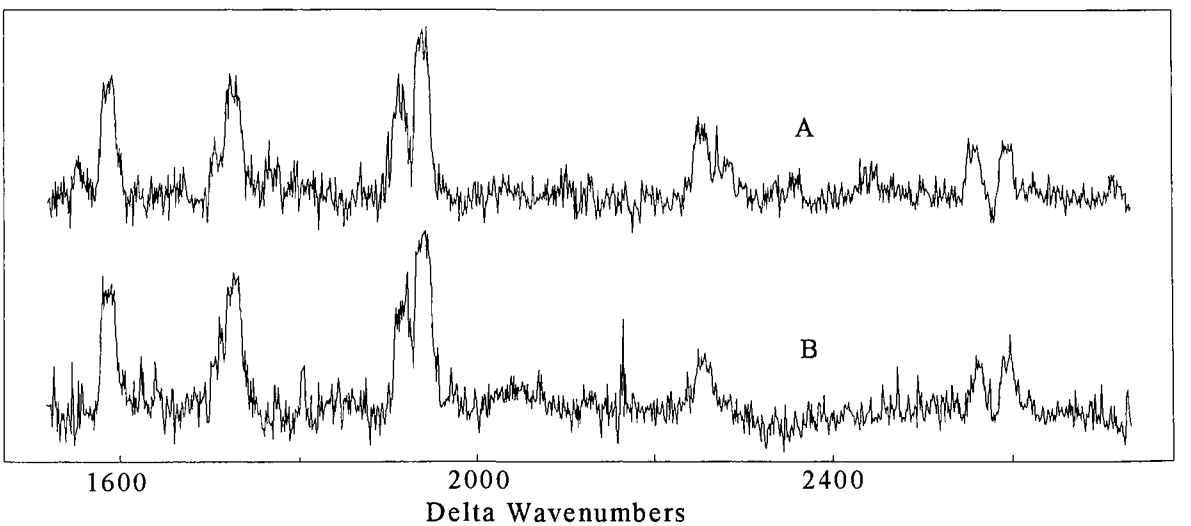


Figure 5 Cyanide region for a core. Both measurements made at approximately the same position on the core, but on different days. Curve A, one minute, curve B, 10 minute integration.

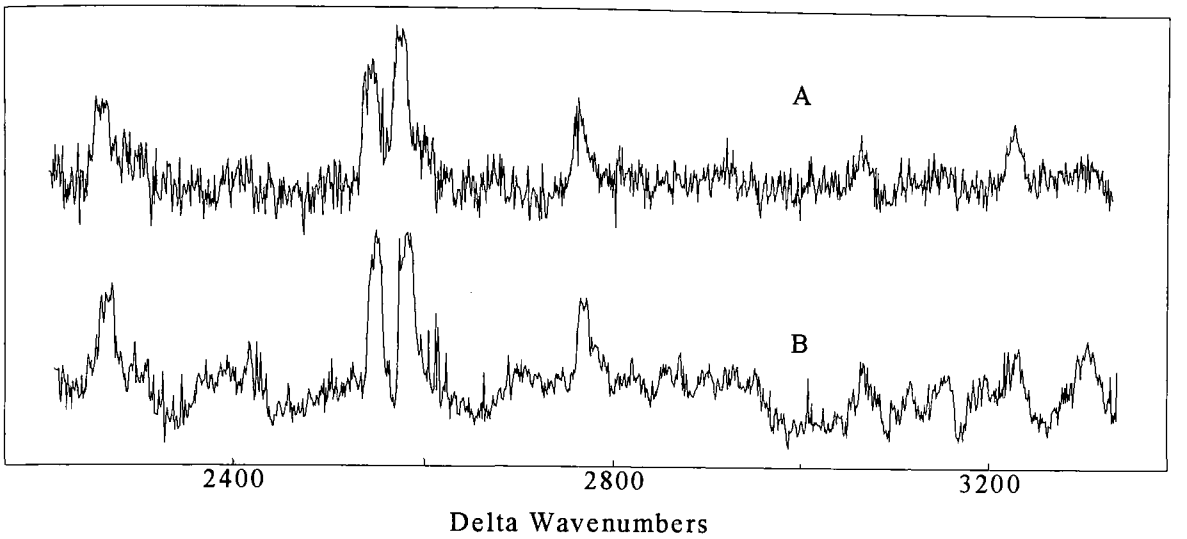


Figure 6 CH region for the same core represented in Fig. 5. A. One minute integration. B. Ten minute integration. Spectra recorded on separate days.

is shown for comparison. These spectra have had both the silica and fluorescence signal components removed. Most of the peaks are common to all three regions. However, varying peak ratios show that the the core is not is not homogeneous. One of the uses for Raman measurements in this effort is to provide preliminary screening to guide the sampling operation that is used to prepare samples for wet chemical analysis of core material.

Figure 5 shows the CN region of a core. The spectra were recorded on different days but at approximately the same location on the core. This gives some perspective on the repeatability of the measurements. In this figure, the upper curve is a one-minute integration, while the lower represents a 10-minute exposure. The S/N is pretty much the same for both. This reflects difficulty in positioning the probe in the sample. The operation was carried out using remote manipulators with the sample several feet away from the operator.

Figure 6 shows two measurements on the same core that was used for the measurements of Fig. 5. These were also made on different days, with one- and ten-minute integration times. The spectrometer was moved to show the CH region. Again this demonstrates that the visible features are reproducible spectral peaks. In addition, note that there is some overlap between Fig. 5 and Fig. 6. Peaks that occur in the common region appear in the expected positions.

Analyses of Slurry Samples

Raman scattering differs from other optical vibrational spectroscopy in that sample particle size has no direct effect on the shape of the spectrum. Accordingly, it does not make a qualitative difference if the sample is changed from a solid to the same material dispersed as a slurry. Similarly, the presence of the solid particles in the slurry does not affect the shape of the spectral features of the liquid components. Changing from a clear solution to a slurry does affect the intensities of the responses because it alters the effective depth of penetration of the laser beam into the sample.

The upshot of this is that reference spectra that are made on the individual sample components can be used in analysis of slurries, providing that calibration shifts caused by variations in beam penetration are taken into account. As an illustration of this capability

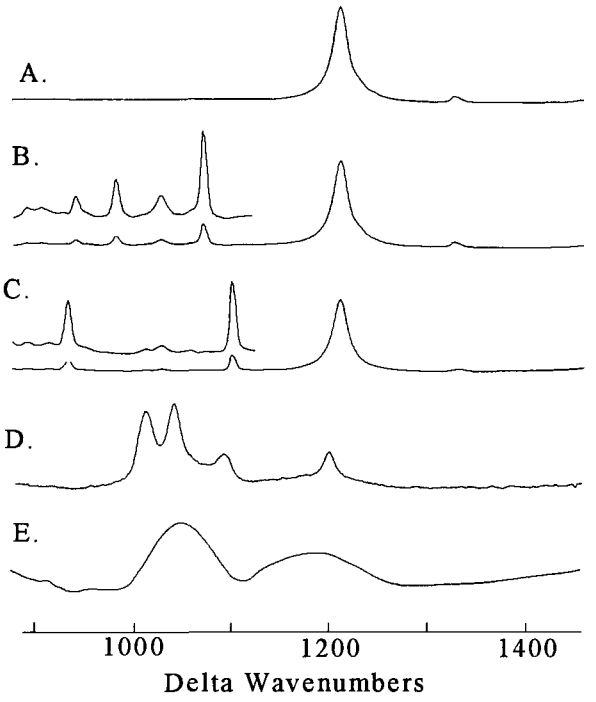


Figure 7 A. Chloroform. B. 0.1 M Quadricyclane in $CHCl_3$. C. 0.1 M Norbornadiene in $CHCl_3$. D. $CuSO_4$ powder. E. Raman Spectrum of silica from the fiber optic probe.

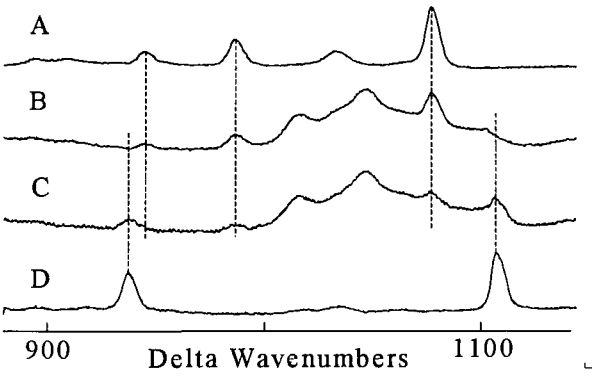


Figure 8 A. Quadricyclane. B. Starting reaction mixture. C. Ending reaction mixture. D. Norbornadiene

we present some results from a study of the heterogeneous catalytic conversion of quadricyclane to norbornadiene.[4] The reactants are dissolved in chloroform. The reaction is catalyzed by dispersed solid copper sulfate.

In Fig. 7 the spectra of the individual components are shown. The region of principal interest is from 850 to 1150 cm^{-1} In Fig. 8 the spectra of the reactant and product are shown along with spectra of the reaction mixture taken at the start and near the end of the reaction. This is a complex system. The Raman signals due to the probe and the suspended $CuSO_4$ powder almost hide the strongest features of the reactant and product. The chloroform line at 1216 cm^{-1}, which we wish to use as an internal standard, overlaps significant features of $CuSO_4$ and the two organic compounds. This was dealt with by using least-squares fitting for quantification because it handles spectral overlap efficiently. The fit values were used in a standard addition procedure for which one of the calibration curves is shown in Fig. 9. As is pointed out in the paper cited, a plot of the responses of the reactant and product vs. time shows the expected decrease of one and growth of the other.

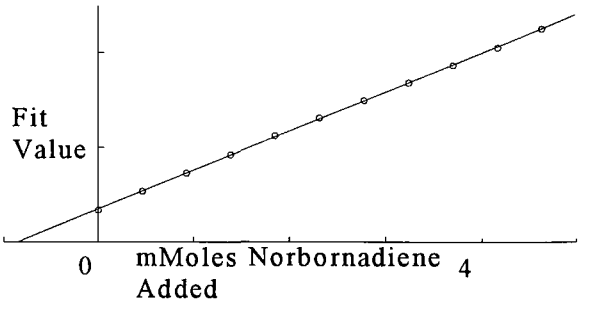


Figure 9 Standard addition curve.

Aging of Paint Films

Since Raman measurements are based upon examination of scattered light, it is possible to do chemical analysis on the surfaces of totally opaque samples. As an example we cite some results from an accelerated aging test that was run on a water based paint.[5] After a normal drying time, paint films were exposed for varying periods to UV, primarily in the 275...350 nm range. Although there is no perceptible change in color during the period of

these tests, measurable changes in spectra of the pigments occurred in less than three hours of exposure.

The paint was blue. It contained a proprietary film material, together with four principal pigment materials: titanium dioxide, carbon black, copper phthalocyanine and carbazole dioxazine violet. The film produced a relatively weak spectrum which did not have much effect on these measurements. TiO_2 produces strong peaks which are outside the window of interest and carbon black produces only a weak and featureless response. Accordingly, the spectra were dominated by the two organic pigments. This is illustrated in Fig. 10 with the spectra of the individual pigments and that of the dried paint. The paint film appears to be the sum of the spectra of the pigments. Actually, if they are removed, one is left with a recognizable spectrum of the binding polymer.

Figure 11 shows the result of an exposure test. There are readily apparent changes in the relative intensities of several peaks. Two pairs are marked on the figure. The intensity of the 1529-cm^{-1} peak of copper phthalocyanine, marked **c** on the figure, increases relative to the 1341-cm^{-1} peak of the same compound, **a**, and also relative to the 1391-cm^{-1} peak of carbazole dioxazine violet, **b**. Peak **c** represents the vibration of a functional group that is photochemically unreactive. In fact, its absolute intensity varied little during the period of the test and it was used as an internal standard.

Measurement of these peaks demonstrated that both of the pigments are degraded by UV exposure. The carbazole violet response decayed more rapidly than the phthalocyanine response.

Dynamic Range

Chemical analysis of mixtures generally involves detecting and measuring minor components in the presence of major components which may not be of interest. The process usually boils down to exclusion of the major component signal in order to make the minor component visible. There are a great many ways of doing this. When the phenomenon is

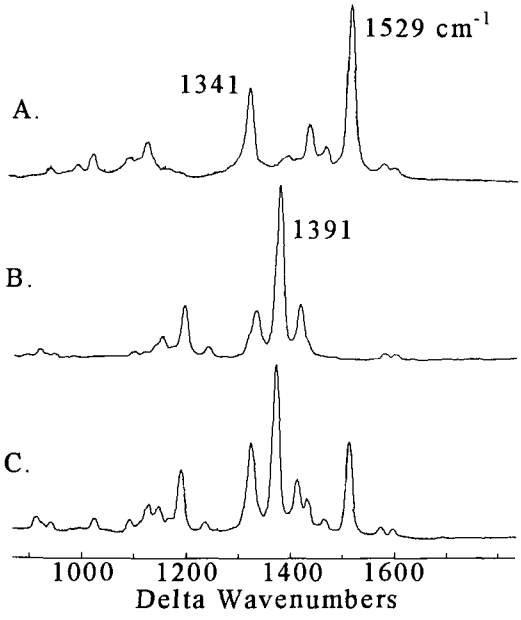


Figure 10 A. Copper Phthalocyanine. B.Carbazole Dioxazine Violet. C. Dried paint film.

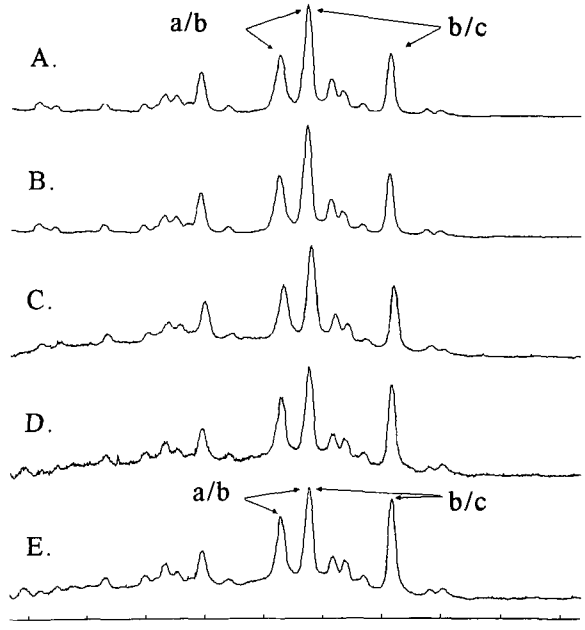


Figure 11 Effect of exposure to UV. A. Unexposed. B. After 3 hours. C. 25 hours. D. 86 hours. E.100 hours.

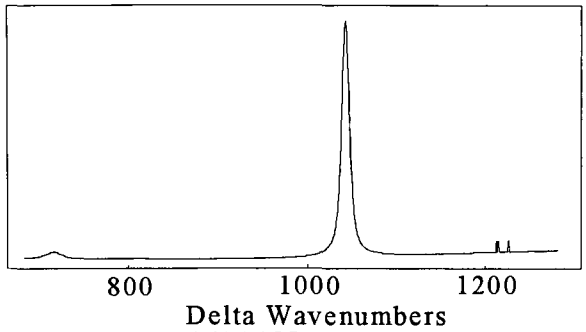


Figure 12 1 *M* $NaNO_3$

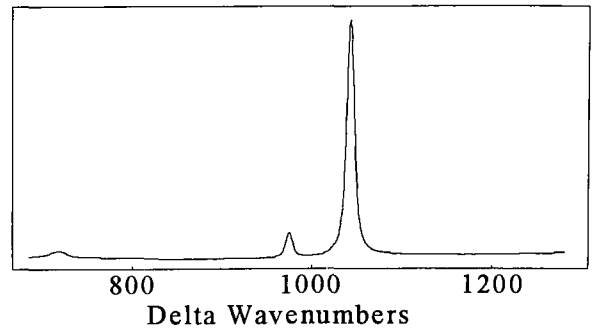


Figure 13 0.1 *M* $(NH_4)_2SO_4$ in 1 *M* $NaNO_3$

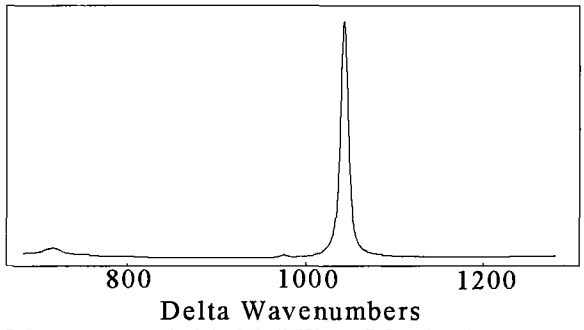


Figure 14 0.01 *M* $(NH_4)_2SO_4$ in 1

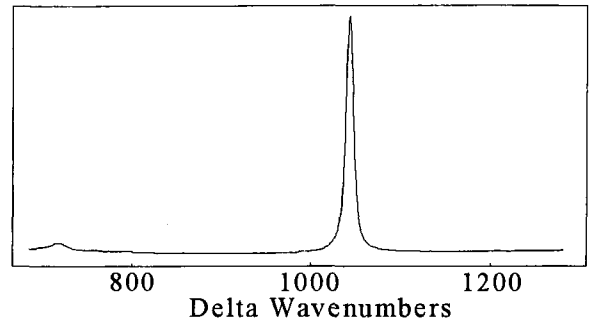


Figure 15 0.001 *M* $(NH_4)_2SO_4$ in 1 *M* $NaNO_3$

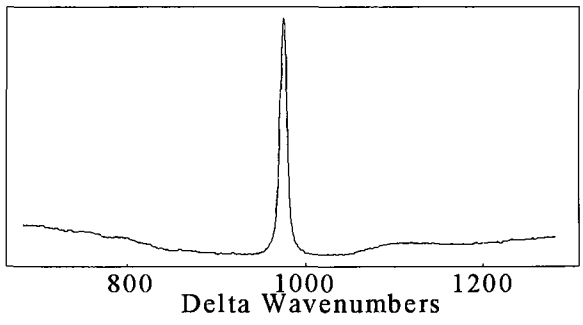


Figure 16 0.1 *M* $(NH_4)_2SO_4$ in Water

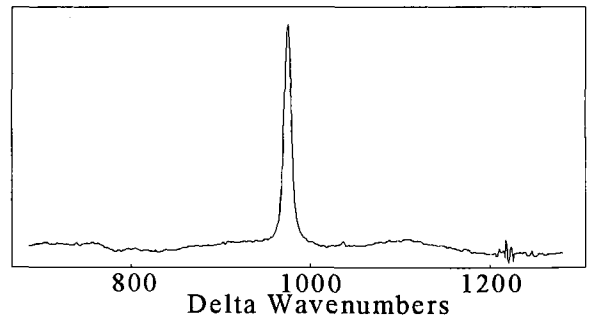


Figure 17 0.1 *M* $(NH_4)_2SO_4$ in 1 *M* $NaNO_3$

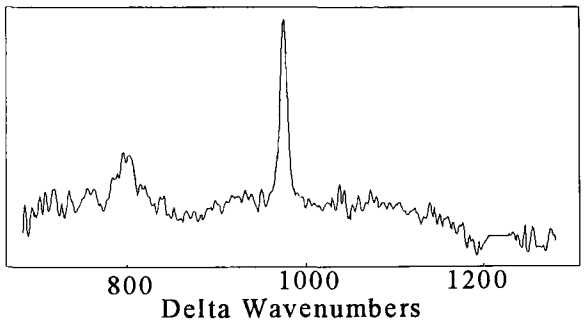


Figure 18 0.01 *M* $(NH_4)_2SO_4$ in 1 *M* $NaNO_3$

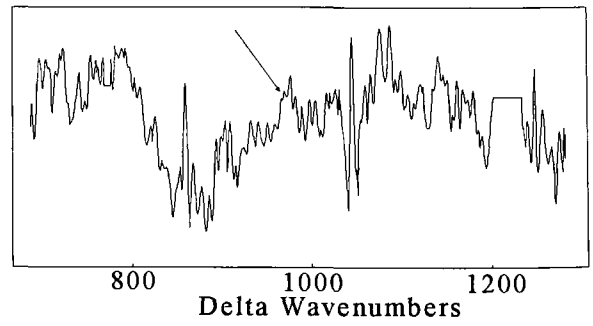


Figure 19 0.001 *M* $(NH_4)_2SO_4$ in 1 *M* $NaNO_3$. Sulfate peak marked.

linear, it can be done by simple subtraction. In the case of Raman scattering, the phenomenon is linear, providing that the chemical environment in the sample is held constant. Limits on the dynamic range are set by the apparatus, at the present time primarily by detector response.

To demonstrate this we present measurements on solutions that are 1 *M* in $NaNO_3$ and 0.1, 0.01 and 0.001*M* in sulfate. A nitrate reference and the sulfate containing samples are shown in Fig. 12...15. In these, the Raman spectrum of silica from the fiber optic sample is appreciable and has been subtracted from the sets. Figures 17...19 are Fig. 13...15 after subtraction of the nitrate signal. Figure 16 shows 0.1 *M* sulfate for comparison.

After removing 1 *M* nitrate from one tenth to one thousandth that concentration of sulfate, the sulfate is visible in all cases. In Fig. 19, scale expansion is sufficient to reveal two artifacts which were produced by the small degree of nonlinear response that is present in this system. This indicates that the practical dynamic range is around 1000:1 with current equipment.

Summary

In this paper we have demonstrated that Raman scattering is capable of supporting direct chemical analysis on a variety of types of samples. The examples have been solid mixtures, slurries of solids suspended in liquids and opaque surface layers. In addition we demonstrate a dynamic range of around three orders of magnitude. When applied to quantitative determination of target substances, the limit of detection will range from 0.005...5 percent, with most falling around 0.1 percent. Measurements are made without sample preparation and normally require from one to ten minutes. Complete systems can be obtained for around $80,000 at the present, may weigh around fifty pounds and can be housed in a ten cubic foot enclosure. Remote operation is feasible. This is a technology that is sufficiently mature to be used in routine applications.

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INTEGRATED SAMPLE AUTOMATION FOR CONCENTRATION, EXTRACTION, AND CLEANUP

MARK CAVA Zymark Corporation, Zymark Center, Hopkinton, MA 01748

The maturing environmental services industry is characterized by a commodity situation where it is difficult for buyers to distinguish sellers. Oversupply, a new national administration, and a flat period for government contracts have forced lab industry consolidation. To compete, management must lower costs and improve margins. The easiest way to do this is to apply sample automation to standard operating procedures. Implementing sample automation technology requires change. To make change easy companies let their most important assets, their best people, drive sample automation projects. These companies achieve growth by automating to obtain excellent QC, lowest cost, and fast delivery. For these leading labs, automation is a solution for improved competitiveness and profitability in a changing market.

Innovative concentration workstations have revolutionized laboratories by providing consistent results, low cost per sample, and twice the throughput. Payback periods of less than 3 months are normal for the automated concentration of trace organics. Related to sample concentration is the increasing use of solid phase extraction(SPE) as the medium for simultaneous extraction and concentration.

A unique automated SPE workstation takes the advantages of solid phase extraction, low solvent costs and extraction selectivity, and combines them with the efficiency and control of automation. Workstation extraction provides improved consistency for large volume SPE, fast turnaround, and payback within 6 to 12 months. Even when extraction and concentration is done, many crude isolates or extracts are too laden with high molecular weight compounds or coellutant interferences. This adds cleanup as a necessary step in sample processing.

Companies using multimethod robotic workstations for sample cleanup see more than 60% annual return on investment, 60 % improved consistency, and a dramatic 60% improvement in sample turnaround. Payback periods for mutimethod cleanup automation ranges from 6 months to 18 months.

Workstation automation of sample concentration, extraction, and cleanup for drinking water, groundwater, waste water, and soil will be discussed. Results are for compounds regulated under RCRA, NPDES, and SDWA. Sample automation for concentration, extraction and cleanup will be examined. PCB, GPC (8080 and 8270 compounds), and Florisil Pesticide cleanup (a GPC companion for 8080 compounds) will be discussed. The automation methods, GC results, HPLC results and payback are examined.

ANALYSIS OF ASH RESIDUES FOR VOLATILE ORGANIC CONSTITUENTS BY USING A MODIFIED SW-846 METHOD 8260

Richard P. Grese, Sr. Chemist, Tennessee Eastman Division, Marsha D. Edwards, Sr. Technician, Tennessee Eastman Division, Eastman Chemical Company, Kingsport, Tennessee, 37662

ABSTRACT

Application of SW-846 Methods 8240 or 8260 for volatile organic analysis (VOA) of some ash residues is limited because of suppression of spiked analytes by the adsorptive matrix. The suppression of internal standard recoveries produces large biases in the quantitation of analyte concentrations. In addition, suppression of spiked analytes prevents the use of normal QA/QC criteria for validation of the data. A slightly modified Method 8260 is proposed to minimize the biases and to improve the data quality of the VOC analysis of ash residues. The modification of Method 8260 described here allows most laboratories to improve the quality of he data without extensive development of a new method or without resorting to a more expensive approach such as "isotope-dilution" GC/MS.

In this work, the adsorptive behavior of specific analytes for a given matrix were determined, and analytes were assigned to internal standards with similar adsorptivity. Five internal standards and five surrogates were recommended for the analysis of fly ash samples. The modified method was used to evaluate fly ash from two sources by determining spike recovery acceptance criteria and biases for each analyte studied. Of the analytes studied, recoveries (based on the new internal standard assignments) were generally between 85 to 120%. Matrix-induced decomposition of 1,1,2,2-tetrachloroethane by one type of boiler fly ash is reported.

INTRODUCTION

Regulations permitting the burning of hazardous waste in a boiler or industrial furnace require that the resulting residue (e.g. fly ash) be analyzed for contaminants that are in the waste or that may be generated by products of incomplete combustion. The residue may be excluded from the definition of a hazardous waste if the analysis demonstrates that the hazardous waste did not significantly affect the residue. The regulations also require that the analyses be in conformance with procedures in SW-846.[1] The analyses of ash residues for trace level volatile organic constituents (VOC's) represent one of the most difficult challenges to the environmental laboratory.

SW-846 methodology for volatile organic analysis (VOA) of solid wastes cannot be reliably used for the analysis of some ash residues, especially those containing a large percentage of activated carbon. The adsorptive capacity of these matrices for volatile organic compounds effectively suppress the recovery of spiked analytes and thus limit the quality and usefulness of the purge-and-trap analysis. The suppression of spiked analytes in effect prevents the use of normal QA/QC criteria for validation of the data. The data reviewer or regulator must be knowledgeable of the matrix interactions and how they affect data quality prior to using the final data.

In the VOC analysis, the analyte must partition initially from the solid matrix into the water prior to being purged out of the water and onto the trap. If the analyte adsorbs more strongly to the solid matrix than the water, the analyte will not be available for purging onto the trap and recovery is poor. The adsorptive behavior of an analyte is thought to be related to various physical and chemical properties of both the ash and the analytes, and may be quite different for ash samples collected from different sources. The poor recovery of spiked analytes appears to be directly proportional to boiling point, and has been suggested to be a result of the adsorptive potential and the adsorptive surface area of the ash, the temperature, physical characteristics of the analyte, and the amount of time during which the analytes are in contact with the ash matrix.[2] Prior attempts by this laboratory to increase partitioning of volatile analytes into the water have had limited success.[3] Procedural changes include: use of smaller sample size, increased heating of sample during purging, and addition of a matrix modifier to the water to compete with active binding sites on the fly ash.

The poor recovery of internal standards from the ash matrix is an especially serious problem as it may produce a large bias in the data when the adsorptive behavior of a specific analyte is different to that of its assigned internal standard. This bias can be either positive or negative depending on the measured amount of the internal standard. The actual recovery of an analyte from the matrix, as determined by comparison to external standards, is also not an attractive quantitation alternative as the low recoveries of some compounds will under-estimate the contamination of the fly ash. External standard quantitation methods, in addition, provide no correction for changes of instrument sensitivity during the analysis.

The low "actual" recovery of analytes (0 to 10% for some compounds), however, may not be critical for quantitation if an internal standard method is used which corrects for the bias. This is essentially the approach of an "isotope-dilution" GC/MS method in which isotopically-labelled standards of every analyte are added to each sample, thus continually correcting the calibration for each sample's matrix effects. Ideally, a method employing isotope-dilution GC/MS methodology is an attractive approach for analyzing volatile organics in an adsorptive matrix such as fly ash. However, the cost of procuring isotopically-labelled standards for all analytes inhibits most laboratories from this approach.

The goal of this research was to develop a method, only slightly modified from SW-846 Method 8260, that improves the quality of the analysis of boiler fly ash. A simple way to minimize the biases resulting from poor recoveries is to assign internal standards based on adsorptivity to the matrix rather than GC retention time as is usually done. The new method was developed by first determining the adsorptive behavior of specific analytes for a given matrix, and then assigning the analytes to internal standards with similar adsorptivity. Fly ash generated by two boiler types were included to investigate how differences in the matrix affect the data generated by the modified method.

EXPERIMENTAL

Reagents and Procedures. The deionized water used in these experiments was purified by passing through a Millipore (Bedford, MA) Milli-Q filtering system and activated carbon prior to use. All GC/MS standards, unless otherwise noted, were obtained from Supelco (Bellefonte, PA) as certified standard solutions. Fluorobenzene and pentafluorobenzene were obtained as neat

Three compounds need additional comment in **Sample-B**. Trichloroethene (164%), tetrachloroethene (164%) and 1,1,2,2-tetrachloroethane (16%) gave percent recoveries quite different from those from **Sample-A**. It is known the 1,1,2,2-tetrachloroethane is converted to trichloroethene by a based-catalyzed dehydrohalogenation reaction.[4] Similarly, tetrachloroethene may be formed by loss of hydrogen from 1,1,2,2-tetrachloroethane. Ten replicate samples of **Sample-B** were prepared and loaded onto the autosampler and analyzed sequentially. Figure 2 shows the recoveries of the three analytes overtime as well as the total (combined) recoveries. This data points to decomposition of the 1,1,2,2-tetrachloroethane as the possible source of the increased amounts of the two other analytes. Calcium hydroxide present in the fly ash is thought to be responsible for the decomposition of 1,1,2,2-tetrachloroethane; addition of HCl may be useful to prevent this reaction.

CONCLUSIONS

Analysis of fly ash with SW-846 Methods 8240 or 8260 is difficult because of adsorption of analytes onto the ash. The poor recovery of internal standards is especially troubling due to the biases it creates in the quantitation of analytes. The modification of Method 8260 described here allows most laboratories to improve the quality of the data without extensive development of a new method. It also allows the laboratory to develop data quality objectives for recovery of matrix spikes and surrogates. Once these objectives are determined, a more reasonable and accurate assessment of volatile organic constituents in the ash can be made. A disadvantage of this approach is that most laboratories can not devote the time to develop data quality objectives for every adsorptive matrix. However, if a large number of analyses of a specific matrix type is anticipated, development of a specific method may be a worthwhile endeavor. We have developed a method on a "worst case" matrix, speculating that the method would be useful for less adsorptive matrices as well.

By definition, an "internal standard" should not be affected by method or matrix interferences. Therefore, strictly speaking, the modified method described here should not be termed an "internal standard method." We have, however, used the terminology here to contrast the quantitation method in which external standards are used. Our approach has been to select "internal standards" which respond similarly to the matrix as the analytes assigned to them. In this regard, the approach is more like an "isotope-dilution method" without the use of labelled analytes. Realistically, as long as purge-and-trap is used for extraction of fly ash there continues to be opportunities for improvement in this method.

Future work in this laboratory will include the investigation of method detection limits (MDL's) and the application of this method to other ash matrices.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. Craig Hoyme for the preliminary work with analysis of fly ash, and to Dr. Darrel Wilder for his support of this research.

TABLE 1
GC/MS INSTRUMENTAL PARAMETERS

Purge-And-Trap

Instrument: Tekmar LSC2000
AutoSampler: Tekmar ALS2016 with Tekmar Sample Heater
Trap: Supelco VOCARB 4000 adsorbent trap, 30.5 cm x 0.125" OD x 0.105" ID (Carbopack C, Carbopack B, Carboxen 1000, Carboxen 1001)
Method 2:

- Sample Temp: 40°C
- Purge Preheat: 3 min.
- Purge Time: 11 min
- Desorb Preheat: 245°C
- Desorb Time: 2 min
- Desorb Temp: 250°C
- Bake Time: 4 min
- Bake Temp: 260°C
- Transfer Line Temp: 80°C
- Purge Flow: 40 mL/min

Gas Chromatograph

Instrument: Hewlett-Packard 5890 Series II
Column: Rtx-5, 60 m, 0.25 mm ID, 1.00 μ df (Restek)
Oven Temperature: 35°C for 2 min, then 35-200°C @ 10°/min, 6 min hold
Oven Temperature (for BFB) : 100°C for 0.5 min, then 100-220°C @ 10°/min
Injector: Split 25:1 (EPC constant flow)
Injector Temperature: 200°C
Transfer Line Temperature: 280°C
GC/MS Interface: Direct
Carrier Gas: He (1 mL/min)

Mass Spectrometer

Instrument: Hewlett-Packard 5972MSD
Scan Limits (Low): 35 amu
Scan Limits (High): 300 amu
Scans/Second: 2

TABLE 2

PERCENT RECOVERY FROM FLYASH
Spiked at 4 mg/kg (n=5)
External Standard Calculation

	No.	COMPOUND	Sample-A	Sample-B
	1.	Iodomethane	123	136
	2.	1,4-Dioxane	106	104
	3.	Isobutanol	105	93
	4.	Methylene chloride	105	71
	5.	Acrylonitrile	97	89
*	6.	Bromochloromethane	94	102
	7.	Carbon tetrachloride	90	102
	8.	Chloroform	90	106
	9.	Acetone	89	77
*	10.	1,2-Dichloroethane-d4	88	98
	11.	Bromomethane	87	99
	12.	Dibromomethane	87	101
	13.	2-Butanone (MEK)	86	104
	14.	1,1-Dichloroethene	84	103
	15.	1,1,1-Trichloroethane	83	101
	16.	Methacrylonitrile	81	98
	17.	Bromodichloromethane	80	99
*	18.	2-Bromo-1-chloropropane	61	93
	19.	Trichloroethene	59	145
*	20.	Benzene-d6	55	91
	21.	Benzene	54	90
	22.	Crotonaldehyde	48	79
*	23.	Fluorobenzene	38	85
	24.	Bromoform	36	76
*	25.	1,4-Difluorobenzene	30	77
	26.	Tetrachloroethene	25	119
	27.	1,1,2,2-Tetrachloroethane	24	17
*	28.	Pentafluorobenzene	19	71
*	29.	Toluene-d8	19	69
	30.	Toluene	18	72
	31.	cis-1,4-Dichloro-2-butene	14	51
*	32.	Ethylbenzene-d10	8	54
*	33.	Chlorobenzene-d5	7	53
	34.	Chlorobenzene	7	55
*	35.	4-Bromofluorobenzene	2	29
	36.	1,2-Dichlorobenzene	0	15

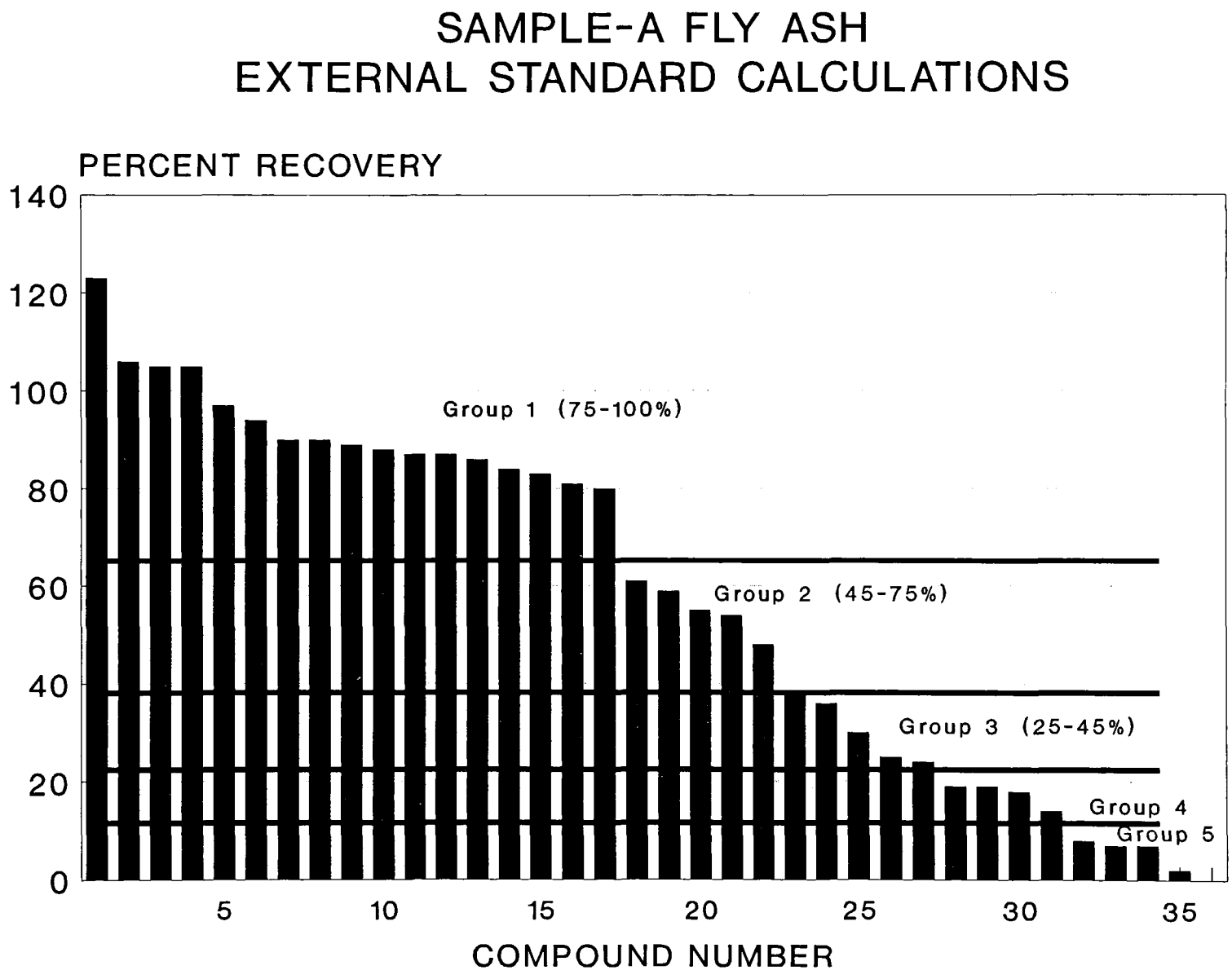
SAMPLE-A FLY ASH
EXTERNAL STANDARD CALCULATIONS
PERCENT RECOVERY
140
120
100
80
60
40
20
0
Group 1 (75-100%)
Group 2 (45-75%)
Group 3 (25-45%)
Group 4
Group 5
5
10
15
20
25
30
35
COMPOUND NUMBER

FIGURE 1

TABLE 3

ASSIGNMENT OF INTERNAL STANDARDS
AND SURROGATES
Percent Recovery of Fly Ash
(External Standard Calculations)

	No.	COMPOUND	Sample-A	Range
	1.	Iodomethane	123	75-100%
	2.	1,4-Dioxane	106	
	3.	Isobutanol	105	
	4.	Methylene chloride	105	
	5.	Acrylonitrile	97	
IS	6.	Bromochloromethane	94	
	7.	Carbon tetrachloride	90	
	8.	Chloroform	90	
	9.	Acetone	89	
SS	10.	1,2-Dichloroethane-d4	88	
	11.	Bromomethane	87	
	12.	Dibromomethane	87	
	13.	2-Butanone (MEK)	86	
	14.	1,1-Dichloroethene	84	
	15.	1,1,1-Trichloroethane	83	
	16.	Methacrylonitrile	81	
	17.	Bromodichloromethane	80	
SS	18.	2-Bromo-1-chloropropane	61	45-75%
	19.	Trichloroethene	59	
IS	20.	Benzene-d6	55	
	21.	Benzene	54	
	22.	Crotonaldehyde	48	
SS	23.	Fluorobenzene	38	25-45%
	24.	Bromoform	36	
IS	25.	1,4-Difluorobenzene	30	
	26.	Tetrachloroethene	25	
	27.	1,1,2,2-Tetrachloroethane	24	10-25%
IS	28.	Pentafluorobenzene	19	
SS	29.	Toluene-d8	19	
	30.	Toluene	18	
	31.	cis-1,4-Dichloro-2-butene	14	
SS	32.	Ethylbenzene-d10	8	0-10%
IS	33.	Chlorobenzene-d5	7	
	34.	Chlorobenzene	7	
	35.	4-Bromofluorobenzene	2	
	36.	1,2-Dichlorobenzene	0	

TABLE 4

PERCENT RECOVERY FROM FLYASH SAMPLE-A
Spiked at 4 mg/kg (n=10)
Internal Standard Method

	COMPOUND	% Rec.	s.d.	Range (3 sigma)	
Analytes	Bromomethane	95	7	75	114
	Acetone	84	10	54	114
	1,1-Dichloroethene	89	7	69	109
	Acrylonitrile	101	6	82	120
	Iodomethane	148	12	113	183
	Methylene chloride	118	43	-10	246
	2-Butanone (MEK)	90	5	77	104
	Methacrylonitrile	89	4	76	102
	Chloroform	96	5	81	111
	Isobutanol	110	15	66	154
	1,1,1-Trichloroethane	89	7	69	108
	Crotonaldehyde	91	5	75	107
	Benzene	98	2	91	104
	Carbon tetrachloride	85	7	66	105
	Trichloroethene	108	3	99	117
	Dibromomethane	95	3	84	105
	1,4-Dioxane	108	9	81	134
	Bromodichloromethane	85	5	70	100
	Toluene	100	6	83	116
	Tetrachloroethene	80	4	69	92
	Chlorobenzene	94	5	80	108
	Bromoform	70	6	52	88
	cis-1,4-Dichloro-2-butene	105	29	19	190
	1,1,2,2-Tetrachloroethane	89	10	60	119
	4-Bromofluorobenzene	24	4	12	35
	1,2-Dichlorobenzene	6	2	-1	12
Surrogates	1,2-Dichloroethane-d4	94	2	88	99
	2-Bromo-1-chloropropane	116	4	105	126
	Fluorobenzene	73	2	66	80
	Toluene-d8	104	6	87	121
	Ethylbenzene-d10	105	8	81	128

TABLE 5

QUANTITATION BASED ON INTERNAL STANDARDS
CONCENTRATION COMPARISON (SAMPLE-A)
AVERAGE % RECOVERY (N=3)

COMPOUND	2 PPM	4 PPM	5 PPM	QA Range (1)		
Bromomethane	91	90	88	75	to	114
Acetone	121	93	106	54	to	114
1,1-Dichloroethene	80	84	84	69	to	109
Acrylonitrile	111	105	115	82	to	120
Iodomethane	135	140	141	113	to	183
Methylene chloride	198	149	177	-10	to	246
2-Butanone (MEK)	97	91	101	77	to	104
Methacrylonitrile	89	90	97	76	to	102
Chloroform	93	92	94	81	to	111
Isobutanol	132	120	128	66	to	154
1,1,1-Trichloroethane	80	83	85	69	to	108
Crotonaldehyde	103	90	104	75	to	107
Benzene	97	99	99	91	to	104
Carbon tetrachloride	68	81	84	66	to	105
Trichloroethene	118	109	106	99	to	117
Dibromomethane	93	95	96	84	to	105
1,4-Dioxane	114	113	125	81	to	134
Bromodichloromethane	76	81	83	70	to	100
Toluene	97	97	95	83	to	116
Tetrachloroethene	152	132	121	69	to	92
Chlorobenzene	92	93	94	80	to	108
Bromoform	188	140	120	52	to	88
cis-1,4-Dichloro-2-butene	66	119	85	19	to	190
1,1,2,2-Tetrachloroethane	227	159	137	60	to	119
4-Bromofluorobenzene	12	21	22	12	to	35
1,2-Dichlorobenzene	0	5	5	-1	to	12
1,2-Dichloroethane-d4	93	94	95	88	to	99
2-Bromo-1-chloropropane	138	119	114	105	to	126
Fluorobenzene	152	139	133	66	to	80
Toluene-d8	101	103	101	87	to	121
Ethylbenzene-d10	100	101	100	81	to	128

(1) Acceptance Criteria from Table 4.

TABLE 6

PERCENT RECOVERY FROM FLYASH SAMPLE-B
Spiked at 4 mg/kg (n=10)
Internal Standard Method

	COMPOUND	% Rec.	s.d.	Range (3 sigma)	
Analytes	Bromomethane	94	4	83	106
	Acetone	77	7	55	99
	1,1-Dichloroethene	100	2	93	107
	Acrylonitrile	87	7	65	109
	Iodomethane	127	9	101	152
	Methylene chloride	95	24	24	166
	2-Butanone (MEK)	108	14	66	150
	Methacrylonitrile	100	8	77	122
	Chloroform	103	2	97	110
	Isobutanol	96	13	58	134
	1,1,1-Trichloroethane	97	3	89	106
	Crotonaldehyde	93	12	57	128
	Benzene	99	1	96	102
	Carbon tetrachloride	99	4	88	110
	Trichloroethene	164	6	145	183
	Dibromomethane	98	3	89	107
	1,4-Dioxane	103	11	71	134
	Bromodichloromethane	96	3	88	104
	Toluene	101	2	95	108
	Tetrachloroethene	155	3	147	163
	Chlorobenzene	102	1	100	104
	Bromoform	85	5	70	100
	cis-1,4-Dichloro-2-butene	64	12	28	101
	1,1,2,2-Tetrachloroethane	16	9	-10	41
	4-Bromofluorobenzene	58	4	46	69
	1,2-Dichlorobenzene	32	5	16	48
Surrogates	1,2-Dichloroethane-d4	95	2	88	102
	2-Bromo-1-chloropropane	102	1	99	106
	Fluorobenzene	100	1	97	102
	Toluene-d8	97	1	93	101
	Ethylbenzene-d10	102	2	97	106

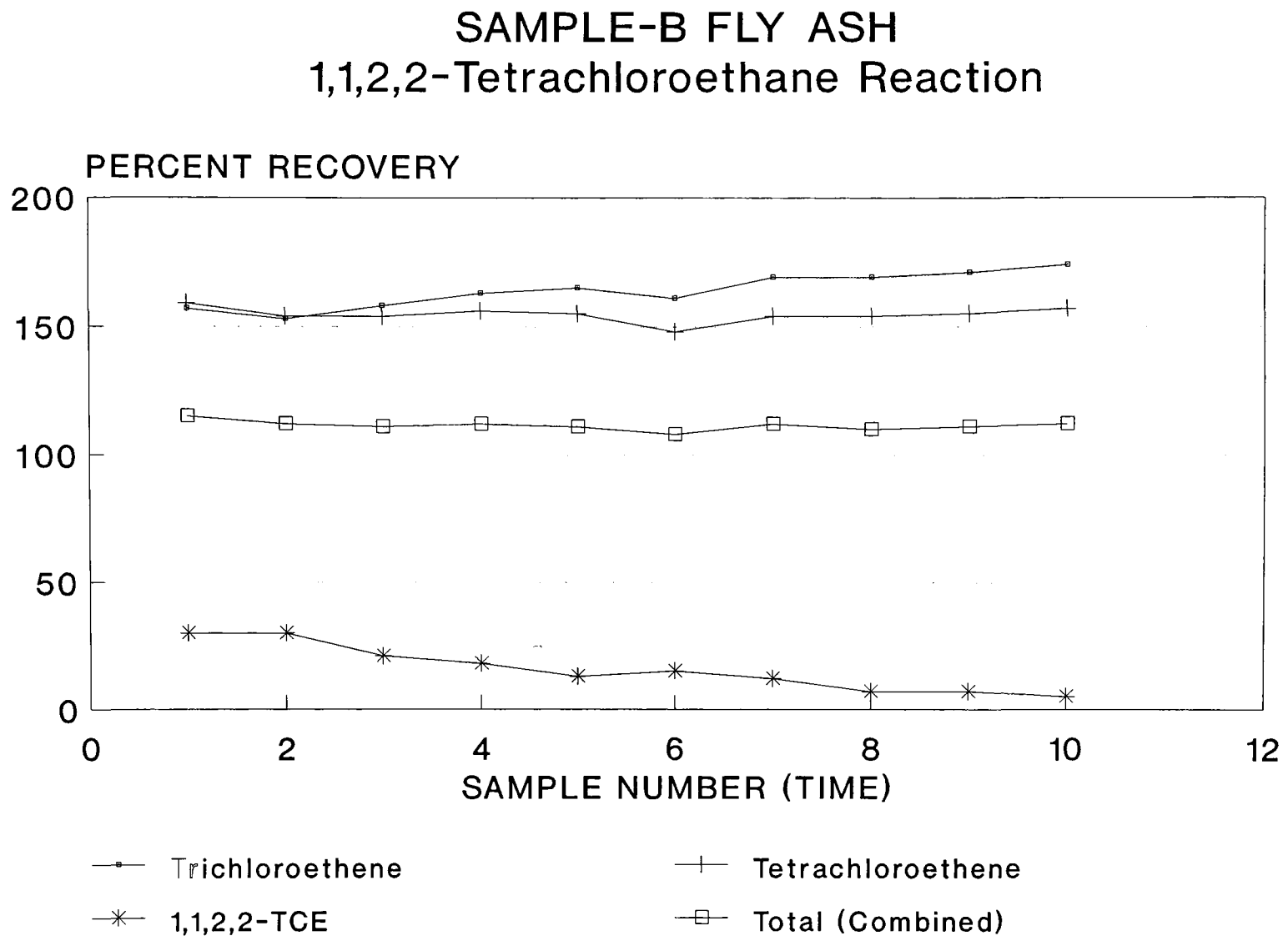
SAMPLE-B FLY ASH
1,1,2,2-Tetrachloroethane Reaction
PERCENT RECOVERY
200
150
100
50
0
0
2
4
6
8
10
12
SAMPLE NUMBER (TIME)
Trichloroethene
Tetrachloroethene
1,1,2,2-TCE
Total (Combined)

FIGURE 2

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PCB FIELD EXPERIENCE USING THE D TECH™ PCB IMMUNOASSAY FIELD SCREENING TEST.

James M. Melby, Development Group Leader, Brian Finlin, Scientist, Strategic Diagnostics Incorporated, Newark, DE, 19713, Mary Knowles, Project Manager, and Tracy Young, Environmental Scientist, Jaycor Environmental, Vienna, VA 22182.

ABSTRACT

PCB testing by immunoassay is gaining acceptance by environmental contractors through validation testing against accepted analytical methods. Though proven as a valid quantitative methodology in medical diagnostics for over 20 years, this technology has only recently been accepted by the EPA as a valid field screening method for PCB. The D TECH™ PCB field screening test kit incorporates immunoassay technology into a user friendly, quick, accurate, and field portable system. Using this technology, over 100 samples were tested in a site evaluation conducted to establish the usefulness, convenience, and cost effectiveness of the D TECH system. The procedure consists of the following 8 steps: 1. sample extraction 2. sample filtration 3. sample dilution 4. reaction of sample with immunoreagents 5. application of reaction mixture to filtration/ detection device 6. wash addition 7. color reagent addition 8. read result. This test detects all of the most commonly found aroclors (1254, 1242, 1248, 1260, 1262, 1268) equally, while the detection of aroclor 1232 is 5-fold less than 1254, and the detection of 1016 and 1221 is about 10-fold less than 1254. A sampling grid design was set up for a 1 acre site that was suspected to have PCB contamination due to its history of use as a storage site for transformers. A total of 117 samples were collected at 50 foot intervals in most cases, attempting to evenly cover the entire site. Most samples were collected at both 1 and 2 foot depths. The samples were tested on site using an EPA-accepted test along with the D TECH method, and 38 selected samples were sent to two analytical laboratories for SW846 method 8080 GC analysis. Results indicated very low level contamination ($\leq$1 ppm) at randomly located sites with all three methods, and most samples (88) were less than the minimum detectable limit for all methods. The EPA-accepted test had 13% false positives and no false negatives when compared to GC and the D TECH method had 9 % false positives and no false negatives. The cost for the D TECH test is $30.00 per sample, which for this study amounted to $3,510.00 for the screening method. Sending 10% of the field screened samples in addition to those indicated as positive by the screening method (a total of 22 samples) for GC analysis cost an additional $3,520.00 at $160.00 per sample. Therefore the total cost for the screening event was $7,030.00. GC analysis of all 117 samples would have cost $18,720.00 at $160.00 per sample. In addition, the field screening offers same day results whereas the GC results typically take from 4-6 weeks. A savings of over $11,000.00 in addition to the time savings offered by using the D TECH PCB field screening test on site demonstrate the significant advantages of this method.

IDENTIFICATION OF HIGH MOLECULAR WEIGHT BIOGENIC N-ALKANES, N-ALKANOLS, N-ALKANALS, AND PLANT STEROLS IN ENVIRONMENTAL SAMPLES AND DETERMINATION OF LEE RETENTION INDICES BY GC/MS EQUIPPED WITH ELECTRONIC PRESSURE CONTROL

Paul H. Chen, William A. Van Ausdale, Athanasios Tomaras, and Dwight F. Roberts

Analytical Services Division, Environmental Science & Engineering, Inc.
P.O. Box 1703, Gainesville, FL 32602

ABSTRACT

Soil samples were analyzed by GC/MS according to EPA methods for semivolatile organics. High molecular weight odd carbon number n-alkanes (C_{25} to C_{33}), even carbon number 1-alkanols (C_{22} to C_{32}) and n-alkanals (C_{20} to C_{32}), plant sterols, and pentacyclic triterpenes were found to be present in some of the soil samples. The constituents and the relative quantities of alkanes, alcohols, and aldehydes are similar to that found in plant waxes reported in the literature. This indicates that these compounds are from plant material in the soil. It is important to know that these high molecular eight compounds are biogenic not anthropogenic. The major plant sterols found are β-sitosterol, stigmasterol and campesterol. These sterols are 24 α-alkylsterols with a ring double bond between C-5 and C-6 positions. It has been reported in the literature that vascular plants principally contain these sterols. Lee retention indices (RI) were determined for the compounds identified in this study. In order to shorten the run time, GC equipped with electronic pressure control was used for analysis. The RIs provide the elution order and position for sterols and also for the homologs of n-alkanes, n-alkanols, and n-alkanals which are very useful for compound confirmation from GC/MS analysis.

INTRODUCTION

In the EPA methods for the analysis of semivolatile organics by GC/MS, samples are generally analyzed for the target compound list (TCL) components by an automated data system and for non-TCL components by a library search of a published mass spectral data base. The non-TCL components are reported as tentatively identified compounds (TIC) or unknowns. In our analysis of thousands of environmental samples for non-TCL components, it was not unusual that we found n-nonacosane and n-hentriacontane, and to a lesser extent, n-heptacosane and n-tritriacontane, in the soil samples. These high molecular weight n-alkanes are not from crude oil or petroleum products because they are all odd carbon number whereas n-alkanes in the petroleum product should not show any odd-to-even carbon predominance. In addition to these high molecular weight n-alkanes, we often found high molecular weight n-alkanols, n-alkanals, plant sterols, and pentacyclic triterpenes in some of these samples. These classes of chemicals have been reported in leaf cuticles (1), leaf surfaces (2), road dust (3), and ambient aerosols (4,5). Presumably many soil samples we have analyzed contained plant materials which contributed to these chemicals in the samples. The objectives of this study were to identify these high molecular weight compounds by GC/MS and to determine their Lee retention indices (RI) by GC/MS equipped with electronic pressure control. The Lee RI can provide a means of confirmation of these compounds along with mass spectral data.

Lee retention indices, based on a series of four polycyclic aromatic hydrocarbons (PAHs) as retention index standards, have been reported by Lee et al. (6) and Vassilaros et al. (7) for a large number of polycyclic aromatic compounds. These Lee RIs are determined using capillary columns GC operated

under temperature programming conditions. Rostad and Pereira (8) reported Lee RIs determined by GC/MS for a large number of PAHs and other organic compounds of environmental interest. We reported last year in this symposium that high reproducibilities of Lee retention indices determined under different GC conditions can only be achieved if compounds of interest and the RI standards such as chrysene and benzo(g,h,i)perylene are eluted during the temperature ramping period. Using the conventional GCs which are normally equipped with the constant pressure control, the column oven temperature programming rate has to be decreased to about 5°C/min in order to have benzo(g,h,i)perylene elute during the temperature ramping period. This will result in a long run time (about 60 min) which is not practical in a routine analysis. Since the compounds of interest in this study are all high molecular weight compounds and mostly elute between chrysene and benzo(g,h,i)perylene, we chose to run these samples by GC equipped with electronic pressure control (EPC) which maintains a constant column flow (9). Using EPC we can shorten the run time to 27 minutes and still achieve the elution of benzo(g,h,i)perylene in the temperature ramping period.

EXPERIMENTAL SECTION

Sample Preparation. Soil samples were extracted with methylene chloride in Soxhlet extractors according to EPA SW-846 Method 3540/8270 (10). Before extraction, each sample was spiked with 1.0 mL of surrogate spiking solution which contains 100 μg/ml each of acid surrogates and 50 μg/ml each of base/neutral surrogates. Methylene chloride extract was concentrated to 1 ml with Kuderna-Danish concentrator and analyzed by GC/MS. Prior to GC/MS analysis, the extract was spiked with 20 μl of an internal standard mixture which contains 2 μg/μl each of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}.

GC/MS Analysis. Sample extracts and standards were analyzed on HP5972 MSD connected to an HP5890 Series II GC which was equipped with an EPC split/splitless injection port. The column used was a 30m X 0.25mm i.d. DB-5MS (25 μm coating) fused silica capillary column (J & W Scientific, Folsom, CA). A starting temperature of 50°C was used. The pressure was pulsed by ramping from 18 psi to 98.9 psi at a rate of 99 psi/sec, held for 0.3 min, then ramped back to 18 psi at 99 psi/sec. The column flow at 18 psi and 50°C was 2.2 ml/min which was maintained at a constant flow for the remainder of the run. The column temperature was held at 50°C for 2 min then programmed at 20°C/min to 120°C and then to 320°C at 10°C/min and held isothermal at this final temperature for 3 min. Under this programming benzo(g,h,i)perylene (the last RI standard) elutes during the temperature ramping period. The mass spectrometer was scanned from 35 to 500 amu at a rate of 2 scans/sec. A forward library search was performed for non-TCL compounds on a Wiley/NBS data base which contains 139,000 different spectra (11). Compounds were tentatively identified by library search or by elucidation of the compound structure from its mass spectrum if no match was found in the library. The tentatively identified compounds were confirmed if possible by agreement of the mass spectra and retention times between the sample components and the authentic compounds. The retention time of the tentatively identified compound or the standard was used for the calculation of Lee RI according to the equation described in the following paragraph.

Calculation of Lee Retention Indices. The Lee retention indices are calculated according to the following equation:

$$RI = \frac{100\,(Tx - Tz)}{Tz+1 - Tz} + 100 * Z$$

Where: Tx is the retention time of compound of interest
Tz is the retention time of the preceding RI standard
Tz+1 is the retention time of the following RI standard
Z is the number of rings in the preceding RI standard

The retention index standards used are naphthalene (RI=200.00), phenanthrene (RI=300.00), chrysene (RI=400.00), and benzo(g,h,i)perylene (RI=500.00). When these compounds are not found in the sample, their retention times are calculated by adding the differences in the retention times between the first three RI standards and their corresponding deuterated internal standards in the daily calibration standard to the retention times of the corresponding internal standards in the sample.

RESULTS AND DISCUSSION

A total ion chromatogram of a soil sample that contains high molecular weight biogenic compounds is shown in Figure 1. This chromatogram does not show all the biogenic compounds we have identified in this paper. However, it does show five classes of compounds from biogenic source discussed in this paper. These five classes of compounds are n-alkanes, n-alkanols, n-alkanals, plant sterols, and pentacyclic triterpenes. The presence and distribution of these compounds are somewhat different from sample to sample presumably due to the presence of different plant materials in the soil sample.

N-Alkanes. The alkanes found are all odd carbon number n-alkanes from C_{25} to C_{33}. Nonacosane (C_{29}) and hentriacontane (C_{31}) were found most frequently and most abundantly. Heptacosane and tritriacontane were also found in the sample. These odd carbon number alkanes are not from petroleum products, they are from plant material in the soil which contains plant waxes. Epicuticular plant waxes are known to have n-alkanes of the odd-to-even carbon number predominance. The distribution of the odd carbon number C_{25} to C_{33} n-alkanes found in the soil samples is similar to the distribution reported in the literature for the leaf surfaces abrasion products (2), road dust (3), and ambient aerosols (4,5).

N-Alkanols. The alcohols found in the soil samples are all even carbon number 1-alkanols from C_{22} to C_{32} generally with C_{28}, C_{26}, and C_{30} the most predominant. Similar predominancy of these even carbon number n-alkanols have been reported by other scientists in the leaf surface abrasion products (2) and road dust (3). This indicates that these alcohols are from plant material in the soil which contains epicuticular plant waxes. Coelutions of C_{25} alkane with C_{22} alcohol, C_{27} alkane with C_{24} alcohol, and C_{29} alkane with C_{26} alcohol in the DB-5 column make the quantitation of these alcohols and alkanes somewhat difficult. Figure 2 shows the mass spectra of C_{29} alkane, C_{28} alcohol, and C_{28} aldehyde. As shown in this figure, C_{29} alkane has high intensity peaks at m/z 57, 71, and 85 with ratios of 57/55, 71/69, and 85/83 calculated from the tabulated form of spectrum to be 3.7, 3.6, and 3.6, respectively. On the other hand, the ratios of these three pairs of peaks for C_{28} alcohol are 1.0, 0.93, and 0.47, respectively. Furthermore, C_{28} alcohol has high intensity peaks at m/z 83, 97, and 111 with ratios of 83/85, 97/99, and 111/113 equal to 2.1, 5.0, and 6.1, respectively. Similar ratios should be observed for other high molecular weight alkanes and alcohols. Using this information, one can estimate the percentage of the alcohol and the alkane in the coeluting peak.

N-Alkanals. The aldehydes found in the samples are even carbon number n-alkanals from C_{20} to C_{32}. The most abundant aldehydes are generally C_{30}, C_{28}, C_{26}, and C_{32}. This distribution is similar to that reported in the literature (2,3). Again these aldehydes are likely from vascular plant waxes in the soil. As shown in Figure 2, the mass spectrum of n-alkanal normally shows strong peaks at m/z 82 and 96. Other less intense even mass peaks are also present in the spectrum. For high molecular weight n-

alkanal, the molecular ion is usually absent. However, [M-H_2O] and [M-H_2O-C_2H_4] ions are occasionally present. Since no authentic C_{20} to C_{32} aldehydes are available for confirmation, chemical ionization (CI) spectra were obtained for one of the samples. The CI spectra gave [M+H] and [M+C_2H_5] ions for the aldehyde which confirm the suspected aldehyde.

Plant Sterols. As shown in Figure 1, a few common plant sterols were found in the soil sample which contains plant wax constituents. β-Sitosterol (stigmast-5-en-3-ol or 24α-ethylcholesterol) was found most frequently and most abundantly, next came stigmasterol (stigmata-5,22-dien-3-ol) and stigmast-4-en-3-one. Stigmast-4-en-3-cone is not a common steroidal ketone in the plant, it is probably from the oxidation of β-sitosterol to the corresponding 5-en-3-ketone, then isomerization to a more stable 4-en-3-ketone which is stigmast-4-en-3-one. The oxidation and isomerization may occur by the microbial enzymes in the soil. Compesterol (ergost-5-en-3-ol), a 24-α-methylcholesterol, was also found in the soil sample. Less commonly, a trace amount of cholesterol was sometimes found to be present in the sample. The mass spectra of four common plant sterols found in the soil are shown in Figure 3. The plant sterols found in the soil sample are dominated by 24α-alkylsterols and with a ring double bond between C-5 and C-6 positions. The plants principally with these sterols have been designated as category I-A (12). Most vascular plants belong to category I-A (12).

Pentacyclic triterpenes. Several pentacyclic triterpenes have been found in the soil samples. We are only able to obtain two of the authentic compounds, i.e., lupen-3-one and friedelin, to confirm their presence in the samples. The mass spectra of lupen-3-one (lup-20(29)-en-3-one) and friedelin (D:A-friedooleanan or friedelin-3-one) are shown in Figure 4. Other pentacyclic triterpenes found in the soil samples but not confirmed by the authentic compound include D-friedoolean-14-en-3-one (taraxerone with M. Wt. of 424) and taraxerol methyl ether (M. Wt. 440). Oleanolic acid and orsolic acid were found in the fine particulate abrasion products from leaves by Rogge et al. (2), but were not found by us probably because they are not amendable to analysis by GC/MS without derivatization of the cabroxyl group.

Other Classes of Compounds. Hexadecanoic acid, and to a lesser extent, octadecanoic acid, were often found in the soil samples. 9-Hexadecenoic acid, 9-octadecenoic acid, lower alkanoic acids (C_{12}-C_{16}) and higher alkanoic acids (C_{20} to C_{24}) were sometimes found in the soil samples. Part of the lower alkanoic acids are probably from microbial lipids. The free fatty acids found in the soil are even carbon number n-alkanoic acids which are likely from the plants material present in the soil. Other biogenic compounds found to be present in the soil samples include dehydroabietic acid, vitamin E, and squalene. Dehydrobietic acid is a resin acid which is known to be present in conifers.

Lee Retention Indices. Table 1 shows the comparison of Lee RI of PAHs determined by the conventional constant pressure GC and constant flow GC. Constant flow GC is achieved by using EPC injection port. As shown in Table 1, Lee RI values determined by constant pressure and constant flow agree very well. This indicates that Lee RI data determined by the conventional GC method such as those reported by Lee et al. (6), Vassilaros et al. (7) and Rostad and Pereira (8), can be applied to RIs determined by GC/MS equipped with EPC. We reported last year in this symposium that high reproducibilities of Lee RI determined under different GC conditions can only be achieved if compounds of interest and the RI standards such as chrysene and benzo(g,h,i) perylene are eluted during the temperature ramping period. Since the compounds of interest in this study are all high molecular weight compounds,in order to shorten the analysis time and still achieve the Lee RI values that can be reproduced by other labs, GC/MS equipped with EPC was used for analysis.

Lee Retention Indices of Biogenic Compounds. Lee RIs of biogenic compounds found in the soil are listed in Table 2. These RI values can not be reproduced under different GC conditions with as good reproducibility as that shown in Table 1. This is because in Table 1 the compounds of interest and the RI standards are all PAHs, the changes in their chromatographic retention behavior under different GC conditions should be similar. The RIs listed in Table 2 provide the elution order and position for plant sterols and also for the homologs of n-alkanes, n-alkanols, n-alkanals, and n-alkanoic acids which are very useful for compound confirmation from GC/MS analysis.

ACKNOWLEDGMENTS

We thank P. Dumas and his department for extracting the samples and S. Keeran, D. Schindler, and H. Adcock for their assistance in GC/MS analysis. We also thank Dr. Dave Powell of University of Florida for obtaining the CI mass spectra for us.

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TABLE 1. COMPARISON OF LEE RETENTION INDICES OF PAH'S DETERMINED BY CONSTANT PRESSURE AND CONSTANT FLOW

Compound	Constant Pressure RI	Constant Flow RI
Phenanthrene	300	300
Anthracene	301.59	301.83
Fluoranthene	344.83	344.43
Pyrene	352.72	352.60
Benzo(a)anthracene	398.53	398.72
Chrysene	400	400
Benzo(b)fluoranthene	442.34	442.24
Benzo(k)fluoranthene	443.05	443.37
Benzo(a)pyrene	454.06	454.02
Indeno(1,2,3-cd)pyrene	492.36	492.09
Dibenzo(a,h)anthracene	493.42	493.22
Benzo(g,h,i)perylene	500	500

TABLE 2. LEE RETENTION INDICES FOR BIOGENIC n-ALKANES, 1-ALKANOLS, n-ALKANALS, PLANT STEROLS, n-ALKANOIC ACIDS, AND PENTACYCLIC TRITERPENES

Compound	RI
Pentacosane	402.40
Heptacosane	430.84
Nonacosane	456.71
Hentriacontane	480.80
Tritriacontane	503.44
Docosanol	402.41
Tetracosanol	430.85
Hexacosanol	457.26
Octacosanol	482.07
Triacontanol	505.21
Dotriacontanol	528.82
Docosanal	393.81
Tetracosanal	421.90
Hexacosanal	448.83
Octacosanal	473.88
Triacontanal	497.50
Dotriacontanal	520.10
Dodecanoic acid	264.11
Tetradecanoic acid	293.86
Hexadecanoic acid	326.41
Octadecanoic acid	356.78
Eicosanoic acid	385.02
Docosanoic acid	412.52
Tetracosanoic acid	439.96
Cholesterol (Cholest-5-en-3β-ol)	484.43
Campesterol (24α-methylcholesterol)	496.58
Stigmasterol ($\Delta^{5,22}$-24α-ethylcholesterol)	498.71
β-Sitosterol (24α-ethylcholesterol)	506.48
Stigmast-4-en-3-one	520.89
Lupen-3-one	514.53
Friedelan-3-one (Friedelin)	534.44
Vitamin E	484.26
Squalene	449.71

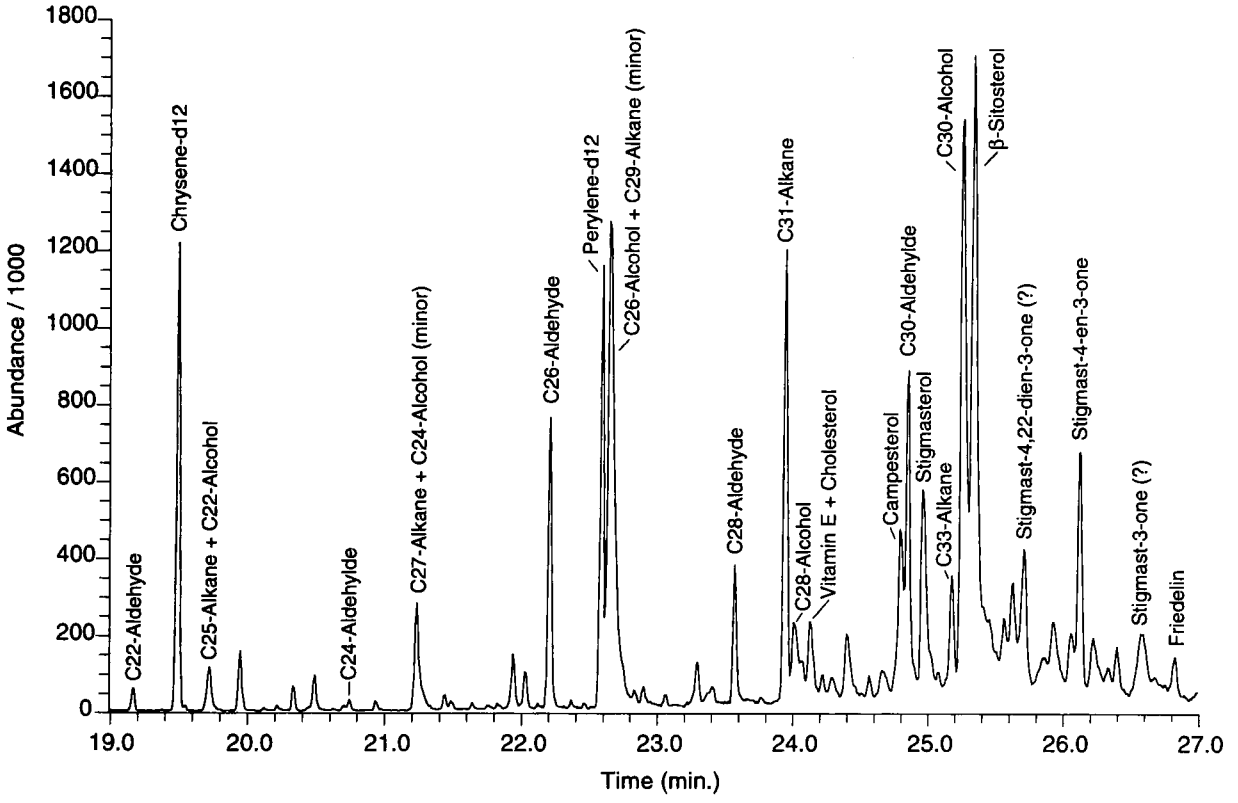

Figure 1. Total ion chromatogram of a soil sample which contains high molecular weight n-alkanes, n-alkanols, n-alkanals, plant sterols, and pentacyclic triterpenes.

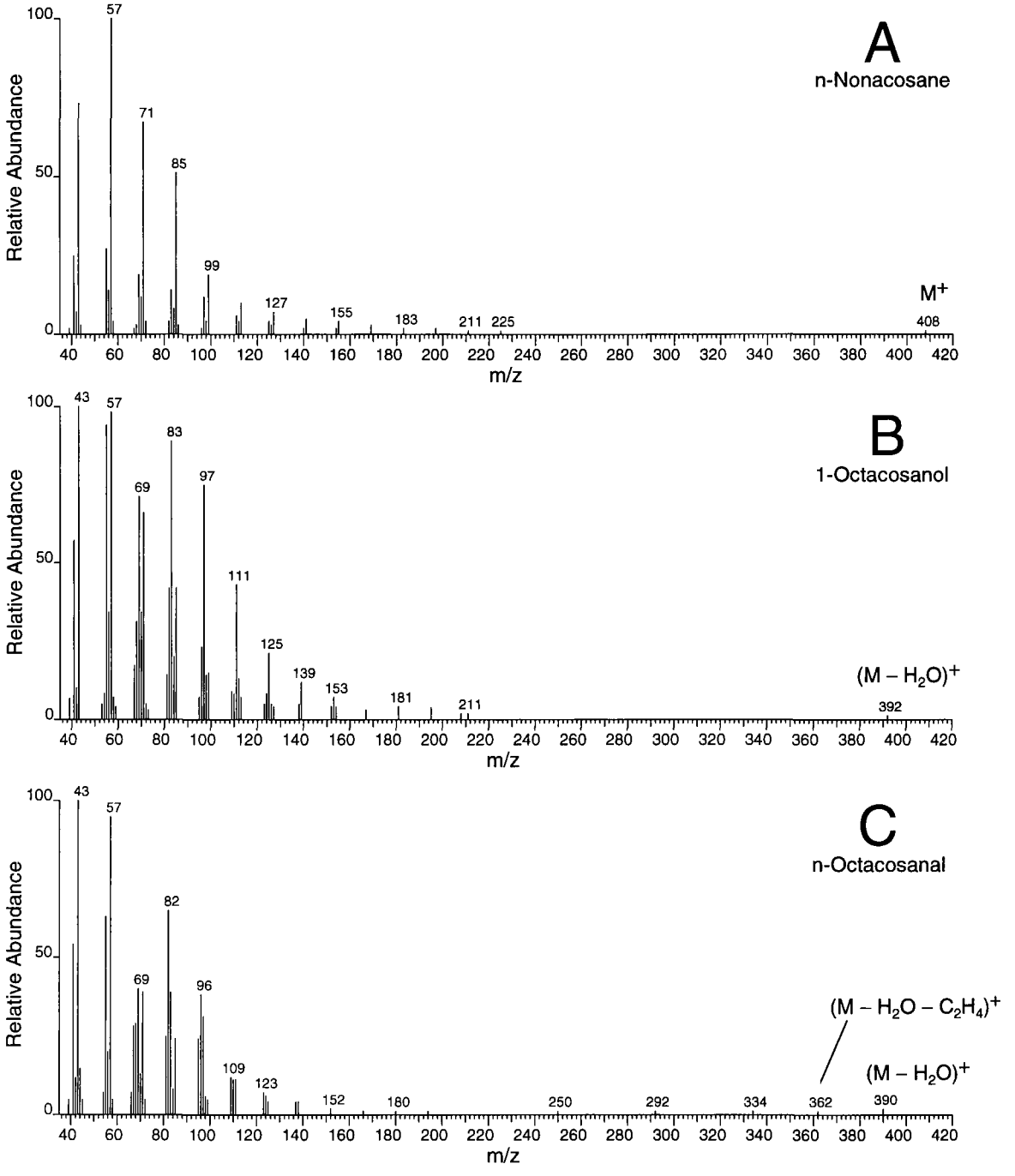

Figure 2. Mass spectra of n-nonacosane (A), 1-octacosanol (B), and n-octacosanal (C).

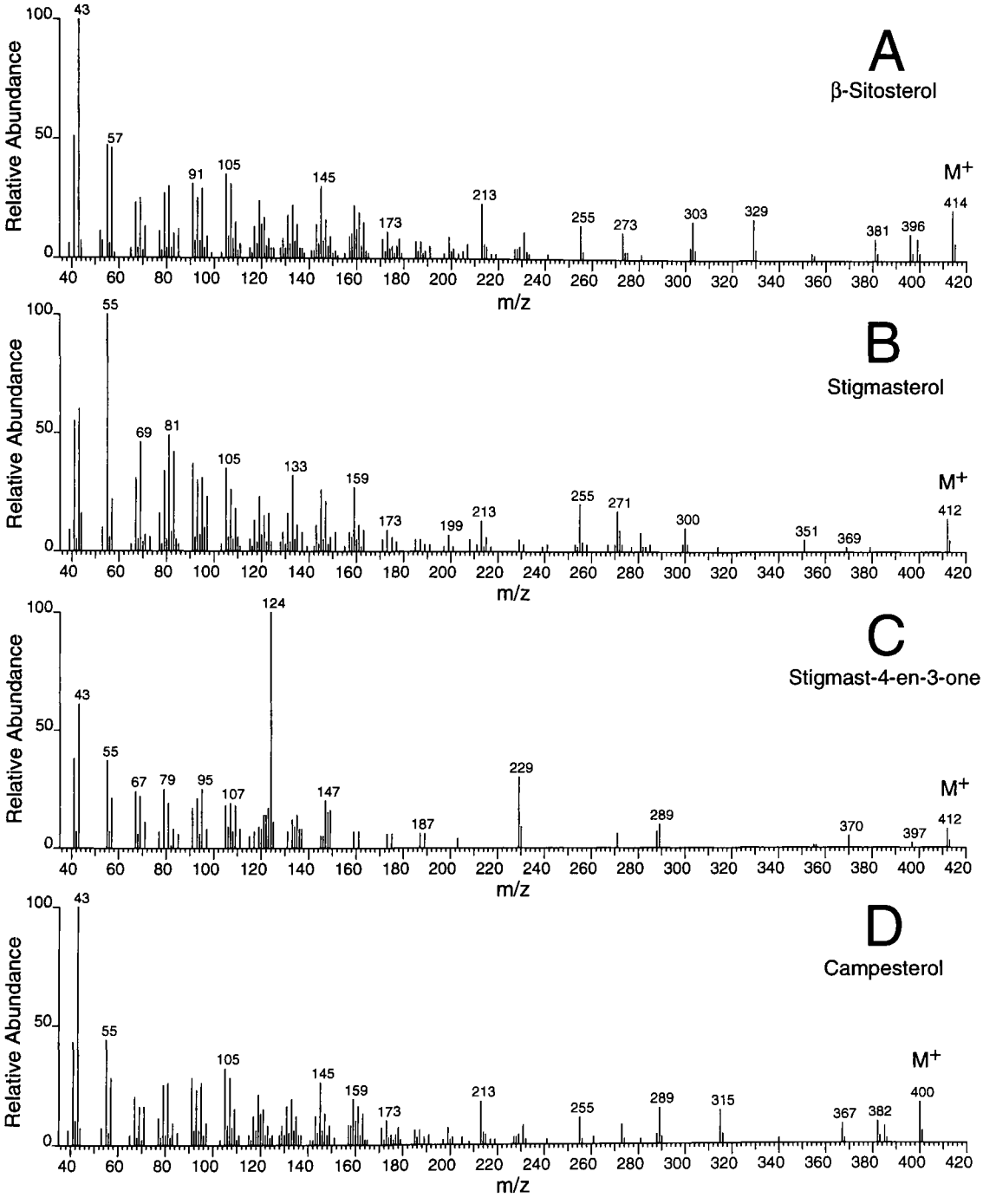

Figure 3. Mass spectra of four common plant sterols found in soil samples: β-sitosterol (A), stigmasterol (B), stigmast-4-en-3-one (C), and campesterol (D).

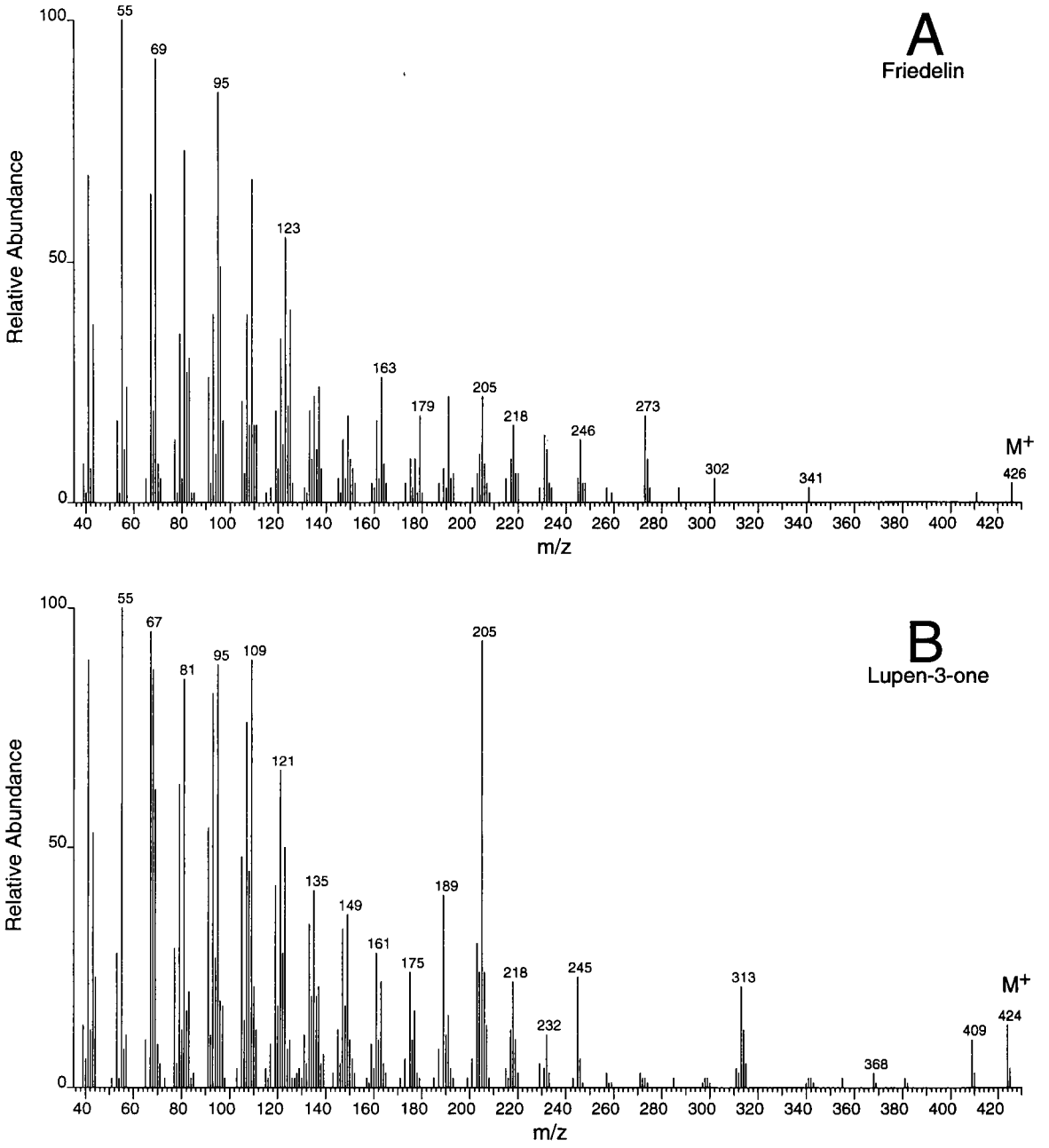

Figure 4. Mass spectra of two common pentacyclic triterpenes found in soil samples: friedelin (A) and lupen-3-one (B).

RAPID DIOXIN SCREENING BY ENZYME IMMUNOASSAY

Robert O. Harrison, ImmunoSystems, Inc., Scarborough, ME 04074
Robert E. Carlson, Ecochem Research Inc., Chaska, MN 55318
Hamid Shirkhan, Fluid Management Systems, Inc., Watertown MA 02172
Theresa Keimig, Midwest Research Institute, Kansas City MO 64110
Wayman E. Turner, Centers for Disease Control, Atlanta, GA 30341

ABSTRACT

A system has been developed for rapid screening of 2,3,7,8-TetraChloroDibenzo-p-Dioxin (TCDD). The system uses a competitive inhibition Enzyme ImmunoAssay (EIA) based on a mouse monoclonal antibody which is specific for TCDD and related congeners. Sample preparation can be performed with a programmable automated extraction and cleanup system which uses disposable Teflon clad columns. The extraction and cleanup system has been extensively validated by GC-MS for a variety of sample types. The sample preparation system allows immunoassay analysis of soil, serum, water, and other matrices by taking each sample type to the same sample preparation endpoint. Concentration factors and endpoint conditions are completely flexible and programmable. Immunoassay analysis is performed by the addition of a prepared sample extract in organic solvent to an antibody coated microwell containing an aqueous sample diluent. This is mixed and incubated for 30 minutes to allow the immobilized antibody to capture analyte from the sample. The liquid is then removed and the well is washed to remove unbound materials. The well is then incubated with a competitor-HRP conjugate capable of binding specifically to the antibody sites not occupied by TCDD. After 30 minutes, the unbound conjugate is washed away and enzyme substrate is added for color development. The color generated is directly related to the amount of competitor-HRP bound in the second step, which is inversely related to the amount of analyte bound in the first step. After 30 minutes, a stop solution is added and the developed color is read on a microplate reader. The total time required for the EIA analysis of a prepared extract is less than 2 hours. Sensitivity for TCDD is better than 0.1 ng/well, allowing sensitive analysis of a variety of environmental matrices. Preliminary results indicate that it is possible to detect 10 ppb 2378-TCDD in soil by direct analysis of crude soil extracts. Work is being directed toward simplification of the extraction procedure and improvement of the interface with the automated sample cleanup system. The data presented here demonstrate that this system should be useful for TCDD screening in many situations for a variety of matrices. The system offers significant improvements in speed, sample throughput, and cost compared to GC-MS.

INTRODUCTION

Reagents and Standards

The EIA for PCDD/F's uses the mouse monoclonal antibody DD3, which has been described previously (1). Competitors which bind specifically to the dioxin binding site of DD3 were conjugated to horseradish peroxidase (HRP) to make conjugates

which can be captured by the immobilized DD3 antibody. The competitor-HRP conjugates were tested for PCDD/F sensitivity and solvent and matrix tolerance. Standard preparation was as follows, based in part on prior work by Sherry et al. (2). PCDD/F standards in toluene or nonane were diluted in the same solvent in silanized glass vials. A small volume of DMSO was added to each vial, then the toluene or nonane was evaporated under a nitrogen stream. The DMSO was diluted with an equal volume of methanol and the standard was mixed vigorously, then sonicated for 15 minutes. Analysis was as described in the EIA procedure below, by adding the DMSO/methanol solution to aqueous diluent in the EIA well.

PCDD/F EIA Procedure and Interpretation of Results

Following is the procedure for the EIA analysis of PCDD/F's: 1) mouse antibodies which recognize the dioxin structure are immobilized on the walls of plastic microwells; 2) PCDD/F's in solvent, in the form of either standards or samples prepared as described above, are mixed with Assay Diluent in the wells, allowing PCDD/F's to bind to the immobilized antibodies; 3) unbound sample is washed away with water; 4) competitor-HRP conjugate is added and allowed to compete with the captured analyte for the limited PCDD/F binding sites on the immobilized antibodies; 5) unbound conjugate is washed away with water, leaving an amount of conjugate on the immobilized antibodies inversely related to the amount of PCDD/F's that were present in the sample; 6) enzyme substrate is added to the wells for color development by the bound enzyme. The intensity of color is proportional to the amount of bound enzyme and is inversely related to the amount of PCDD/F's present in the sample. Therefore, ***more color means less PCDD/F's***. Total run time is approximately 2 hours per test and up to 40 samples can be run in a single batch. The optical density (OD) of each standard and sample well is measured and sample PCDD/F concentrations are calculated based on the standard curve.

RESULTS AND DISCUSSION

Method Sensitivity

The use of heterologous haptens or competitors for improving immunoassay sensitivity has been described previously in detail (3) and has been exploited here using a well studied anti-dioxin antibody. Three heterologous competitors were compared to the homologous competitor. The results of a single experiment (Figure 1) show that the improvement in sensitivity obtained was greater than an order of magnitude for one competitor and approximately one order of magnitude for the other two competitors. Conjugates 1c and 2a were selected for further characterization. Sensitivity to 2378-TCDD in all subsequent experiments with both 1c and 2a has been better than 100 pg/well.

Test Specificity

The specificity of DD3 antibody has been described previously (1) and is primarily directed toward selected tetra- and pentachlorodibenzodioxins, with reduced recognition of the corresponding furans. This recognition profile corresponds roughly

to the I-TEF values given in reference 4. Competitive inhibition tests were performed using a complex mixture of dioxins and furans (Table 1) to assess the possibility of a change in specificity due to the use of heterologous competitors. This mixture contains compounds comprising the full range of recognition by DD3 antibody in the system used by Stanker et al. (1), as well as TEF values covering three orders of magnitude. The results shown in Figure 2 suggest that the specificity of DD3 antibody with competitor 1c does not differ significantly from the previously established pattern. Similar results were seen for competitor 2a.

Interface of EIA with Automated Sample Cleanup System

The system described is capable of analyzing samples in a variety of solvents, but has been designed to accommodate any sample that can be exchanged from a volatile hydrophobic solvent into a non-volatile hydrophilic solvent. This allows the analysis of any sample prepared by standard methods such as the FMS Dioxin-Prep™ System for Automated Sample Cleanup (5). Preliminary experiments indicate no interference in the EIA using a fully cleaned extract from the FMS system. Ultimate method sensitivity is therefore determined primarily by sample size, concentration factor, and interference from the concentrated matrix.

Soil Spiking and Extraction

The possibility of a rapid extraction and analysis for PCDD/F's in soil was investigated as follows. Aliquots of 5 g of soil were weighed into silanized glass extraction vials and air dried overnight. Soils were spiked by adding a toluene solution of 2378-TCDD directly to the soil surface at multiple sites. After mixing the soil and air drying 30 minutes, 3 steel BB's and 5 ml of solvent were added to each vial. Methylene chloride and toluene samples were prewetted with a minimum amount of acetone before adding the other solvent. Vials were sealed with Teflon lined caps and soil samples were extracted by shaking for thirty minutes at 300 rpm on an orbital shaker. The extracts were clarified by centrifugation for 15 minutes at 1-2000g. An aliquot of each extract was removed to a silanized vial, DMSO was added, and the volatile solvents were removed by evaporation under a nitrogen stream. Methanol was added to each sample and further handling and analysis followed the procedure described above for standards. The data of Table 2 show that 2378-TCDD spikes may be recovered and detected with a relatively simple procedure, but that not all solvents will give adequate results. Toluene appears to extract soil components which give strong false positive interference in the EIA, while DMSO appears to give inadequate recovery. Neither methylene chloride nor hexane:acetone gave significant false positive interference and both gave acceptable recovery values. These results will form the basis of further experiments directed toward a rapid soil extraction procedure for low level analysis of PCDD/F's in soil.

CONCLUSIONS

1. The test is capable of analyzing for PCDD/F's in less than 2 hours from prepared extracts, using very little specialized equipment.
2. The heterologous competitor strategy employed here demonstrates significantly improved sensitivity.
3. The specificity of the test appears to parallel the previously established profile for DD3 antibody.
4. The design of the EIA accommodates significant variations in sample preparation, allowing the analysis of PCDD/F's in many matrices.
5. Ongoing work with this kit includes improvement of the rapid soil extraction procedure and validation for a variety of sample matrices.

Table 1. Composition of Native Standard and Toxic Equivalent Concentrations

Congener	pg/µl Used	TEF*	TEC**
2,3,7,8-TCDF	4	0.1	0.4
2,3,7,8-TCDD	4	1	4
1,2,3,7,8-PeCDF	20	0.05	1
2,3,4,7,8-PeCDF	20	0.5	10
1,2,3,7,8-PeCDD	20	0.5	10
1,2,3,4,7,8-HxCDF	20	0.1	2
1,2,3,6,7,8-HxCDF	20	0.1	2
2,3,4,6,7,8-HxCDF	20	0.1	2
1,2,3,7,8,9-HxCDF	20	0.1	2
1,2,3,4,7,8-HxCDD	20	0.1	2
1,2,3,6,7,8-HxCDD	20	0.1	2
1,2,3,7,8,9-HxCDD	20	0.1	2
1,2,3,4,6,7,8-HpCDF	20	0.01	0.2
1,2,3,4,7,8,9-HpCDF	20	0.01	0.2
1,2,3,4,6,7,8-HpCDD	20	0.01	0.2
OCDF	40	0.001	0.04
OCDD	40	0.001	0.04
Total	348		40.08

* TEF = toxic equivalency factor, from reference 4
** TEC = toxic equivalent concentration (pg/µl used x TEF = TEC)

Table 2. Recovery of 2378-TCDD from Soil by Four Extraction Methods. One soil was spiked at 10 ng/g with 2378-TCDD and recovery was compared to a standard evaporated onto a bare vial and recovered with DMSO. Each extraction method and the no soil control included an unspiked sample for evaluation of the matrix effect. Each value is the mean for three replicate wells in one EIA run.

Extraction Solvent	Matrix Effect*	Recovery of Standard**
DMSO	92	36
toluene	56	167
dichloromethane	108	91
hexane:acetone (1:1)	120	94

* optical density (OD) of unspiked soil as a percent of the no soil/no TCDD control OD in the EIA

** percent recovery of 10 ng/ml soil spike relative to spike recovered from vial with no soil

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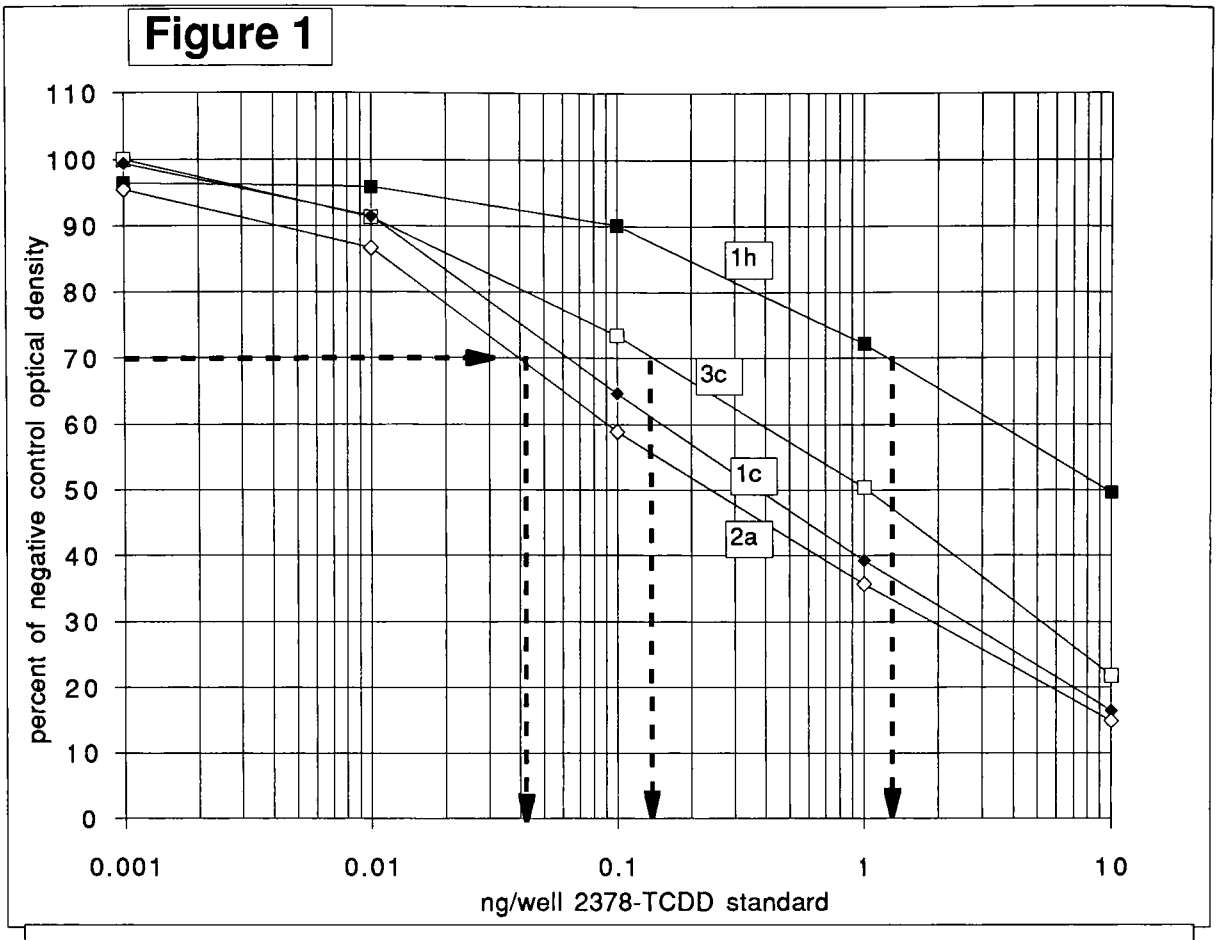
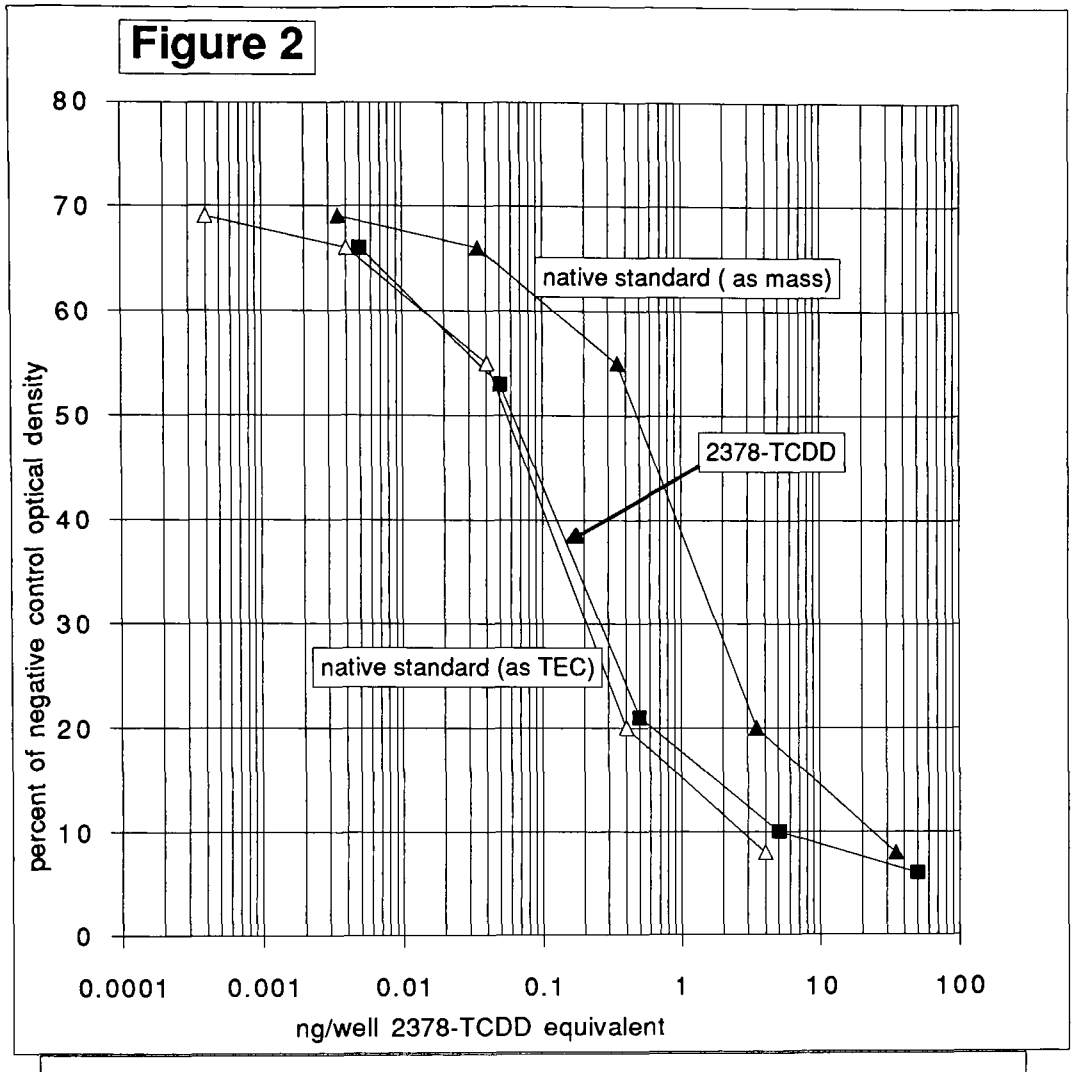


Standard Curves of 2378-TCDD for DD3 with 4 Conjugates. Conjugate 1h is a fully homologous system, where the competitor used for HRP conjugation is the same as the haten used for developing the antibody. The other three conjugates use competitors for HRP conjugation which are different than the hapten used for developing the antibody.



Comparison of EIA Standard Curves of 2378-TCDD and a 17 Congener Native Standard Mixture. HRP conjugate 1c and DD3 antibody were used to detect both 2378-TCDD and native standard (Table 1). The native standard response is expressed both as actual total mass and as toxic equivalent concentration (TEC) according to Table 1.

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EXTRACTION OF ENVIRONMENTAL ANALYTES USING A CARBON MEMBRANE

Steve Miller and Gary L. Nixon, Alltech Associates, 2701 Carolean Industrial Drive, State College PA 16801

ABSTRACT

Membrane extraction disks are increasingly being used in solid-phase extraction of aqueous environmental samples to take advantage of their ability to separate pollutants from an aqueous matrix faster and with a lower solvent usage than alternative techniques. Current methods generally cite membrane disks which employ a reverse phase adsorbent (usually C18). We have developed a membrane using graphitized carbon black as the adsorbent, combining the advantages of the membrane extraction with the efficency of carbon . By embedding graphitized carbon black in an inert support, we are able to demonstrate improved extraction of polar analytes while maintaining high recoveries of non-polar compounds. These results demonstrate that carbon membrane extraction provides a means to apply this technology to a wider range of analytes than was previously possible.

A PRELIMINARY INVESTIGATION OF RETENTION TIMES AND ANALYTE RECOVERIES WHEN USING HIGH EFFICIENCY GEL PERMEATION CHROMATOGRAPHY CLEANUP

E. E. Conrad, N, L. Schwartz, K. P. Kelly, ABC Instruments (a division of Laboratory Automation, Inc.), Columbia, MO 65202

INTRODUCTION

Gel Permeation Chromatography (GPC) is widely used to clean up extracts that are contaminated with various higher molecular weight coextractives. Data published by other workers (T. Willig, J. Kauffman, *9th Annual WT & QA Conference*, **1993**, Paper #65) demonstrate that GPC cleanup of sample extracts protects analytical systems and preserves data quality by preventing the entrance of matrix coextractives into sensitive equipment. High efficiency GPC employs smaller gel particles which provide higher GPC resolution. Packing the small particle resin into short, stainless steel columns decreases processing time and reduces solvent consumption relative to larger, traditional, glass-barrelled GPC columns.

Establishing that retention properties observed during GPC cleanup are the same for high efficiency versus traditional columns will allow analytical laboratories to reduce waste generation and save money by decreasing solvent consumption while increasing sample processing speed. Results reported here compare retention times and analyte recoveries for some semivolatile target analytes chromatographed on traditional or high efficiency columns and assess column matrix handling capacity.

PROCEDURES

Spiked solvent aliquots (5 mL) were injected and eluted through an Envirosep-ABC high-efficiency GPC cleanup column set (23 mm i.d. x 410 mm bed length, 5 mL per minute flow rate) by using an ABC Instruments Autoprep 1000 GPC. A UV detector (254 nm) was used in-line when retention times were measured. The calibration solution used was prepared per the directions provided within proposed EPA Method 3640A. Analyte recoveries were calculated by GC analysis. GC response for the collected fraction, which was evaporated to a final volume of 5 mL, was compared to GC response for the same analytes using the standard solution injected in the GPC.

Matrix loading capability was assessed by injecting 5 mL of solvent containing some amount of non-volatile matrix coextractive, such as corn oil or potting soil extract. The dumped eluent fraction was collected, transferred to a tared aluminum pan and evaporated to dryness in a fume hood. The residue was weighed and the result was compared with the amount that had been injected.

EXPERIMENTAL PROGRAM

Representative subsets of analytes were chosen from target lists given in semivolatile organic analysis methods. GPC cleanup is well known and has little tendency to capture or destroy target analytes. While high-efficiency columns differ slightly from GPC columns suggested in EPA methods, the differences are of a physical rather than a chemical nature, therefore lower recoveries are not expected. However, since analyte retention time is based primarily on physical factors, relative retention times of analytes may shift. The analyst must be able to recover analytes from the collected fraction using the calibration procedure that is provided in the method (or a workable adaptation of it). Therefore, a principal goal of these experiments was determining elution order for a number of common target analytes with high-efficiency columns and comparing results obtained when using traditional (glass-barreled, low-pressure) columns. In particular, analytes having elution times which are retarded (relative to elution times based solely on size exclusion behavior) by adsorptive effects and which may elute near the elution times of perylene and sulfur were examined in this study.

Another difference between traditional and high-efficiency columns is the capacity to handle matrix loading without excessive loss of chromatographic resolution. Some column capacity is given up when switching to high efficiency columns in order to achieve benefits of reduced solvent usage and faster sample processing. Compared to using traditional columns, high-efficiency columns may use up to 50% less solvent because samples are processed at up to twice the speed.

Matrix handling capacity was rated by measuring the amount of non-volatile soluble material removed from a sample at several matrix loading levels. The column and instrument were calibrated using the recommended EPA procedure, in which 125 mg of corn oil is loaded onto the column and dump time is adjusted to remove at least 85% of the oil while retaining at least 85% of *bis*-(2-ethylhexyl) phthalate (DEHP). Then a methylene chloride solution containing corn oil or extract of potting soil was injected in the system. Each dumped fraction was collected and evaporated to determine the amount of non-volatile material removed in the dumped fraction. NOTE: Although high efficiency columns provide greatest resolution when small injection volumes are used, in practice the 5 mL injection has been retained so that viscosity effects or high solute loadings of concentrated solutions do not degrade chromatographic performance or damage columns.

Capacity in this context is defined as ability to process samples while maintaining the degree of coextractive removal equivalent to the specification (85%) given in the method calibration instructions. Although results show that high-efficiency columns have less matrix handling capacity than traditional columns, many environmental samples can be processed without exceeding capacity.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL BY ENZYME IMMUNOASSAY

Robert O. Harrison, ImmunoSystems, Inc., Scarborough, Maine 04074
Robert E. Carlson, Ecochem Research Inc., Chaska, Minnesota 55318

ABSTRACT

A competitive inhibition Enzyme ImmunoAssay (EIA) has been developed for the determination of Polycyclic Aromatic Hydrocarbons (PAH's) in soil. PAH derivatives were attached to carrier proteins and these conjugates were used to immunize rabbits. The resulting anti-PAH antibodies were used to develop a class-specific field-portable PAH EIA, parallel to the earlier development of PCB and other test kits for field analysis of soil, water, and other matrices. The PAH EIA has sensitivity better than 20 ppb for pyrene, which is the most prevalent PAH compound in environmental samples. The test is formatted as a semiquantitative soil test with 95% confidence of detection when the total PAH level is 1 ppm or greater. Decisions at other levels can be made by use of different dilution protocols. The test detects the key PAH indicator compounds pyrene, fluoranthene, benzo(a)pyrene, and phenanthrene at less than 1 ppm (each compound alone) in soil using a semiquantitative protocol. This protocol also detects 10 other PAHs at less than 8 ppm (each compound alone). The test does not recognize PCB's, pentachlorophenol, BTEX, motor oil, or hydraulic fluid, but some positive interference was observed with petroleum fuels such as diesel, fuel oils, Bunker C and crude oil, which have PAH as a significant component. The data described here demonstrate the usefulness of this EIA for screening PAH in soil in many field and laboratory situations. The lab and field data developed during the validation of the test have been submitted to the EPA Office of Solid Waste for evaluation as screening method 4035 of the SW846 compendium of solid waste methods.

INTRODUCTION

Reagent and Method Development

The development of the EIA for PAH's followed these steps: 1) PAH derivatives were synthesized for conjugation to proteins; 2) one of these PAH derivatives was conjugated to a carrier protein and the resulting conjugate was used to immunize animals, which then produced antibodies recognizing both the PAH derivative and PAH's; 3) a PAH derivative was conjugated to horseradish peroxidase (HRP) to make a conjugate which can be captured by anti-PAH antibodies; 4) the PAH-HRP conjugate was used to screen and select antibodies; 5) the selected system was optimized for PAH sensitivity and solvent and matrix tolerance, then characterized for specificity; 6) the sample preparation method used previously for PCB in soil analysis was applied and validated; 7) the method was validated in the lab by verifying sensitivity, false positive/false negative rates and spike recovery and

testing the effect of pH and water content; 8) the method was validated using field samples.

Sample Preparation

Soil sample preparation is summarized as follows: Weigh 5 g soil on portable balance and place in polyethylene extraction bottle; extract soil by adding 5 mL of methanol and shaking vigorously for two minutes. Filter extract and collect for storage or immediate EIA analysis. Analyze extract as described in the EIA procedure below, diluting the extract in methanol for decisions other than 1 ppm. All components required for this method are commercially available in kit form, including materials, protocol, and instructions for analysis of diluted extracts.

PAH EIA Procedure and Interpretation of Results

The procedure for the analysis of samples containing PAH's is as follows: 1) rabbit antibodies which recognize the PAH structure are immobilized on the walls of plastic test tubes; 2) PAH's in solvent, in the form of either calibrators or samples prepared as described above, are mixed with Assay Diluent in the tubes, allowing PAH's to compete with the PAH-enzyme conjugate for the limited PAH binding sites on the immobilized antibodies; 3) unbound sample and conjugate are washed away with tap water. The amount of conjugate retained by the immobilized antibodies is inversely related to the amount of PAH present in the sample; 4) enzyme substrate is added to the tubes for color development by the bound enzyme. The intensity of color is proportional to the amount of bound enzyme and is inversely related to the amount of PAH present in the sample. Therefore, ***more color means less PAH***. Total run time is less than 30 minutes per test. The EIA is formatted as a semiquantitative test only. The optical density (OD) of each sample tube is compared to the OD of the calibrators. If a sample OD is greater than a calibrator OD, then the sample has less PAH in it than that calibrator. If a sample OD is less than a calibrator OD, then the sample *may have* more PAH in it than that calibrator. A slight false positive bias is designed into the test to guarantee the false negative rate is less than 5%.

RESULTS AND DISCUSSION

Test Specificity

The test response to the target PAH compounds of EPA methods 8100 and 8310 is shown in Table 1. Other compounds and mixtures of compounds expected to be found in conjunction with PAH contamination are also listed in Table 1. The test has measurable, but low crossreactivity for several of these, mostly fuel oils. These have a significant aromatic component, primarily naphthalene, alkylnaphthalenes, and other low molecular weight PAH's. Other materials such as mineral oil, new motor oil, and hydraulic fluid do not contain significant aromatic components and therefore are not crossreactive in the EIA. The PAH's most strongly recognized by the EIA are pyrene, fluoranthene, phenanthrene, and benzo(a)pyrene. Eckel et al. (1) have shown that this group of four compounds together is the most effective indicator group for prediction of soil contamination by other PAH's. Thus, the specificity of the

EIA for these PAH's allows screening for soil contamination with a high level of confidence in the results.

Method Sensitivity

Method sensitivity was determined by assaying 8 different soils which did not contain PAH greater than 1 ppm. Each of these soils was extracted in triplicate and each extract was assayed in three different assays. The mean and the standard deviation of the resulting response values (percent of negative control) were calculated and the sensitivity was estimated at two standard deviations below the mean [mean – 2SD = 79.5% – 2x6.4% = 67%]. Based on this technique and the average assay response, the method sensitivity is 0.25 ppm total PAH at a 95% confidence level.

False Positive and False Negative Rates

False positive and false negative rates were estimated by fortifying eight soil samples at 20% and 200% of the 1 ppm action level. Each sample was extracted and each extract was tested in three different assays. Results obtained by comparison to the 1 ppm PAH calibrator were correct 88% of the time, with 4% false negatives and 8% false positives.

Effect of Water Content

The effect of water content of the soil samples was determined by assaying three different untreated soil samples which had subsequently had water added to a final concentration of 30% (w/w). Aliquots of these samples were then fortified with PAH. Both the fortified and unfortified samples were extracted and each of these extracts were assayed three times. It was determined that water in soil up to 30% had no significant effect on the method.

Effect of pH

The effect of the pH of the soil extract was determined by adjusting the pH of three soil samples. Soil samples were adjusted to pH 2 to 4 using 6N HCl and pH 10 to 12 using 6N NaOH. These soil samples were then fortified with PAH and the unfortified and fortified samples were extracted. Each extract was assayed three times. It was determined that soil samples within the pH range tested had no detectable effect on the performance of the method.

Spike and Recovery

For the purpose of this experiment, quantitative results were obtained using a pyrene standard curve. Three different soil samples were fortified at two levels, 0.2 and 0.8 ppm. The spike solution was a mixture of 3 PAH's equivalent in expected assay response to 86 and 340 ppb pyrene. Three fortified samples of each soil were extracted and each extract was assayed three times. Recovery values were calculated based on the expected assay response to the mixture of the three spiked compounds. Recovery for individual determinations ranged from 48% to 105%.

Average recovery by individual extract ranged from 68% to 83%. Overall average recovery for all samples was 76%.

Field Trial- Correlation with GC-MS Results

A field trial was conducted at a creosote contaminated site using the PAH EIA. Samples were split for analysis by two EIA operators and also for GC-MS if the EIA indicated an acceptable concentration for the correlation study. EIA Operator 1 was experienced, while Operator 2 was trained specifically for this field trial. For this work, quantitative EIA results were obtained using a negative control and a three point pyrene standard curve. Duplicate tubes were run for all negative controls, but all EIA results are based on single tubes for both standards and samples. EIA results from Operator 2 were scored semiquantitatively and correlated to GC-MS results for 42 samples. There was agreement for 83.3% of the samples tested, with 2 false negative results (4.8%) and 5 false positive results (11.9%). The semiquantitative correlation data shown in Figure 1 demonstrate that the method is comparable in accuracy to Method 8270.

Field Trial- Precision of GC-MS and EIA

Four sets of field duplicates were run by both enzyme immunoassay (EIA) operators and the GC-MS lab. Precision results were calculated as coefficients of variation for total PAH concentration for each pair of field duplicates. The results shown in Table 2 demonstrate that the method is comparable or superior in precision to Method 8270.

Field Trial- Correlation Between EIA Operators

EIA results from both operators were scored semiquantitatively and correlated for 98 samples. The semiquantitative correlation data shown in Figure 2 demonstrate that the test performs well even when performed by a newly trained operator in a field situation.

CONCLUSIONS

1. The test is capable of analyzing for PAH's in soil in the field in less than 30 minutes, using no specialized equipment.
2. Screening of soils containing PAH's can be performed at multiple levels from 1 to 10,000 ppm with 95% confidence of detection of contaminated samples.
3. The use of the same extraction protocol as for other kits such as PCB and BTEX allows analysis of multiple analytes in a single sample extract.
4. The design of the EIA accommodates significant variations in sample type and protocol, allowing the analysis of PAH's in other matrices.
5. Method 4035 is acceptable for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method for documentation of data quality.
6. Ongoing work with this kit includes sediment analysis and water analysis. Field testing and validation are proceeding for these applications.

Table 1. Cross Reactivity of Different Compounds in the PAH EIA

Compound	Concentration (ppm) Required for Positive Interpretation at 1 ppm
Acenaphthene	3.7
Acenaphthylene	2.4
Anthracene	7.6
Benzo(a)anthracene	4.9
Benzo(b)fluoranthene	2.7
Benzo(k)fluoranthene	6.2
Benzo(ghi)perylene	5.3
Benzo(a)pyrene	0.8
Chrysene	4.3
Dibenz(ah)anthracene	356
Fluorene	3.4
Fluoranthene	0.3
Indeno(123cd)pyrene	6.5
Naphthalene	40
Phenanthrene	0.9
Pyrene	0.2
Creosote	3.5
Diesel Fuel	75
Home Heating Oil	80
#2 fuel oil	150
#6 fuel oil	150
Bunker C oil	125
K-1 kerosene	500
crude oil	800
Gasoline	1000
BTEX	>300
pentachlorophenol	>1000
new motor oil	>1000
hydraulic oil	>1000
mineral oil	>1000
Biphenyl	250
Aroclor 1242	>200
Aroclor 1248	>200
Aroclor 1254	>200
Aroclor 1260	>200

Table 2. Precision Within Laboratory and EIA Operators

Coefficients of variation for total PAH concentration for one 8270 lab and both EIA operators for four pairs of field duplicates. EIA Operator 1 was experienced, while Operator 2 had been trained specifically for this field trial.

	%CV for total PAH concentration		
Sample Pair	8270 Lab (GC-MS)	EIA Operator 1	EIA Operator 2
1	28	2	12
2	96	93	47
3	77	49	0
4	47	7	20
Means	62	20	38

REFERENCE

1. Eckel, W.P., Jacob, T.A., Fisk, J.F.; "Co-occurrence Patterns of Polycyclic Aromatic Hydrocarbons in Soils at Hazardous Waste Sites"; presentation at Data Analysis and Interpretation for Environmental Surveillance Conference, Lexington KY, February 1990.

Figure 1. Correlation of Semiquantitative EIA and 8270

total n = 42

* This sample contained several pebble-like lumps which were not included in the subsamples analyzed by immunoassay. Subsequent analysis indicated these lumps to be coal or coal-like material which contained more than 10% total PAH by weight by EIA.

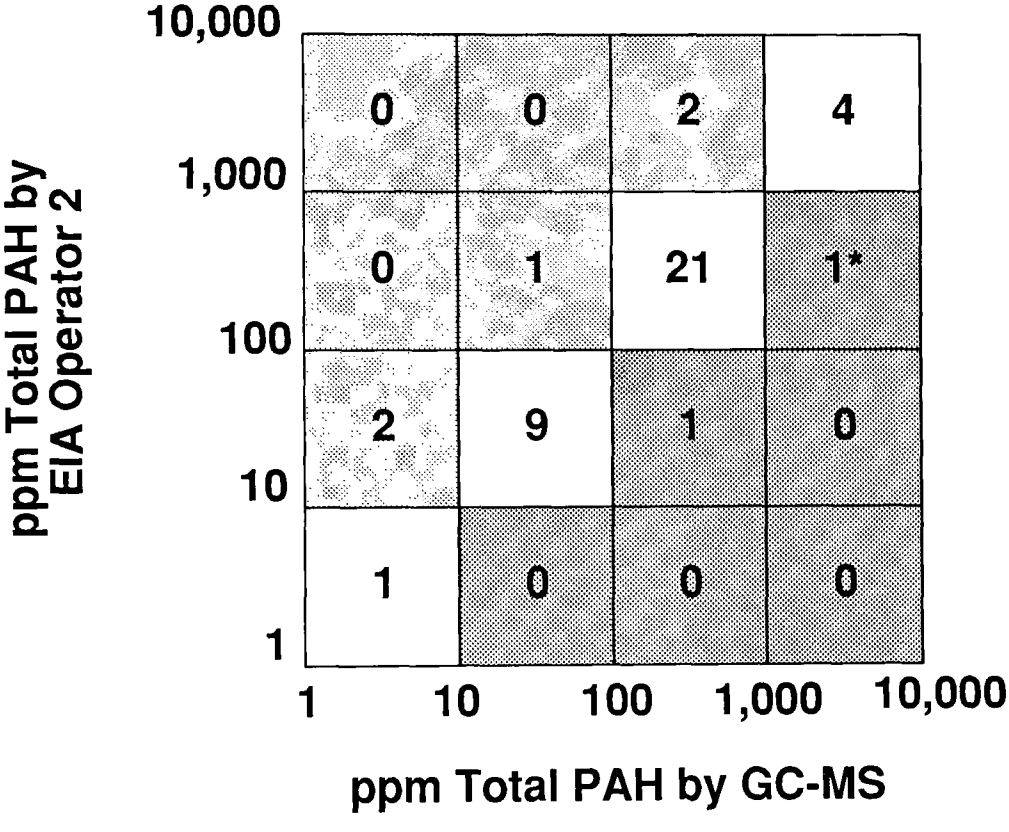
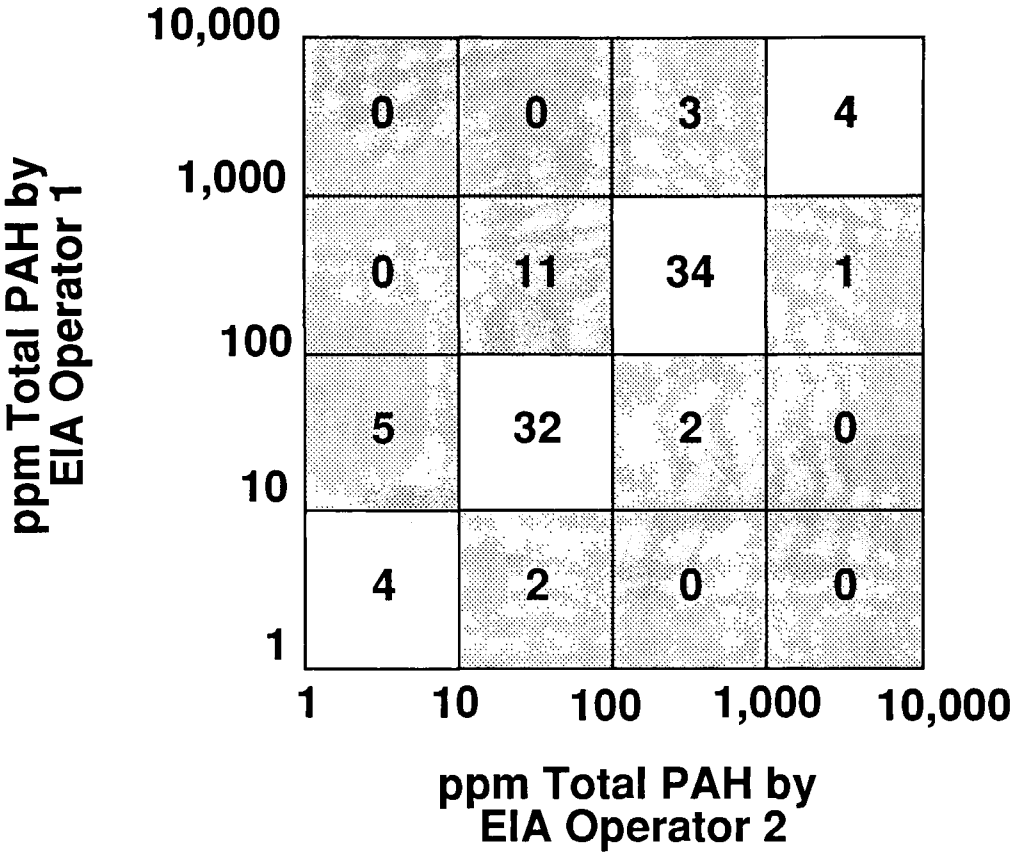


Figure 2. Correlation of Semiquantitative EIA by Two Operators

total n = 98



IMMUNOASSAY DETECTION OF POLYCYCLIC AROMATIC HYDROCARBONS SIMPLIFIES FIELD ANALYSIS OF SOIL AND WATER

Michael C. Mullenix, Scientist, Robert T. Hudak, Scientist, and James W. Stave, Director of Research and Development, Strategic Diagnostics Incorporated, 128 Sandy Drive, Newark, Delaware 19713

ABSTRACT

The carcinogenic and mutagenic nature of polycyclic aromatic hydrocarbons (PAH) has led state and federal agencies to regulate their levels in the environment. Until now, site assessment of PAH levels was limited by the high cost and long turnaround time associated with the analytical laboratory techniques for measuring PAH. An immunoassay for the semi-quantitative detection of PAH was developed as a part of the D TECH' environmental detection systems line of products. This PAH immunoassay is designed to simplify the process of site assessment by providing a rapid, reliable, and low cost alternative to analytical laboratory techniques. In the immunoassay, PAH in a water sample or extract from a soil sample inhibits the binding of a latex-immobilized anti-PAH antibody to an alkaline phosphatase labeled PAH analog. This test detects the majority of the compounds on the EPA's list of 16 PAH priority pollutants and its specificity is directed toward the 3,4 and 5 ring compounds. The assay detects the carcinogen benzo(a)pyrene and does not detect BTEX, PCB, or other priority pollutants. Contaminated field samples of PAH were collected and the PAH concentrations were determined by both the immunoassay and a commercial laboratory using the EPA SW-846 method 8270. The immunoassay results correlated wth method 8270 and displayed a sensitivity range of 0.3 to 10 ppm PAH in soil and 8 to 500 ppb PAH in water. The low number of false positive and false negative results confirmed the specificity of the immunoassay for PAHs. The use of immunoassay simplifies field analysis by providing the advantages of a rapid onsite analysis, minimum sample preparation, and lower cost per result. An additional advantage is that only minimal training is required to run the D TECH immunoassay. Inclusion of this easy to use test in PAH field screening protocols is a cost effective way to simplify site assessment.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are aromatic compounds consisting of from two to six fused carbon rings. Many of the four, five, and six ring PAHs are highly carcinogenic causing them to be routinely measured environmental pollutants (1). PAH pollution enters the environment from both petrogenic and pyrolytic sources. Petrogenic PAH waste sources such as diesel fuel and crude oil are formed during low temperature processes. Pyrolytic PAH waste sources such as coal tar and creosote are the result of high temperature fossil fuel combustion. The abundance of carcinogenic and mutagenic PAHs entering the environment through various industrial processes has led state and federal agencies to regulate their levels in both soil and water. The EPA lists 16 PAHs as priority pollutants and regulates their levels in the environment..

In general, site assessment of PAH contamination is carried out by collecting soil and water samples and sending them to an analytical laboratory for chemical analysis by high performance liquid chromatography (HPLC) or gas chromatography-mass spectraphotometry (GC-MS). This costly and time consuming approach prompted the development of field analytical techniques that can be carried out on site thus reducing the

need for laboratory analysis (2). Using field analysis techniques provides the advantages of faster turnaround time, more accurate detection the semivolatile PAHs that may be lost due to sample handling, and a significant cost savings.

A recent advance in field analysis occurred with the introduction of immunoassays for detecting and and measuring PAH. Immunoassays offer several advantages to commercial laboratory analytical techniques: portability, cost, turnaround time and ease of use. PAH immunoassays are designed for field screening applications allowing multiple samples to be run simultaneously. When used as a screening procedure only positive results must be verified by an analytical method. This limits the number of samples sent off for lab analysis by instrumental methods. This approach saves both analysis time and the overall analysis cost of the traditional analytical techniques.

In this study an immunoassay developed as a part of the D TECH environmental detection systems line of products was used to determine PAH concentrations in both soil and water. The assay is shown to crossreact with the majority of compounds on the 16 PAH priority pollutants. Spike and recovery studies in both soil and water demonstrate the assay's reproducibility and accuracy. The results of immunoassay analysis of real world samples and standard reference materials are compared to the SW-846 method 8270 (GC/MS). We conclude that immunoassay directed field screening simplifies and allows a more complete site assessment for PAH contamination.

MATERIALS AND METHODS

Immunoassay format: PAH in soil samples is extracted with isopropanol by shaking a small soil sample for three minutes (figure 1). After extraction the sample is diluted twice in a pH 8.5 aqueous buffer. The diluted sample is filtered directly into the immunoreagent test reaction vial containing lyophilized latex-antibody and a PAH derivative-alkaline phosphatase conjugate. An identical reference vial is prepared by adding buffer to a similar reaction vial that contains the same lyophilized components with the addition of a small amount of analyte. The reference vial sets the maximum color level and incubation time of the test under field conditions. In addition, it serves as a procedural control since color development occurs only if the appropriate reagents are used in the correct order. The mixtures are resuspended and incubated for five minutes. After incubation, the reaction mixture is poured onto the appropriate test or reference well on a membrane filter device and allowed to drain. The filter will retain the antibody-latex and any alkaline phosphatase conjugate bound to the latex. Increasing concentrations of analyte will inhibit antibody-latex binding to the alkaline phosphatase conjugate. The test or reference wells are then washed with a buffered detergent solution. Next the alkaline phosphatase substrate BCIP is added to each of the wells and incubated until color development in the reference well reaches the endpoint. As the concentration of free PAH increases in the sample the amount of blue color in the test well decreases. The percent of reference reflectance of each test well is determined using a hand held reflectometer or by color comprison to color card reference card. The results are reported in percent relative reflectance. The PAH immunoassay for water follows a similar assay format using only a single dilution step into the aqueous buffer.

Cross reactivity determinations: The ability of the immunoassay to detect individual PAH compounds was examined by determining the percent cross reactivity of the

individual PAHs at their minimum detection limit. All PAH solutions were prepared in aqueous buffer from individual commercially available PAH standards.

Spike and recovery studies: Negative soil and water samples were spiked at various concentrations with a mixture of commercially obtained PAH standards. Immunoassay results were interpreted from a previously generated standard curve.

Immunoassay correlation with EPA SW-846 method 8270 (GC/MS): Real world soil samples containing PAH and PAH standard reference materials were collected or ordered from commercial sources. The real world samples were analyzed by immunoassay and by method 8270 (GC/MS) at a commercial laboratory.

RESULTS

Immunoassay cross reactivity: To be used as an effective field screening assay, the immunoassay must cross react with as many of the 16 PAH priority pollutants as possible. The percent cross reactivity of the individual PAHs is shown in figure 2. The results indicate the assay detects the 3,4, and 5 carbon ring PAHs best. Ten of the PAHs demonstrate cross reactivity above 10 percent and include the most carcinogenic PAHs such as benzo(a)pyrene and benzo(b)fluoranthene. Three PAH not detected above 10 percent cross reactivity are naphthalene, acenaphthylene and acenaphthene. These three PAHs are less carcinogenic and vary widely in concentration in various sources of PAH waste. In addition, the immunoassay was shown not to crossreact with BTEX, PCBs or other priority pollutants (data not shown).

Soil spike and recovery: The D TECH soil immunoassay has a sensitivity range of 0.3 to 10 ppm of PAH. To demonstrate the linearity of the dose response, negative soil samples were spiked with various levels of PAH and analyzed using the immunoassay. The results were plotted verses their corresponding spike concentrations and fitted to a linear curve (figure 3). The dose response remains linear throughout the assay sensitivity range. the $R^2 = 0.987$ indicates the high degree of sample correlation and reproducibility in the assay.

Water spike and recovery: The D TECH water immunoassay has a sensitivity of 8.0 to 500 ppb of PAH in water. The higher sensitivity can be attributed to a smaller dilution factor in the assay. The water immunoassay, unlike the soil assay, does not require a large dilution to compensate for the effects of an extraction solvent on assay performance. Immunoassay results were plotted verses the their corresponding spike concentrations and fitted to a linear curve (figure 4). The dose response remains linear over the assay sensitivity range . the $R^2 = 0.97$ indicates a high degree of sample correlation and reproducibility in the assay.

Immunoassay correlation with EPA SW-846 method 8270: Real world samples collected at sites with both petrogenic and and pyrolytic sources of PAH contamination were analyzed by immunoassay. PAH concentrations in the real world samples were determined by a commercial analytical laboratory using method 8270 (GC/MS). Immunoassay results were compared to method 8270 results (tables 1, and 2). The immunoassay results correlated with the method 8270 results in all cases.

SUMMARY

The advantages immunoassays offer simplify site assessment in the following ways: they are portable and allow onsite testing, they are fast and allow results to be obtained in nearly real time, multiple samples can be analyzed simultaneously, they are less expensive than analytical analysis, and their format is often simple enough to be used by personnel with only minimal technical training (3). The development of an immunoassay capable of detecting PAH has added an important new weapon the effort of regulating levels of these common and highly carcinogenic compounds in our environment.

This study demonstrates the ability of a PAH immunoassay to detect and crossreact with a wide range of PAH priority pollutants. Spike and recovery experiments with soil and water samples served to underline the accuracy and reproducibility of the PAH immunoassay. PAH immunoassay results were also shown to correlate well with both real world samples and standard reference materials analyzed by EPA SW 846 method 8270 (GC/MS).

Immunoassays are gaining widespread acceptance and applications in the field of pollution monitoring. The low cost, speed, specificity, and accuracy inherent to immunoassay technology makes them especially suited to field screening (3). Immunoassay screening methods for the detection of various priority pollutants have reached both "proposed" and "draft" status for inclusion into EPA SW 846 method.

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2. Abraham, B. M.; Liu, T-Y.; Robbat, A."Data Comparison Study Between Field and Laboratory Detection of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons at Superfund Sites." 1993. Hazardous Waste and Hazardous Materials 10(4):461-473.

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Figure 1. PAH Immunoassay

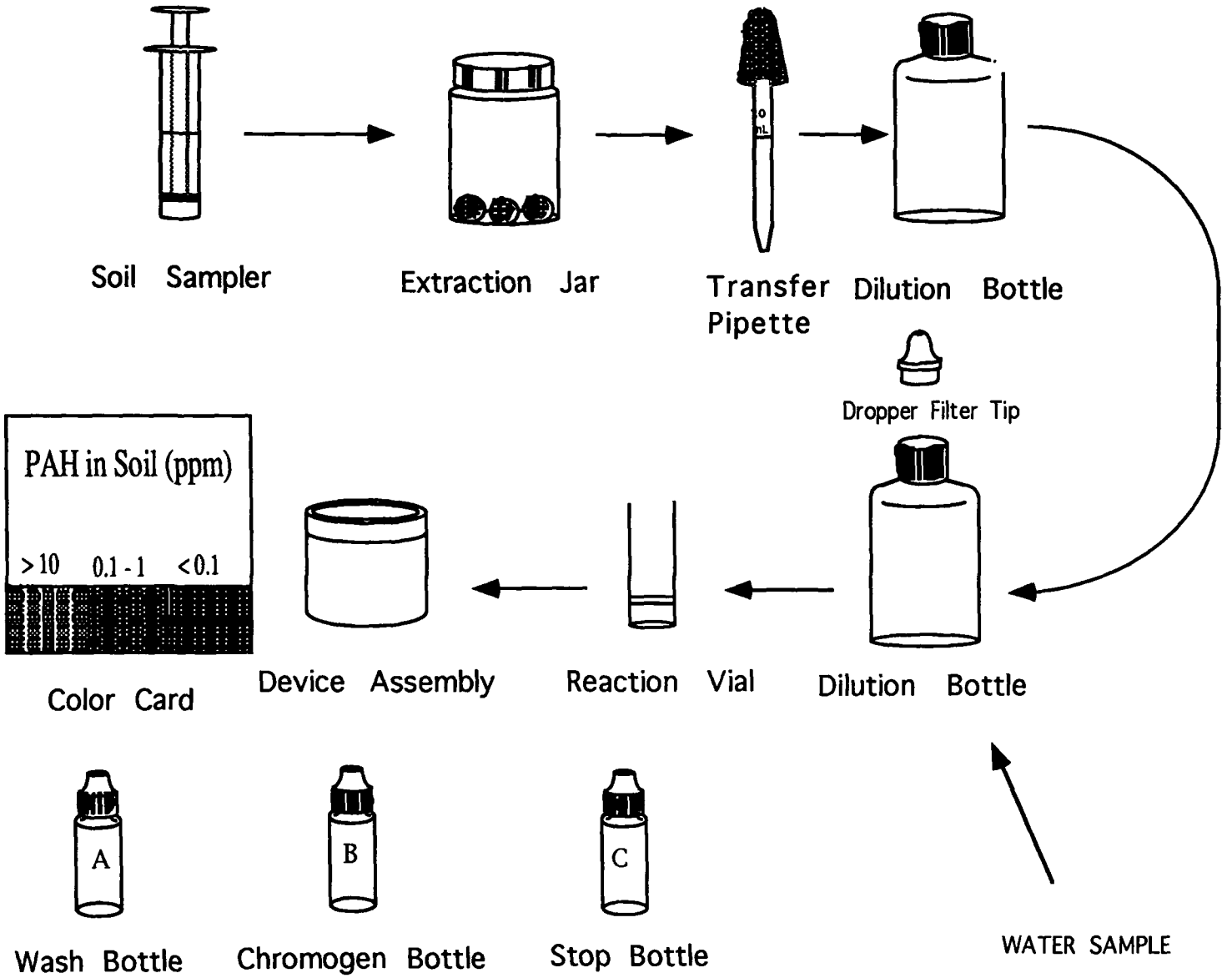

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Figure 2. PAH Assay Cross Reactivity

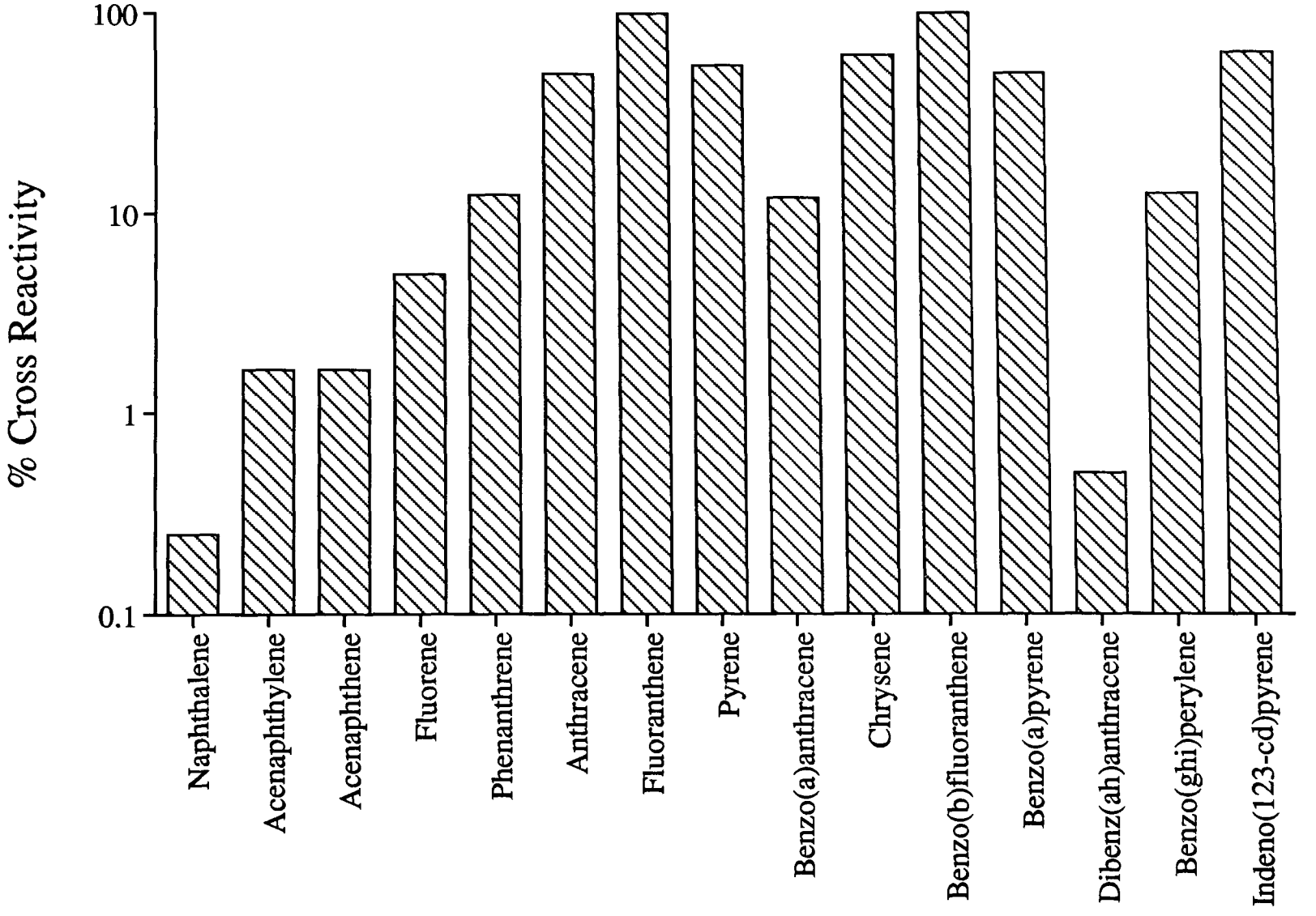

Figure 3
Soil Spike and Recovery Sample Correlation

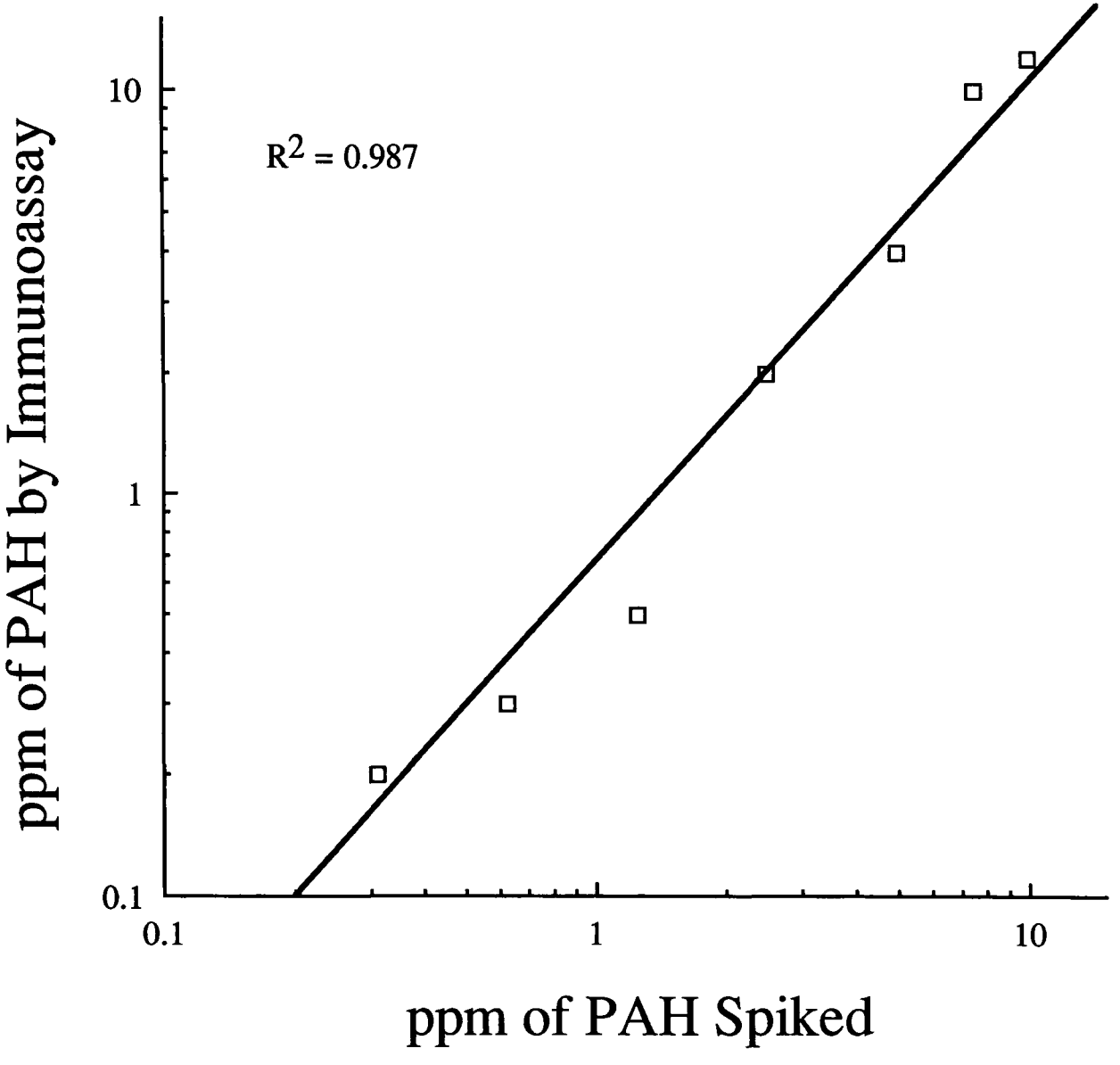

Figure 4

Water Spike and Recovery Sample Correlation

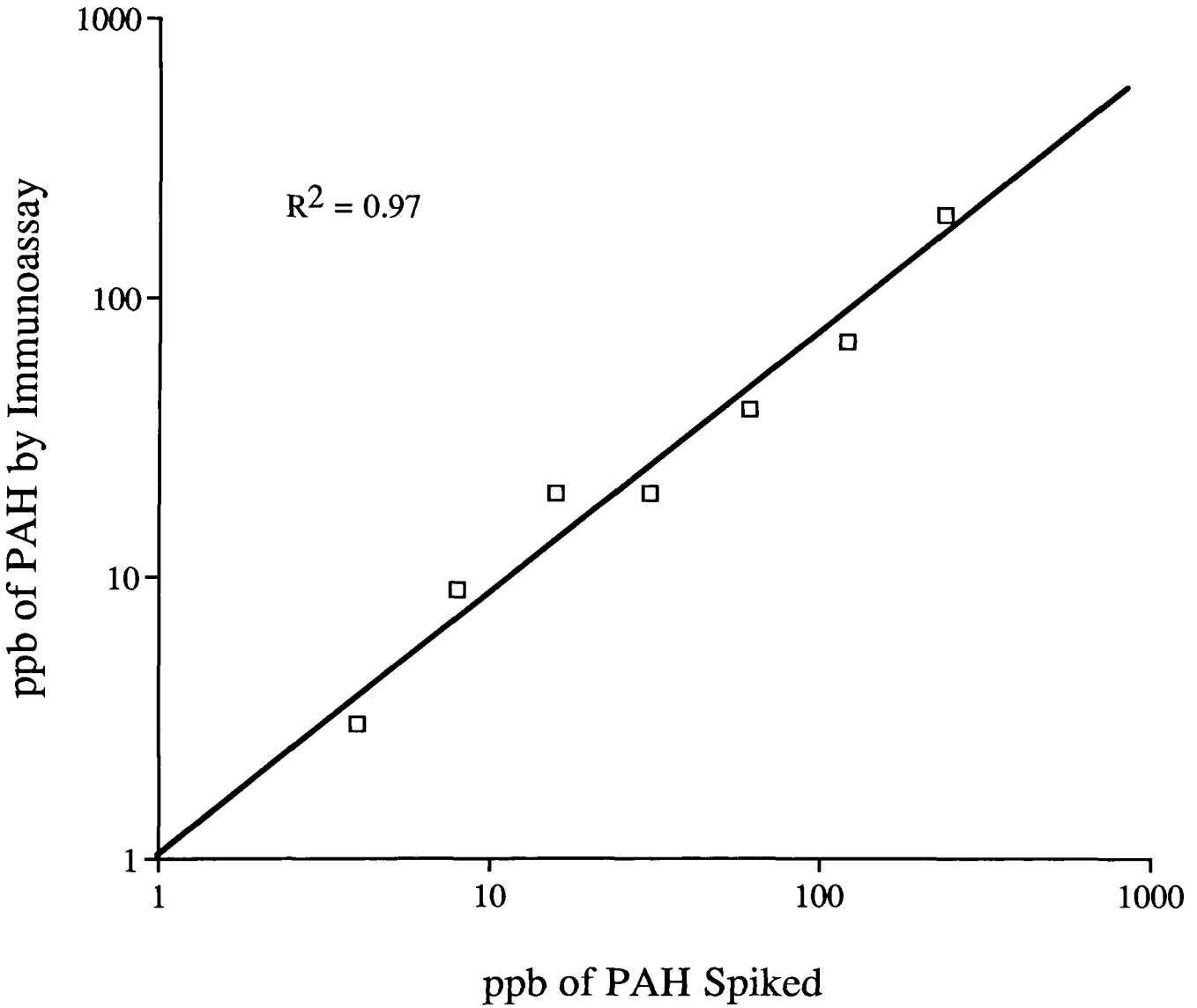

Table 1
Immunoassay Correlation with GC/MS Method 8270
Results are in ppm of PAH

Certified Reference Material*	Immunoassay Results	Method 8270
CRM 103-100	0.90	1.10
Priority PollutnT™/CLP Semivolatiles in Soil	3.00	1.90
SRM 1941a	0.37	0.55

* Certified reference materials are diluted to within assay sensitivity range by homogenization in PAH negative soil.

EXTRACTION CONDITIONS IN SUPERCRITICAL CARBON DIOXIDE RESULTING IN PARTIAL BREAKDOWN OF DDT FROM CONTAMINATED SOILS

ALICIA L. WILSON, Environmental Protection Agency/Oak Ridge Institute for Science and Eduction, 26 W. Martin Luther King Drive, Cincinnati, OH 45268; and Barry M. Austern, Environmental Protection Agency, RREL, 26 West Martin Luther King Drive, Cincinnati, OH 45268.

ABSTRACT

Under some extraction conditions in supercritical carbon dioxide DDT has been observed to break down to DDE and other similar compounds. When DDT was extracted from soil by supercritical fluid extraction (SFE) using carbon dioxide with methanol cosolvent, recoveries could be comparable to those obtained with Soxhlet extraction by EPA Method 3540B. Eleven samples were extracted by SFE and the results were compared to four samples of the same soil extracted by Soxhlet. 96% of the identified compounds recovered by Soxhlet were recovered by SFE. Only 93% of the 4,4 DDT extracted by Soxhlet was extracted by SFE. Some of this may have been due to analytical error and differences in the soil samples, but decomposition of DDT to DDE and other compounds were also observed in most of the soil samples extracted by SFE. A significant increase in the amount of DDE recovered was observed when supercritical carbon dioxide was used without methanol for the initial extraction steps. Less decomposition of DDT to DDE was observed when methanol cosolvent was used to give a more rapid extraction than when carbon dioxide was used alone. Carbon-13 labeled DDT and DDE were spiked onto soil that has been contaminated with DDT and related compounds for more than 20 years to determine whether spiked material was less likely to break down during extraction. No breakdown of the spiked material was observed. A choice of rapid extraction conditions appears to be desirable, not only to increase the throughput of samples, but also to improve the quality of the analytical results.

INTRODUCTION

DDT has been used extensively throughout the world and is still in use in some countries, primarily for vector control. However, there have been extensive reports of adverse effects on wildlife (1-3) as well as an increasing concern about risks of cancers and reproductive problems in humans (4,5). Even in countries where DDT is now banned, significant levels of contamination remain in temperate climates due to the relatively slow rate of degradation.

There is a need for a rapid and efficient means of analyzing soil in areas where high levels of DDT still persist. Traditional extraction methods such as Soxhlet and sonication are labor-intensive and require the use of relatively large amounts of solvents with the consequent safety and disposal costs. Supercritical fluid extraction using supercritical carbon dioxide is relatively safe and should be relatively easy to automate as the technology advances.

Method development for SFE of soils is complicated by matrix effects and the significant differences in adsorption of analytes to the wide range of binding sites available on the soil. Aging of a contaminant such as DDT in a non-homogeneous matrix such as soil results in more of the contaminant being bound in relatively inaccessible pores on strongly adsorbing portions of the soil. Since supercritical carbon dioxide generally becomes a better solvent at increasing densities, extracting a soil sample initially with carbon dioxide at a low density should only remove the least tightly bound molecules of DDT. Repeatedly extracting the same soil at successively greater densities of carbon dioxide should give information about the proportion of DDT molecules which are most and least easily extracted. In an attempt to develop a method for an aging study, it was observed that the total amounts of DDT and DDE recovered varied considerably depending on the conditions during the first few extraction steps.

The degradation of DDT to DDE is commonly observed under a variety of conditions, including those found at hazardous waste sites, so the presence of DDE in DDT contaminated soils is unsurprising. Therefore, conditions during SFE need to be chosen to avoid poor apparent recoveries of DDT due to the breakdown of DDT during extraction of analytical samples.

EXPERIMENTAL

The hexachlorobenzene was 98% technical grade from Aldrich. The 2,4 DDT and 2,4 DDE were analytical grade from Supelco. Optima grade hexane and HPLC grade methanol were from Fisher Scientific. SFC/SFE Grade carbon dioxide from Air Products was used for extractions. Wright Brothers, Inc. supplied the carbon dioxide was used for cooling in the extractor and the prepurified nitrogen and high purity helium for the gas chromatograph.A Hewlett-Packard Model 7680A SFE Module Supercritical Fluid Extractor was used. A Hewlett-Packard Model 5890, Series II Gas Chromatograph with a Supelco SPB-1 30 meter x 0.32 millimeter capillary column and a HP7673 GC/SFC injection tower. A Heat Systems, Inc. sonication bath was used for cleaning extraction thimbles and syringes.

Soil which had been contaminated with DDT for more than 20 years was obtained from a Superfund site. The soil refrigerated until it was air dried in a hood at least a week prior to use. All soil was ground in a mortar and pestle, and rocks larger than 2 mm were removed. After grinding, the soil was stored at room temperature in a stoppered glass bottle.

The Soxhlet extractions were done according to EPA Method 3540B using 1:1 (v/v) acetone/hexane as the solvent. Four grams of soil were extracted in each Soxhlet extractor with about the same weight of sodium sulfate. The extractions were run for 24 hours.

For the standard SFE extraction procedure two to four grams of soil were weighed into a SFE extraction thimble and covered with a wad of glass wool. One milliliter of methanol was then squirted onto the glass wool from a syringe just before the sample was placed into the extractor.

Supercritical carbon dioxide at a density of 0.75 g/ml was held in the thimble for 15 minutes at a flow rate of 2 ml/minute. The thimble temperature was 95°C and the extracted material was trapped at 65°C on stainless steel beads. After the SFE extraction was completed, the trap temperature was changed to 45°C and the trap was rinsed with hexane which was collected in vials containing hexachlorobenzene as an internal standard.

For the sequential extraction procedure one to four grams of soil were weighed into the thimble. For the ECD data in Tables I through IV one milliliter of methanol was added with a syringe. For the work done on the GC/MS, 10% methanol was added with a modifier pump. The soil sample was extracted for fifteen minutes at 95°C with carbon dioxide at a density of 0.25 g/ml. This was repeated with the same soil for step 2. For steps 3 and 4 the density was increased to 0.50 g/ml, and for steps 5 and 6 a carbon dioxide density of 0.75 g/ml was used on the same soil sample. Then the soil sample was extracted four times for steps 7 through 10 using the standard extraction conditions described above.

The extracts for Tables I through IV were analyzed by GC using an ECD detector. The initial temperature of 170°C was held for one minute then ramped to 220°C at a rate of 10°C/min.; the temperature was then held at 220°C for 18 minutes. Then temperature was ramped to 230°C at 2°C/min. and followed by a ramp of 10°C/min. to 300°C where it was held for 10 minutes.

The 13C-spiked samples were analyzed on a Finnigan Incos 50B GC/MS.

SUMMARY

DDT concentrations determined after sequential SFE are much lower than values obtained from the same soil after Soxhlet extraction and the standard SFE method (see Table I). However, the DDE values are much higher after the sequential extraction suggesting that the DDT is undergoing a dechlorination to form DDE. The total recovery of DDT and DDE together after sequential extraction is less than would be expected from the Soxhlet and standard SFE values. This may be due to degradation of DDT to form other compounds for which standards were not available.

During the sequential extraction most of the DDT extracted is removed from the soil during the first few extraction steps, while greater amounts of DDE are recovered during later extraction steps (see Tables II, III and IV). Unpublished data (6) indicate that less decompostion is observed when methanol cosolvent is used than when supercritical carbon dioxide alone is used, especially at lower densities of carbon dioxide. Methanol cosolvent or higher densities of carbon dioxide which result in more rapid extraction give better recoveries of DDT and less formation of DDE and other related compounds. Spiked 13C-labeled DDT was extracted in the first extraction step and no DDE formation was observed. Interactions of the more tightly bound DDT with the soil may be involved in the formation of DDE and other compounds during the extraction of aged soil.

Since DDE is also hazardous, destruction of DDT in soil with supercritical carbon dioxide would not provide adequate remediation under the conditions used for this work, but supercritical carbon dioxide does appear to be effective for the removal of DDT and related compounds from soil when suitable extraction conditions are chosen. For analytical purposes, SFE can give recoveries of DDT and related compounds that are comparable with Soxhlet results without the use of large amounts of organic solvents.

ACKNOWLEDGEMENTS

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TABLE I COMPARISON OF SOXHLET EXTRACTION RESULTS WITH SFE RESULTS BY STANDARD AND SEQUENTIAL PROCEDURES (in ug/g soil)

Compound	Soxhlet	SFE Standard	SFE Sequential
4,4 DDT	1200	1200	250
2,4 DDT	250	250	84
4,4 DDD	78	76	37
2,4 DDD	30	34	27
4,4 DDE	150	160	650
2,4 DDE	28	27	200
TOTAL	1800	1700	1300

TABLE II DDT and DDE EXTRACTED USING SEQUENTIAL EXTRACTION STEPS AT INCREASING DENSITIES FOR EACH SOIL SAMPLE (in ug/g Soil)

Step	CO_2 Density*	ml MeOH	4,4 DDT	4,4 DDE	2,4 DDT	2,4 DDE
1	.25	0	120	59	46	9
2	.25	0	11	11	8	3
3	.50	0	52	200	23	120
4	.50	0	15	140	3	37
5	.75	0	15	140	0.4	13
6	.75	0	4	21	0.2	3
7	.75	1.00	28	72	3	24
8	.75	1.00	5	2	0.2	2
9	.75	1.00	1	0.3	0.1	0.5
10	.75	1.00	0.3	0.2	0.1	0.2
TOTAL			250	650	84	200

*CO_2 Density in g/ml

TABLE III AVERAGE RATIO OF DDE TO DDT EXTRACTED DURING EACH OF FOUR REPLICATE STEPS DONE TO EACH OF SIX SOIL SAMPLES

Step	CO_2 Density*	ml MeOH	4,4 DDE / 4,4 DDT	2,4 DDE / 2,4 DDT
1	.75	1.00	.14	.11
2	.75	1.00	.12	.13
3	.75	1.00	.16	.15
4	.75	1.00	.28	.17

TABLE IV AVERAGE RATIO OF DDE TO DDT EXTRACTED AT EACH STEP OF A SEQUENTIAL EXTRACTION OF EACH OF THREE SOIL SAMPLES.

Step	CO_2 Density*	ml MeOH	4,4 DDE / 4,4 DDT	2,4 DDE / 2,4 DDT
1	.25	0	0.48	0.19
2	.25	0	1.0	0.38
3	.50	0	3.9	4.8
4	.50	0	9.1	13
5	.75	0	10	33
6	.75	0	5.9	17
7	.75	1.00	2.6	8.3
8	.75	1.00	0.45	7.1
9	.75	1.00	0.29	4.6
10	.75	1.00	0.77	1.8

*CO_2 Density in g/ml

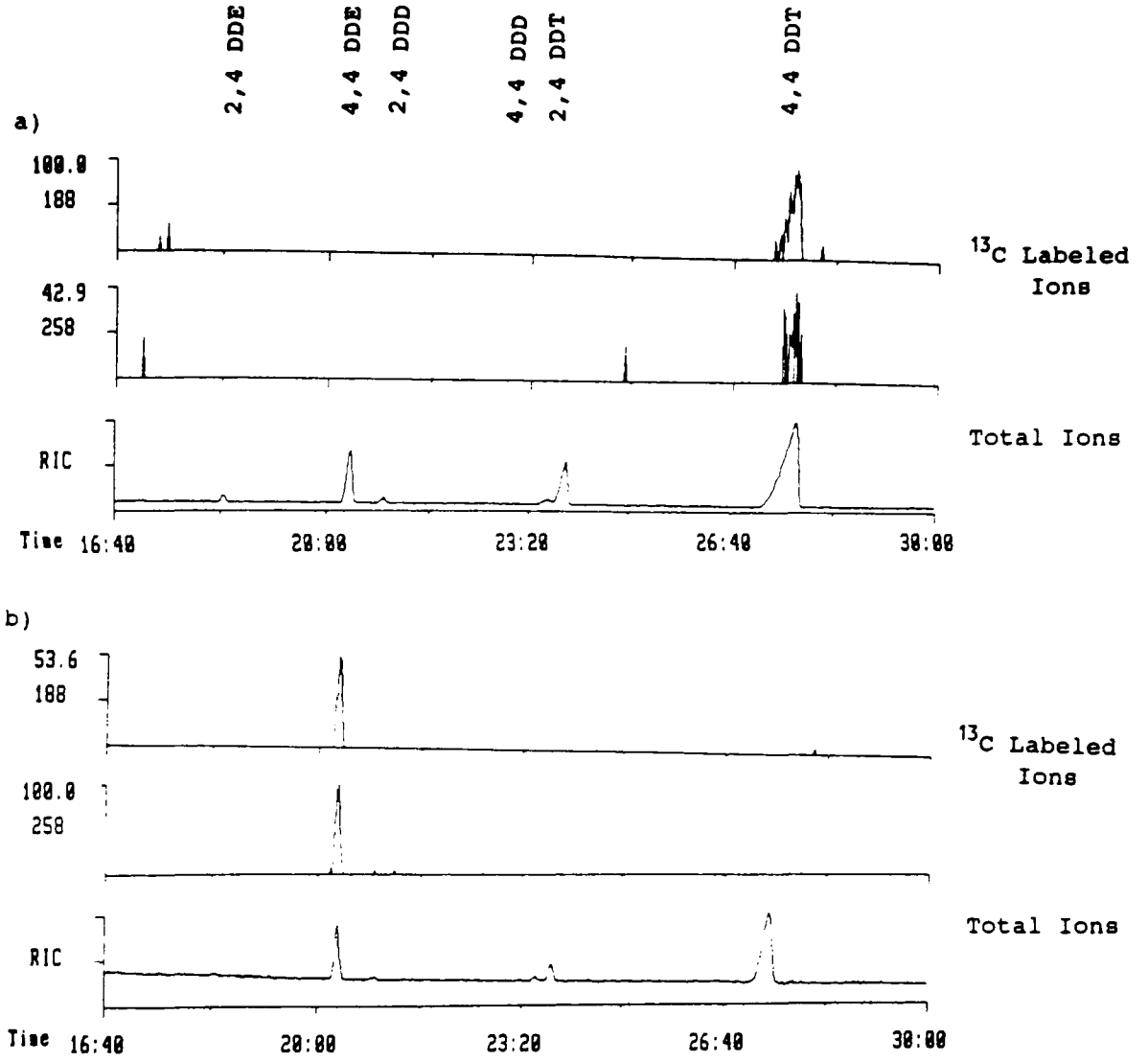

Figure I a) GC/MS of Soil Spiked with Carbon-13 Labeled DDT
b) GC/MS of Soil Spiked with Carbon-13 Labeled DDT

AIR AND GROUNDWATER

ABS, FEP, FRE AND FRP MATERIALS: ABILITY TO WITHSTAND ATTACK BY ORGANIC SOLVENTS AND SORPTION OF TRACE-LEVEL ORGANICS

L.V. Parker, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H. 03755; and T.A. Ranney, Science and Technology Corporation, Hanover, N.H. 03755.

ABSTRACT

This paper examines the suitability of four polymeric materials [acrylonitrile butadiene styrene (ABS), fluorinated ethylene propylene (FEP), fiberglass-reinforced epoxy (FRE) and fiberglass-reinforced plastic (FRP)] for potential use as well casings in ground water monitoring wells. Specifically, two of the factors that determine suitability were examined: the ability to withstand attack by organic solvents and sorption of dissolved organic solutes by the well casings. These materials are compared with two commonly used polymeric well casing materials: polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE).

These six materials were exposed to 27 neat organic solvents, one neat organic acid, and 25% solutions of hydrochloric acid and sodium hydroxide for up to 16 weeks. PTFE and FEP were not degraded by any of the organic solvents, while ABS was either dissolved or softened by almost all of the organic solvents and the neat organic acid. FRE was attacked by two organic solvents and the neat organic acid, and FRP was delaminated by eight organic solvents. PVC was dissolved by ten organic solvents and softened/swollen by a number of others.

A six-week laboratory study compared sorption of low mg/L levels of a suite of dissolved organics by these six materials. During this study ABS sorbed analytes much more rapidly and to a greater extent than the other materials, and PVC and FRE sorbed analytes the most slowly and to the least extent of the materials tested.

During this study we found an increasing number of unidentified peaks in the HPLC chromatograms of some of our samples, indicating that organic contaminants were leaching from these materials. By the end of the study (1000 hours), we had 11 additional peaks in the chromatograms of solutions exposed to ABS, 5 in those exposed to FRP, and 1 in those exposed to FRE. There were no spurious peaks in any of the chromatograms of solutions exposed to PVC, FEP and PTFE. Several of the more volatile organic contaminants that leached were identified.

ABS does not appear to be a good material for well casings used to monitor organic contaminants, while FRE looks quite promising.

INTRODUCTION

Ideally any material used as either a well casing or screen in a ground water monitoring well should retain sufficient strength once installed in the well, should resist degradation by the environment, and should not affect analyte concentrations in samples by leaching or sorbing organics or metals. Recent guidance by the U.S. Environmental Protection Agency [1] acknowledged that none of the most commonly used well casing materials in ground water monitoring [polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC) or stainless steel] can be used for all monitoring applications. PVC and especially PTFE are not strong enough to be used in the deepest of wells, and PVC and stainless steel can both be degraded by certain environments. PVC can be degraded by several neat organic solvents or by high concentrations (near solubility) of aqueous solutions of these solvents. Stainless steel will be corroded if any of the following conditions exist: low pH, high dissolved oxygen and carbon dioxide levels, or the presence of high levels of hydrogen sulfide, dissolved solids or chlorides [2, 3]. Previous studies by our laboratory [4–6] and others [7–9] have also shown that PVC, PTFE and stainless steel are not always inert with respect to sorption and leaching of analytes of interest. Specifically PVC and PTFE sorb organics, and PVC and stainless steel sorb and leach metals.

There are other materials that are being used or have been used for well casings or sampling pipe and that perhaps could be used in situations where the previous materials have proven unsatisfactory. Four such materials are acrylonitrile butadiene styrene (ABS), fluorinated ethylene propylene (FEP), fiberglass-reinforced epoxy (FRE) and fiberglass-reinforced plastic (FRP). ABS is a thermoplastic material like PVC and is a terpolymer of acrylonitrile, butadiene and styrene. FEP is a copolymer of tetrafluoroethylene and hexafluoropropylene, and because it is a fluoropolymer it is similar to PTFE in its chemical and physical properties [10]. FRE is constructed of 75% high-silica glass and 25% high-purity, closed-molecular epoxy. It is manufactured from bisphenol-A-type epoxy resins cured with methyl tetrahydrophthalic anhydride [11]. The FRP used in this study consisted of 70% fiberglass and 30% polyester resin (by weight). This study evaluated two parameters used to determine the suitability of materials for ground water monitoring: resistance to chemical attack and sorption of organic solutes from aqueous solutions.

Information on the ability of these materials to withstand chemical attack is sketchy. Most of the information we found was either provided by the manufacturer or taken from the Cole-Parmer catalog [12]. FEP, like all fluoropolymers, is reported to have excellent resistance to attack by corrosive reagents and dissolution by solvents. FRE is reported by its manufacturer to be impervious to gasoline, hydrocarbon products and most solvents and additives. While the Cole-Parmer catalog reports that "epoxy" has good resistance to fuel oils, gasoline, jet fuel and kerosene, it also reports that it is moderately affected by several ketones and is severely degraded by

dichloroethane, dimethylformamide, benzaldehyde and others. Although the Cole-Parmer catalog does not give any details on the type of "epoxy" tested, we suspect that FRE casings will be attacked by the same organic solvents that are reported to attack "epoxy." According to the same source [12], ABS is severely degraded by a number of organic chemicals, including several ketones, chlorinated alkanes and alkenes, and several hydrocarbons such as fuel oils, gasoline and kerosene. Again, there is no detail on the type of ABS material tested. The manufacturer of the FRP casings claims that their product is resistant to corrosion but makes no claims about its resistance to solvents. Thus, it appears that between ABS, FEP and FRE, FEP will be the most resistant polymer to degradation and ABS will be the least resistant.

We found only two studies on the sorption of organic solutes from aqueous solutions by these materials. Gillham and O'Hannesin [8] conducted a study that compared sorption of ppb-levels of six (mono)aromatic hydrocarbons by FRE, SS, PTFE, polyethylene (PE) and rigid and flexible PVC (RPVC and FPVC, respectively). They ranked the sorptiveness of the materials as (going from most sorptive to least): FPVC > PE > PTFE > FRE > RPVC > SS. Jones and Miller [13] also compared sorption of a number of organics from aqueous solution by SS, (rigid) PVC, ABS, FEP, PTFE and polyvinylidene fluoride (PVDF). However, it is not clear what caused the losses they observed since no biocide was added to prevent biological loss and there did not appear to be any controls that losses could be compared with.

MATERIALS AND METHODS

Six materials were selected for these studies: ABS, FEP, FRE, FRP, PVC and PTFE. PVC and PTFE were included so that comparisons could be made with these commonly used materials. Five-cm- (2-in.-) diameter well casing or pipe were used in these studies. For PVC, PTFE, FEP and FRE, we used well casings manufactured specifically for ground water monitoring. We were not able to find a manufacturer that made FEP well casings but did find one that made "pipe for sampling ground water." Since the manufacturers of ABS well casings have gone out of business, we purchased waste and vent pipe. Special care was taken to eliminate contamination from grease or oil during the cutting process. All the cut pieces were washed with detergent and deionized water as described by Ranney and arker [14, 15]. All the studies were conducted at room temperature.

Chemical Attack Study: Test coupons measuring approximately 1-cm^2 were cut from each type of material. The cutting process fractured some of the edges of the two fiberglass materials, and therefore an effort was made to select only those coupons showing little or no fracturing along the edges.

Each coupon was weighed and placed in a 22-mL borosilicate glass vial. Twenty-eight neat organic compounds (including one organic acid), a 25% hydrochloric acid solution, and a 25% sodium hydroxide solution were used in this study (Table 1).

Table 1. Percent weight gain (or loss) of materials after 112 days of chemical exposure.*

Chemical	*PTFE*	*FEP*	*FRE*	*FRP*	*PVC*	*ABS*
Acetic acid (glacial)	0.4	0.3	R†	1.5	0.4	76.8s
Acetone	0.3	0.2	2.7	5.6	157.8s	D
Benzaldehyde	0.0	0.0	0.3	1.3	D	D
Benzene	0.4	0.3	0.0	0.8	48.7s	D
Benzyl alcohol	0.0	0.0	0.1	0.5	0.1	D
Bromochloromethane	0.7	0.6	26.2	L	D	D
N-butylamine	0.2	0.1	R	L	D	D
Carbon tetrachloride	0.6	0.4	0.0	0.2	0.1	317.2s
Chlorobenzene	0.3	0.3	0.2	7.8	159.8s	D
Chloroform	1.0	0.8	7.3	L	223.9s	D
Cyclohexanone	0.0	0.0	–0.1	0.1	D	D
1,2-dichlorobenzene	0.2	0.1	0.1	1.1	217.7s	D
1,2-dichloroethane	0.4	0.3	3.1	L	D	D
trans-1,2-dichloroethylene	1.4	1.2	8.1	L	56.3s	D
Diethylamine	0.5	0.3	2.0	3.5	31.8s	112.8s
Dimethylformamide	0.0	0.1	R	8.3	D	D
Gasoline (93 octane, unleaded)	0.3	0.2	–0.1	0.1	0.1	61.9s
Hexane	0.4	0.2	–0.1	0.0	–0.1	15.1
Hydrochloric acid (25% w/v)	0.0	0.0	–4.7	–5.0	0.3	1.2
Kerosene (K-1)	0.0	0.0	0.0	0.2	0.0	8.9
Methyl alcohol	0.0	0.0	7.7	1.9	0.4	27.8
Methyl ethyl ketone	0.3	0.2	3.0	4.8	D	D
Methylene chloride	0.9	0.8	15.6	L	D	D
Nitrobenzene	0.1	0.0	0.4	1.0	D	D
Sodium hydroxide (25% w/v)	0.0	0.1	0.2	1.5	0.1	0.9
Tetrachloroethylene	0.9	0.6	0.0	0.5	1.7	251.2s
Tetrahydrofuran	0.3	0.3	3.3	L	D	D
Toluene	0.2	0.2	0.0	0.9	51.4s	D
Trichloroethylene	1.3	1.1	0.3	L	70.9s	D
o-xylene	0.1	0.1	-0.1	0.2	65.7s	D

* For most materials, degradation (R,L,D,s) occurred before the 112-day sampling time.
†R: resin came off coupon
L: fiberglass sheets delaminated
D: dissolved or so soft material broke up on handling
s: material swollen and/or softened

Most but not all of the test compounds were EPA priority pollutants. Five mL of the test chemical was added to each vial, and the vial was closed with a Teflon-lined screw cap. There were no replicates in this study. There were seven sampling times: 1, 7, 14, 21, 28, 56 and 112 days. On the day of sampling, each coupon was removed from the vial, blotted dry on a paper towel, and air dried for one minute prior to being weighed, as described by Ranney and Parker [15]. Softening was determined

by trying to indent the coupon using forceps. After the weights were taken and all other observations were made, the coupon was returned to its vial and recapped.

Sorption of Organics Study: This experiment investigated sorption of 11 organic solutes: cis-1,2-dichloroethylene (CDCE), trans-1,2-dichloroethylene (TDCE), benzene (BENZ), *m*-nitrotoluene (MNT), trichloroethylene (TCE), chlorobenzene (CLB), *o*-dichlorobenzene (ODCB), *o*-xylene (OXYL), *p*-dichlorobenzene (PDCB), *m*-xylene (MXYL) and tetrachloroethylene (perchloroethylene or PCE). The test solutions were prepared by adding each of the neat organics directly to well water in glass volumetric flasks as described by Ranney and Parker [14]. Forty mg/L of $HgCl_2$ was added to the test solutions to prevent biological losses of the organics. Initial concentrations of analytes varied from 1 to 2 mg/L except for BENZ, which had a concentration of approximately 0.5 mg/L.

Two pieces of one type of casing material were placed in individual 40-mL borosilicate glass vials. The vials were filled with aqueous test solution so that there was no headspace and capped with Teflon-lined plastic caps. Vials with test solution but no casing material served as controls. These controls allowed us to correct for any effects that might be due to the vials or caps. The ratio of material surface area to solution volume was 0.79 cm^2/mL, which is typical for a 2-in.-diameter well. Separate vials were used for each sampling event so that the test solution could be discarded after sampling. For each material and time, there were three replicates. The vials were filled randomly in sets of seven, with each vial containing one of the six materials or empty (the controls). The samples were kept in the dark for: 1 hr, 8 hr, 24 hr (1 day), 72 hr (3 days), 168 hr (1 week), 500 hr (3 weeks) and 1000 hr (6 weeks).

For analysis of each sample, a small aliquot of solution was transferred (using a glass Pasteur pipet) to an autosampler vial (1.8 mL), which was (gently) filled so there was no headspace and then capped. Teflon-backed silicone septa were used in the autosampler vial caps. Analytical determinations of the organic solute concentrations were by reversed-phase high-performance liquid chromatography (RP-HPLC). A modular system was employed that consisted of a Spectra Physics SP 8810 isocratic pump, a Spectra Physics SP 8490 variable-wavelength UV detector set at 210 nm, a Spectra Physics SP 8875 autosampler with a 100-μL injection loop, and a Hewlett-Packard 3396 series II digital integrator. Separations were obtained on a 25-cm × 4.6-mm (5 μm) LC-18 column (Supelco) eluted with 62/38 (v/v) methanol/water at 1.5 mL/min. The detector response was obtained from the digital integrator operating in the peak height mode. Retention times of the analytes ranged from 4.0 to 16.3 min. Analytical details can be found in Ranney and Parker [14].

Leaching of Contaminants Studies: When we compared the chromatograms of samples exposed to the casings with those for the control samples, we saw additional peaks in some of the samples. Thus, we decided to analyze the 1000-hour samples using purge-and-trap GC/MS to determine the identity of at least some of

these peaks. For these analyses, EPA method 8240 for volatile organics by GC/MS [16] was used. The PT/GC/MS system consisted of a Tekmar LSC-2 liquid sample concentrator, a Hewlett Packard 5890 series II gas chromatograph, and a Hewlett Packard 5970 series mass selective detector. One sample for each type of material plus a control sample were analyzed.

To confirm that the organics we had found in the test solutions resulted from leaching from the casing materials, we placed two pieces of the cleaned casing material (the same size as used previously) in 40-mL glass vials. These vials were then filled with the well water that contained 40 mg/L of $HgCl_2$ to prevent any biological activity. These samples were analyzed after approximately 500 hours of contact time, using the same method as described previously. We tested only those materials that had leached contaminants in the previous study (ABS, FRE, FRP) and a blank (water only); there were no replicates in this study.

RESULTS AND DISCUSSION

Chemical Attack Study: Table 1 shows which samples were degraded by chemical exposure and the final percent weight gain for those samples that were not destroyed. Although both fluoropolymers, PTFE and FEP, are generally recognized as being inert to chemical attack, there were slight (1%) weight gains in samples exposed to five chlorinated organic solvents by the end of the study. The weight gains were slightly lower in the FEP samples than in the PTFE. There were no apparent signs of softening, swelling or decrease in strength in any of these the FEP or PTFE samples.

The FRE well casing material had a glossy external surface and a dull internal surface. The external surface of these samples flaked when exposed to three chemicals (N-butylamine, acetic acid and dimethylformamide), although these particles did not subsequently dissolve. These samples appeared to remain strong, and no further observations were made on them. Thirteen samples had weight gains exceeding 1%; the samples exposed to bromochloromethane (26.2%) and methylene chloride (15.6%) had the largest weight gains. The sample exposed to the hydrocholoric acid solution had a slight weight loss (~5%). None of the FRE coupons appeared to swell or soften, even the sample with the 26% weight gain. Some fraying of the edges was observed on some coupons, but it is not clear whether this was due to exposure to the chemicals or due to handling.

FRP was more severely degraded than the previous materials. Eight chemicals delaminated it, i.e. the fiberglass sheets separated. This occurred within the first 1–4 weeks and for one chemical within the first 24 hours. The samples that were delaminated more slowly had weight gains of ~1–16% and showed signs of swelling (i.e. liquid could be squeezed out of the material) prior to the sheets separating. Eleven other chemicals caused weight gains of 1–10%, although there were no signs

of swelling or softening. Again, some of the coupons showed frayed edges, although this may have resulted from handling and not chemical exposure. As with FRE the hydrochloric acid solution caused a slight loss in weight (5%).

PVC appears to be much more readily degraded than the previous materials. By the end of the study, ten chemicals dissolved or so softened PVC that the test piece could not be weighed because it fell apart. Four of the chemicals had this effect within the first day. Twelve other chemicals appeared to soften PVC, and for seven of those chemicals, weight gains exceeded 100%. Squeezing the swollen coupons forced out some of the liquid. Only 9 of the 30 chemicals used in this study had little or no effect on PVC. These chemicals were glacial acetic acid, the acid and hydroxide solutions, alcohols, hydrocarbons (gasoline, hexane and kerosene) and carbon tetrachloride.

ABS was by far the most readily degraded polymer tested. After only one day of exposure, 19 of the 30 chemicals evaluated either dissolved ABS or softened it to the point where it fell apart. Four other chemicals caused degradation (i.e. swelling and/or softening) of the coupon on the first day. By the end of the study, only the acid and hydroxide solutions had little effect (~1% weight gain). Clearly ABS is a poor choice where exposure to neat organic solvents may be involved.

Generally where comparisons could be made, we had good agreement between our results and those given by Cole-Parmer. This was especially true for the PTFE and the ABS. (There were no listings for FEP or FRP.) The largest disparity is between their ratings for "epoxy" and our findings for FRE. For FRE we would change the ratings for 11 of the 30 chemicals tested. The differences between "epoxy" and FRE most likely accounts for these differences.

We would rank the materials used in this study, from greatest to least resistance, as: FEP = PTFE > FRE > FRP > PVC > ABS. This ranking should be used only as a general guide, not as a rule. For chemicals that haven't been tested, we suggest testing them with the casing material, especially ABS, FRE, FRP and PVC.

Sorption of Organics: Figures 1–4 show the losses of CDCE, TDCE, TCE and PCE and are fairly typical for the losses we observed. The complete results are presented elsewhere [14]. Generally we found that 1) ABS always sorbed analytes the most rapidly and to the greatest extent of all the materials tested; 2) PVC and FRE sorbed analytes the most slowly and to the least extent; and 3) neither PTFE, FEP nor FRP performed consistently better than the others. The data are summarized in Table 2, which shows the first sample time where a 10% loss in analyte concentrations were observed. For several organics, 10% losses were observed in 8–24 hours for PTFE, FEP and FRP, and in 1–8 hours for ABS. This was not the case for PVC and FRE. For PVC the earliest a 10% loss was first observed was 500 hours, and for FRE the earliest a 10% loss was observed was 72 hours. Losses of some compounds never reached 10%; this is especially true for FRE and PVC.

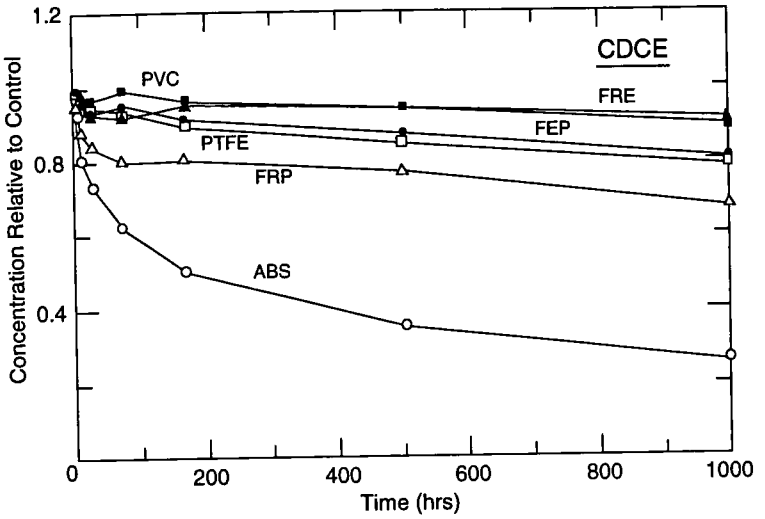

Figure 1. Sorption of CDCE.

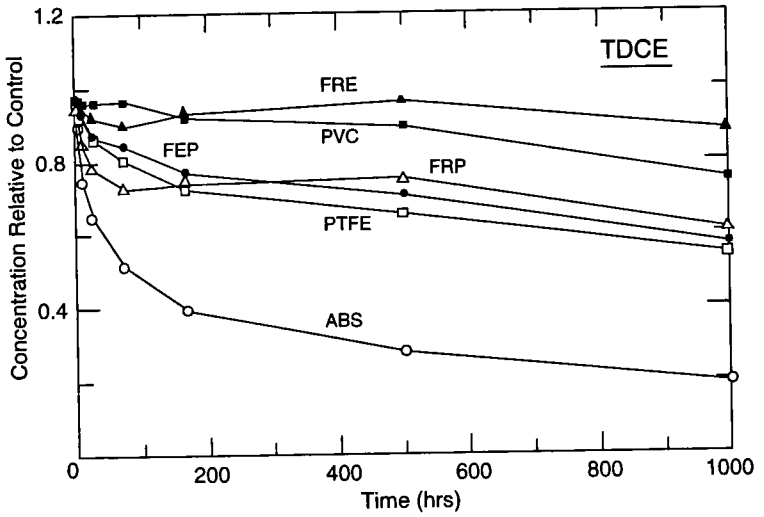

Figure 2. Sorption of TDCE.

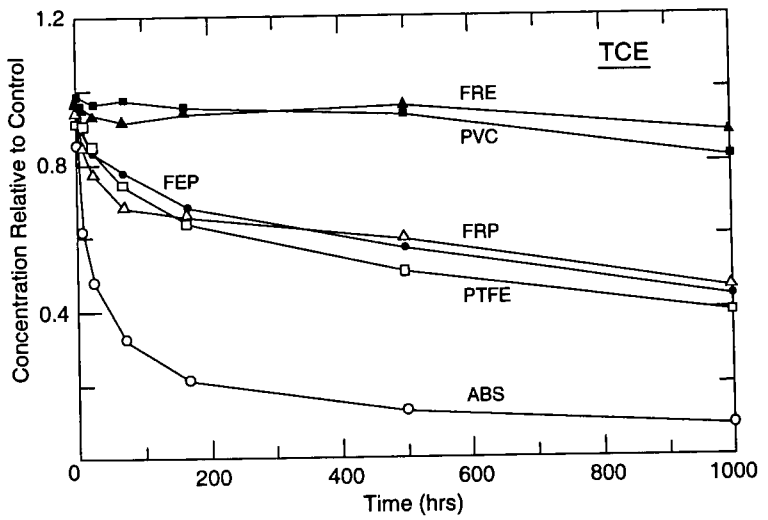

Figure 3. Sorption of TCE.

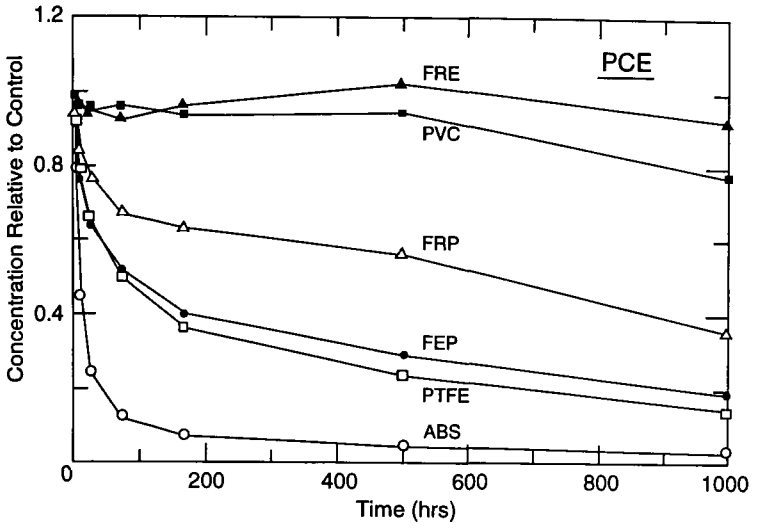

Figure 4. Sorption of PCE.

Our results generally agree well with those of Gillham and O'Hannesin [8] except that they found that the rate and extent of sorption of the compounds they tested [(mono)aromatic hydrocarbons] were always greater for FRE than for PVC. Generally we did not find this to be the case in our study. By the end of the study, we found no significant difference between PVC and FRE samples exposed to two of the same three compounds tested by Gillham and O'Hannesin [8]. Since both studies used a constant surface-area/solution-volume ratio (which differed between the two studies), we suspect that the reason their results differed some from ours is because they tested materials other than well casings; they tested FRE tubing and PVC pipe. The composition and densities of these materials may be quite different.

Leaching of Contaminants: When we examined the HPLC chromatograms, we saw additional peaks in some of the samples when compared with the control samples. By the end of the study, there were additional peaks in the chromatograms for the ABS, FRE and FRP samples but not for the FEP, PTFE and PVC samples (Fig. 5). These results agree reasonably well with what we found when we reviewed the

Table 2. Sampling time (hours) when material sorbed 10% or greater analyte.

Material	*CDCE*	*TDCE*	*TCE*	*PCE*	*BENZ*	*CLB*	*ODCB*	*PDCB*	*OXYL*	*MXYL*	*MNT*
PVC	1000	500	1000	1000	NL*	1000	1000	500	NL	1000	NL
PTFE	168	24	8	8	168	24	24	8	24	8	1000
FEP500	24	8	1	168	24	8	8	24	8	NL	
ABS	8	1	1	1	8	1	1	1	1	1	8
FRE	NL	72†	1000	NL	NL	1000	1000	72	NL	NL	NL
FRP	8	8	8	8	24	8	8	8	24	8	72

* NL: Never lost 10% by the end of the study.
† Subsequently, losses were only 7 and 4% at 168 and 500 hr, respectively.

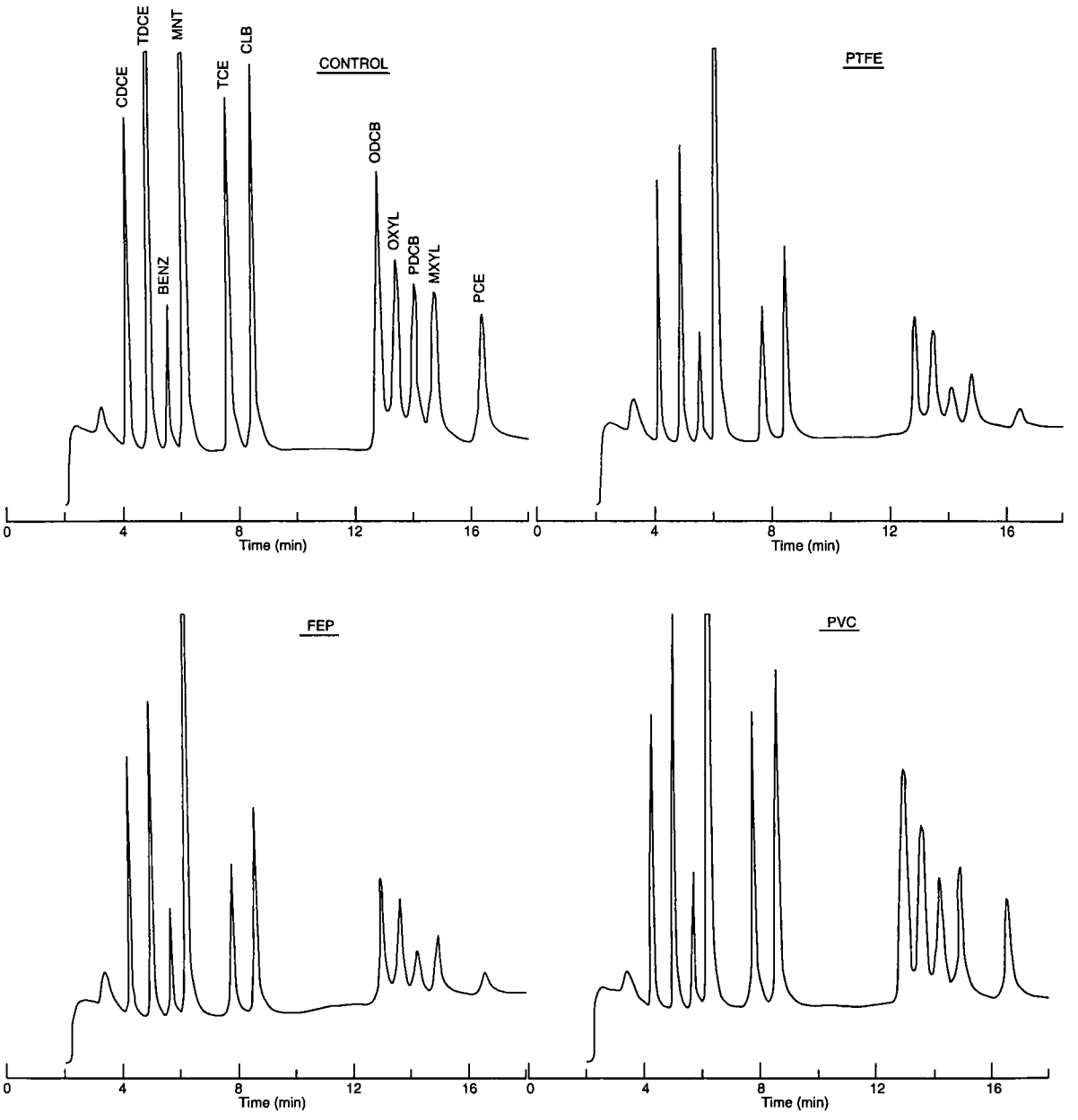

Figure 5. HPLC Chromatograms for 1000-hour samples: a. Control, b. PTFE, c. FEP, d. PVC.

literature on leaching of organic contaminants from these materials. Several studies [17, 18] have shown that PTFE leaches relatively few organic impurities. Presumably FEP would behave similarly to PTFE. Leaching of organics from PVC has been found to be considerably less problematic for rigid PVC, such as pipes and casings, than for flexible tubing [17]. This is mainly because rigid PVC products contain almost no plasticizers (<0.01%) [19].

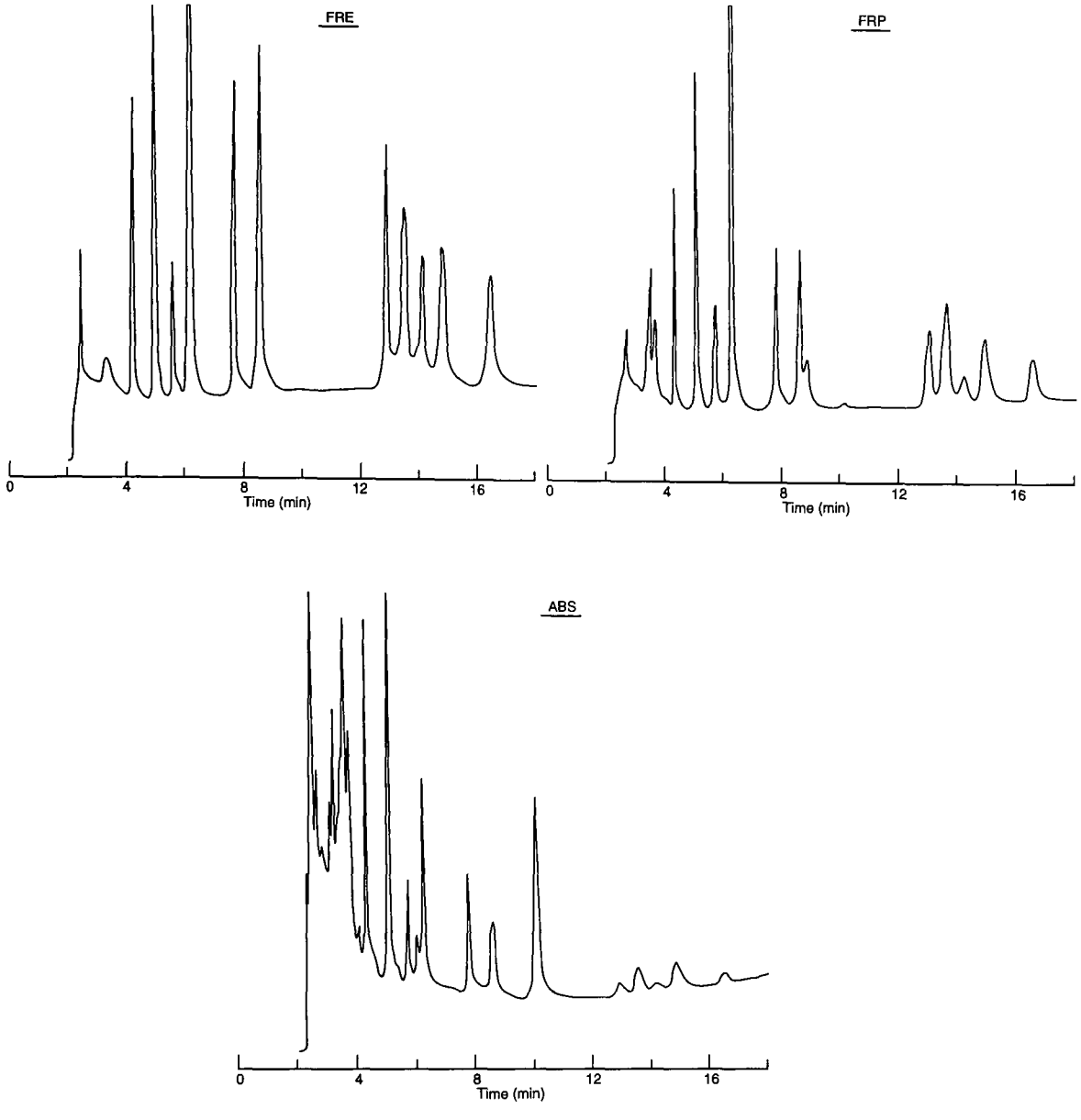

Figure 5. HPLC Chromatograms for 1000-hour samples: e. FRE, f. FRP, g. ABS.

The ABS samples appeared to leach the most contaminants since these samples had the most additional peaks in their RP-HPLC chromatograms. The RP-HPLC chromatogram for the last (1000-hour) samples had 11 additional peaks (Fig. 5g). However, even the one-hour samples had one extra peak, and the size of these peaks increased as time continued [14]. The chromatograms for the FRP solutions had one additional peak after 72 hours [14] and five additional peaks by the end of the study

(Fig. 5f). There was only one additional peak in the chromatograms for the FRE samples (Fig. 5e); this peak first appeared in the 72-hour samples [14]. With both of the FRE and FRP samples, the size of the peaks increased as time continued.

To determine the identity of at least some of these peaks, we analyzed the 1000-hour samples by purge-and-trap GC/MS. When we ran the ABS sample, we observed six peaks and were able to identify four of them. This sample contained acrylonitrile and styrene (two of the three components of ABS), chloroform and ethylbenzene (which is an intermediate in the production of styrene). The concentrations of these compounds in this sample were quite low (<10 mg/L). The other peaks that we had observed previously in the HPLC chromatograms apparently were due to the presence of either nonvolatile or semivolatile organics or inorganic compounds (e.g. metal salts). We only found one peak when we ran the FRP sample, and this was determined to be toluene (which may be used as a solvent or degreaser in the production of FRP). The concentration of the toluene was approximately 100 mg/L. Again, the other four peaks that we observed previously in the HPLC chromatograms may be due to the presence of either nonvolatile or semivolatile organics or inorganic compounds. The one peak we observed in the HPLC chromatograms for the FRE samples is apparently not a volatile organic, since we did not observe any peaks in the chromatograms for the purge-and-trap GC/MS analyses of these samples. These results agree well with those of Cowgill [11], who tested intact FRE well casings and a ground powder of these casings for leaching of any substance involved in its manufacture and EPA priority pollutants. Low levels of diethylphthalate and bisphenol A leached from the powdered well casings after three weeks but not from intact well casing. Cowgill noted that bisphenol A is a component of manufacture, and diethylphthalate is a commonly used plasticizer.

When we conducted a leaching study to confirm that the substances we found in the previous samples had leached from the casing material, we found essentially the same analytes in these samples as we did previously. We were able to identify two of five peaks we found in the chromatograms of ABS leachate: ethylbenzene and styrene. We did not find any spurious peaks in the FRE leachate sample. For the FRP leachate samples, we found five peaks and were able to identify three of them. In addition to finding toluene again, we also found 1,1,1-trichloroethane and ethylbenzene. (This particular sample was run twice with similar results.) These solvents may be used in either the manufacture of this product or cleaning some of the equipment used in its manufacture.

With respect to leaching of contaminants, our results agree well with what is found in the literature for FRE, FEP, PTFE and PVC. As expected, FEP and PTFE performed similarly and did not appear to leach any contaminants. FRE appeared to leach only one compound; most likely this is the same component (bisphenol A) Cowgill [11]

observed leaching from ground FRE casing. Given that we used a waste and vent ABS pipe rather than well casing manufactured for monitoring ground water, it is not surprising that we found a number of contaminants leaching from this product.

CONCLUSIONS

Based on the results from these studies and others, it appears that FRE would be an excellent material to be used for monitoring organics. It is relatively nonsorptive of organic solutes from aqueous solutions, appears to leach few organic contaminants, and is relatively inert to chemical attack (more so than PVC). FEP is inert to chemical attack and does not appear to leach any organic contaminants. However, it is relatively more sorptive of organic solutes than PVC and FRE. It does not appear to offer any clear advantage or disadvantage over PTFE at this time. FRP leaches several contaminants and is relatively sorptive of organics, but it is relatively resistant to degradation by organic solvents. By far, ABS appears to be the poorest choice of a material for monitoring organics. It is degraded by a large number of organic solvents, sorbs organics very rapidly, and leaches a number of contaminants. However, while we feel this material would not be a good casing material, we realize we tested waste and vent pipe rather than well casings and that quality well casings may provide better performance, especially with respect to leaching. Since ABS well casings are not available at this time, we do not see any point testing these materials further. We also realize that those materials that initially sorb organics rapidly (FEP, FRP and ABS) would eventually reach equilibrium and sorption would then be less of a problem, depending upon how the sample was taken. Although, desorption of sorbed analytes could also possibly be a problem for these materials if ground water quality were to improve.

Our lab is currently evaluating FRE, FRP and FEP casings with respect to sorption and leaching of metals. This information will allow us to better determine the overall suitability of these materials.

ACKNOWLEDGMENTS

We thank Martin H. Stutz, Project Monitor, and the U.S. Army Environmental Center (USAEC, formerly USATHAMA), Aberdeen Proving Ground, Maryland, for their support of this work. We also thank Dr. Thomas Jenkins and James Cragin, CRREL, for their technical reviews of this manuscript.

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SAMPLING AND ANALYTICAL METHODS FOR HOUSE DUST AND DERMAL EXPOSURE

J. P. Hsu, Paul Geno, Tapan Majumdar and David Camann, Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78228

ABSTRACT

The indoor exposure to pesticides and polynuclear aromatics is becoming important issue. Pesticides and polynuclear aromatic hydrocarbons are usually present in both house dust and air. There is a strong correlation between the pesticide levels in house dust and air. Due to complex matrix of house dust, it present a challenging problems for chemical analysis. The house dust is sampled from carpet using a validated HVS3 (high Volume, Small, Surface Sampler). However, dermal sampling is also quite important since infants and toddlers have more frequent floor contact since crawling around floor or carpet and hand-to-mouth behavior. The dermal sampling is performed by using a PUF roller, which is developed by Southwest Research Institute. The dust samples will be extracted, clean-up and analyzed by GC/MS in single ion monitoring mode for the target compounds listed in Table 1.

Table 1 Target Compound List

Alachlor	Aldrin	Atrazine	Bendiocarb
Captan	Carbaryl	α-Chlordane	γ-Chlordane
Chlorothalonil	Chlorpyrifos	Dacthal	p,p'-DDE
p,p'-DDT	Diazinon	Dichlorvos	Dicofol
Dieldrin	Folpet	Heptachlor	Hexachlorobenzene
Lindane	Malathion	Methoxychlor	*cis/trans*-Permethrin
Propoxur	*o*-Phenylphenol		Resmethrin
Benz(a)anthracene		Benzo(g,h,i)perylene	
Benzo(a)pyrene		Benzo(b)fluoranthene	
Benzo(k)fluoranthene		Coronene	
(-)Cotinine			

CO_2 MANAGEMENT FOR TO-14 ANALYSES USING A CONTROLLED DESORPTION TRAP (CDT)

R. Jesser and S. Reiss Graseby Nutech, RTP, NC 27703-9000

Large quantities of CO_2 injected onto capillary columns can complicate the quantitation and identification of closely eluting components by GC or GC/MS. Normally, the 330ppm CO_2 in ambient air presents no significant problem for analyzing the trace Volatile Organic Compounds (VOCs) in EPA Method TO-14. However, bioremediation approaches to environmental cleanup can increase CO_2 levels by more than 100 times. In addition, source sites and sealed systems can also contain extreme levels of CO_2. Consequently, the need has arisen for CO_2 management in whole air methodology.

TO-14 suggests a Nafion® dryer for water management. Alternate approaches must be employed when quantitating water soluble compounds under TO-14 protocol. This paper will describe a modification of a water management technique employed with TO-14 protocol for water soluble compounds. Data will be presented showing that sample recoveries and Relative Standard Deviations (RSDs) are good. This CDT approach can lend itself to a wide variety of sample matrices.

STATUS AND NEED FOR FUEL TOXICITY CHARACTERISTICS LEACHING PROCEDURES (TCLP)

Ajmal M. Ilias, Chemist, and George J. Medina, Chemist, U.S. Army Corps of Engineers, North Pacific Division Laboratory, 1491 N.W. Graham Ave., Troutdale, Oregon, 97060.

ABSTRACT

Approximately fifty targeted analytes of volatiles, semi-volatiles and metals have been included under the Toxicity Characteristics Leaching Procedure (TCLP) extraction procedure. Studies on the extraction and leaching potential for petroleum hydrocarbon fuels have not been formally investigated and published. It has been noted that an acidified (HCL) TCLP extraction using semi-volatile organic procedures, followed by methylene chloride extraction, has yielded substantial levels of hydrocarbon fuel but significantly less than the conventional total soil extraction procedure using sonication or soxhlet techniques with freon or methylene chloride solvents. Higher levels of fuels, such as kerosene or diesel fuel No. 6 were found when water samples were subjected to TCLP condition compared to the conventional EPA 3510 extraction without acidification. Advantages to fuel leaching potential in soil (in particular landfill disposal and underground storage tank sites) using this proposed TCLP procedure, coupled with the Corps of Engineers Fuel Identification and Quantitation Method (FIQ) will be discussed.

INTRODUCTION

Currently, the U.S. EPA has relinquished the underground storage tank (UST) authority and responsibility to the states for issuing permits, inspection and determining mandatory cleanup of fuel/oil contamination in the environment. It is estimated that over a million leaking USTs have been excavated. Evidence of leakage in the form of contaminated soil have been found with up to 100 ppm of gasoline, and 200 ppm of diesel, including lubricating oil. In certain states, this may trigger clean-up action procedures. Because of the loosely regulated guidelines, the cost impact on small businesses and gas stations (many of which are independently owned) has been so dramatic, many have been forced to close in the State of Oregon alone. It is suggested that if the EPA, state or both agencies would jointly regulate fuel contamination and remediation criteria on the basis of TCLP, many of the storage sites may not need remediation or clean up. Small businesses, which are going out of business due to non-compliance may not need to close, if regulated under the proposed TCLP (1) guidelines.

Presently, no guideline for fuel TCLP is established but about one half of the targeted analytes are components of fuel. If the sum of critical components of fuel compounds are added, it is estimated that a maximum level of 10 ppm would not be exceeded for fuels in the soils. This could serve as liberal but realistic guideline. Utilizing

this "cut-off" standard may save billions of dollars and an untold number of jobs from unnecessary UST Tank removal, servicing or expensive remediation.

EXPERIMENTAL DATA

Fuel contaminated soil samples were extracted using EPA TCLP Method 1311. The TCLP extracts were re-extracted with methylene chloride and analyzed for diesel range organics DRO (2) and total recoverable petroleum hydrocarbons as diesel, TPH-D (3), with the use of a gas chromatograph equiped with a flame ionization detector (FID). These two methods are modified methods derived from EPA Method 8100 (4). The TCLP extracts were also re-extracted with freon 13 (trichloro, trifluoro ethane) for TRPH analysis using EPA Method 418.1 (5). For the purposes of control, a split of the soil sample was subjected to TCLP and was extracted using methylene chloride. The other split was subjected to sonication/extraction technique, Method 3550 (6) and subsequently analyzing for TRPH using EPA Method 418.1.

Water samples were split. One of the splits was non-acidified and extracted, following the protocols of EPA 3510 (7) and analyzed for various fuels using Army Corps of Engineers Fuel Identification and Quantitation procedure, FIQ (8). The other split was acidified, following TCLP protocols. The TCLP extract was re-extracted with methylene chloride (EPA 3510) and also analyzed using the FIQ procedure. Details are presented in Table 3.

RESULTS AND DISCUSSION

Table 1 details the TPH-D results of fuel contaminated soil samples obtained from an UST/landfill site using TCLP extraction and total extraction (EPA 3550). No TCLP TPH-D were detected between the concentrations of 0.05 through 5.0 parts per million (ppm) in the extract fraction subjected to TCLP and re-extraction with methylene chloride, indicating no fuel leachability. TPH-D was found in the same samples which were directly extracted with methylene chloride using EPA method 3550. The concentrations ranged between the detection limit of 1 ppm through 2300 ppm.

Table 2 presents data comparison of soil samples subjected to TCLP/methylene chloride re-extraction (EPA 3510) and classically extracted with using EPA Method 3550 (sonication), followed with GC/FID analysis for DRO. Inclusive in Table 2 are data of the same samples, sonicated extracted and analyzed for TRPH (EPA 418.1), using an infra-red spectrophotometer (IR). The average recovery of TCLP/methylene chloride extraction and analyses for DRO is 0.805 ppm. The average recovery of straight soil sonication extraction and analyses for DRO is 782 ppm. The average recovery of TRPH is 2165. The State of Alaska's regulatory clean-up level III for DRO and TRPH are 1000 and 2000 ppm, respectively. Both, the straight sonication/extraction analysis using a GC/FID for DRO and IR method of analysis for TRPH provide data that are close to the State of Alaska's

regulatory clean-up levels. Since no guidelines have been established for fuel TCLP, data generated by TCLP for DRO may not trigger clean-up action.

Table 3 describes the result of fuels where water samples were subjected to TCLP conditions. The TCLP extract was re-extracted with methylene chloride using EPA method 3510. Splits of the samples were also extracted without TCLP treatment. Both methylene chloride extracts were analyzed using Army Corps of Engineers Fuel Identification and Quantitation procedure (8). Recovery of gasoline was about one third less after TCLP than the conventional extraction and analysis. However, concentration of kerosene and bunker C fuel were greater after TCLP extraction, indicating, perhaps, that the acidified water matrix yields more fuel, contrary to the non-acidified extracted water samples. Low gasoline recoveries levels found in the TCLP treatment are probably due, in part, to volatilization during the filtration process. Loss may be minimized if zero head space TCLP extraction is employed.

CONCLUSION AND RECOMMENDATIONS

If we are to accept the premises that TCLP simulates field leaching trends, coupled with the data presented, it is permissible to assume that TPH-D does not leach out in any appreciable amounts. No leachable TPH-D was evident after the leachate was subjected to re-extraction with methylene chloride (Table 1). Consequently, no remidiation would be warranted. Following the normally prescribed methodologies, based on the state of Alaska's clean-up levels, the location in question could conceivably require stringent monitoring and/or remediation. Less than 1 ppm of TCLP DRO was found in the samples of Table 2, indicating non-leachable fuel contamination.

With the exception of low boiling fuels, such as gasoline, water samples subjected to TCLP conditions, meaning filtration and a lower pH, yielded higher recovery concentrations of kerosene and heavier fuels (Table 3). The results suggest the need to modify the extraction procedure currently being used (EPA 3510) in order to maximize fuel recoveries; in particular at low levels.

Soil samples (as well as waste and water samples) subjected to a TCLP (semi volatiles) extraction procedure will undergo loss of low boiling fuel compounds. To avoid the loss of these low boiling compounds, the use of zero head space TCLP procedures are recommended. Following zero head space extraction, the use of a purge and trap/GC-FID analyses or the FIQ method of analysis with a GC-FID is recommended (see figure 1). The FIQ method may be developed to classify and quantitate low boiling fuels such as gasoline, certain jet and kerosene, mineral spirit, naphtha, etc. (Figure 1). The advantage of TCLP extraction and application of the FIQ method is the potential for analysis of a broad range of fuels, i.e., from gasoline through heavy lubricant oils.

Without the implementation of more realistic criteria to evaluate clean-up levels for fuel contaminated sites, many small businesses, such as local gasoline stations may have to suffer from the expensive repair or remediation based on data that may erroneously provide evidence of leachable fuels. Similarly, costly corrective action to landfills such as the placement of dikes or liners may not be required. The presented data is far from being conclusive. More controlled studies are required. However, the data clearly suggests that there is room for the investigation into fuel migration in soil, the use of TCLP to evaluate contaminated soil leachability and the implementation of more realistic clean-up level criteria.

ACKNOWLEDGMENTS

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Figure 1

Flow Diagram for Soil
Fuel TCLP
and Analyses

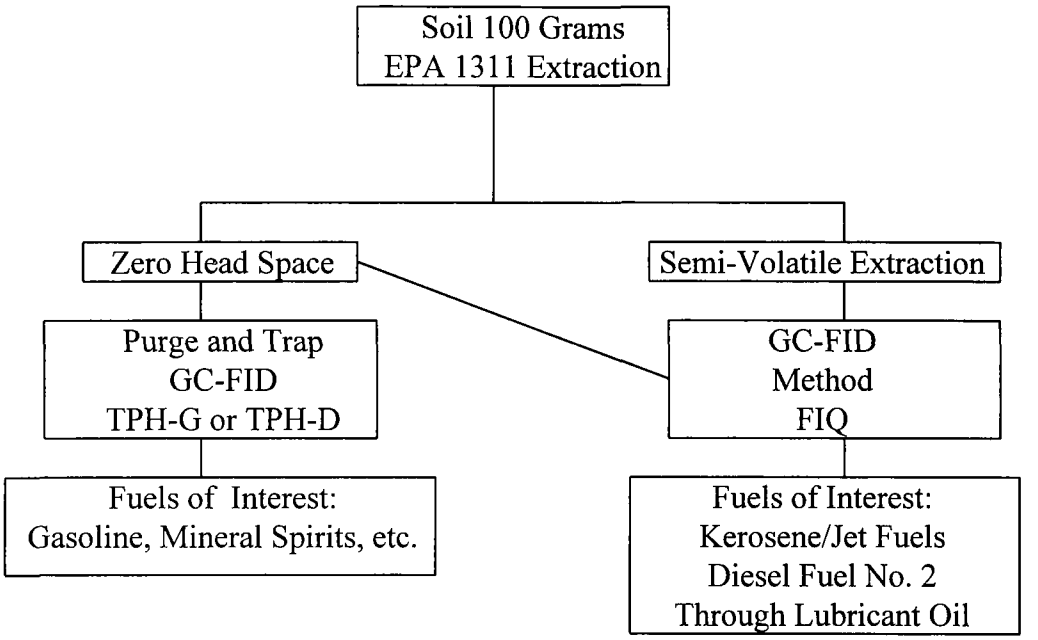

Table 3: Comparison of analysis data of fuel contaminated water using TCLP extraction procedures (EPA 1311) followed by re-extraction of the extract with methylene chloride and water extracted using EPA Method 3510 utilizing a GC-FID.

Fuel Detected	TCLP(EPA 1311) with EPA 3510 RE-EXTRACTION GC-FIQ Result mg/l	WATER EXTRACTED / EPA 3510 GC-FIQ Result mg/l
Gasoline	440	660
Kerosene	310	280
Diesel Fuel No. 2	780	620

Table 1: Comparison of analysis data of fuel contaminated soil using TCLP extraction procedures (EPA 1311) followed by re-extraction of the extract with methylene chloride and soil extracted using EPA Method 3550 to determine the leachability potential from the soil utilizing a GC-FID.

Sample Description	TCLP(EPA 1311) with EPA 3510 RE-EXTRACTION Result	Detection limits mg/l	SOIL EXTRACTED with EPA 3550 Result	Detection limits mg/kg
sp-5	ND	0.05	39.0	1.0
5-4	ND	0.05	ND	1.0
5-1	ND	0.05	44*	1.0
B-3	ND	0.5	100	1.0
1-8	ND	5.0	2300*	5.0

* Positive result for petroleum hydrocarbon as diesel appears to be due to the presence of heavier hydrocarbons rather than diesel.

Table 2: Comparison and assessment of data for DRO/TRPH determination using three different types of extraction and analyses procedures.

SAMPLE DESCRIPTION	TCLP (EPA 1311) with EPA 3510 RE-EXTRACTION DRO RESULT	DETECTION LIMITS mg/l	SOIL EXTRACTED with EPA 3550 GC-FID DRO RESULT	DETECTION LIMITS mg/kg	SOIL EXTRACTED with EPA 3550 418.1/IR TRPH RESULT	DETECTION LIMITS mg/kg
93UNKL01S	0.880	0.100	675	5.0	1320	20
93UNKL02S	0.730	0.100	890	5.0	3010	20
AVERAGE	0.805		782		2165	

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ANALYSIS OF AIR CANISTER SAMPLES FOR POLAR AND NON-POLAR VOLATILE COMPOUNDS USING MODIFIED TO-14

Paul E. Kester, Edmund T. Lewis, Alan T. Madden, Valerie J. Naughton, Tekmar Company, P.O. Box 429576, Cincinnati, OH 45242-9576

ABSTRACT

Recent air studies in urban areas have revealed a suprising number of polar compounds[1] Polar compounds are a particular challenge because they can be highly unstable. Canisters permit the effective sampling and analysis of both polar and non-polar VOCs in one analytical run. Canisters present the additional challenge of analyzing this broad range of analytes in the same sample with relatively high water concentrations.

A complete method for the analysis of the volatile range is necessary. Water removal is an important aspect for successfully achieving this goal. A condensation trap is described which selectively eliminates water without climinating analytes of interest.

Approximately ninety (90) analytes, including selected CLP method compounds, are investigated. Complete system performance is evaluated using different levels of relative humidity and sample concentrations. Data to be presented includes response factors, relative standard deviations, and calibration curves which exhibit the effectiveness of the moisture control system.

[1] Ramamurthi, Mukund; Kelly, Thomas; and Spicer, Chester, "Temporal and Spatial Variability of VOC Area Sources in Urban Air", Measurement of Toxic and Related Air Pollutants Conference, Durham, NC, 1993.

RADIATION

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RADIOCHEMICAL METHODS AND DETECTION LIMITS

Edmond J. Baratta, U.S. Food and Drug Administration, Winchester Engineering and Analytical Center, Winchester, Massachusetts 01890

ABSTRACT

The methods for radiochemical analyses had been originally used to determine the products of fission from the splitting of uranium and plutonium atoms. They were also used to determine the properties and isotopes of the artificially produced actinides. Later, radiochemical methods were used to determine the extent of contamination from various sources. These included world-wide fallout from above ground testing, emissions from nuclear power plants and other nuclear facilities. New emphasis is now on decontamination of decommissioned nuclear power plants and other facilities and sites. Traditionally, gamma spectrometry has been used as one means of identifying these radionuclides. However, for the analysis of "pure" beta-emitters, such as strontium-89 and 90, this is not possible. Also, alpha-emitters from the actinides and some of their decay products require radiochemical analyses. The levels of activity at which these radionuclides pose a hazard are low, so that the use of gamma spectrometry is not feasible. In addition, identification and quantification of various isotopes of the same element, such as uranium, is not possible. The matrices that can be analyzed include air, water, soil, food and other media.

The limits of detection that is required for the radionuclides of interest has improved. This is due to the more sophisticated instrumentation and improved methodology. This paper discusses the radiochemical methodology available and the limits of detection that the U.S. Environmental Protection Agency has set from its collaborative and inter-comparison studies over the years.

INTRODUCTION

The methods for radiochemical analyses had been originally used to determine the products of fission from the splitting of uranium and plutonium atoms [1,2,3,4]. They were also used to determine the properties and isotopes of the artificially produced actinides. Later, radiochemical methods were used to determine the extent of contamination from various sources. These included world-wide fallout from above ground testing, emissions from nuclear power plants and other nuclear facilities. New emphasis is now on decontamination of decommissioned nuclear power plants and other facilities and sites. Traditionally, gamma spectrometry has been used as one means of identifying these radionuclides. However, for the analysis of "pure" beta-emitters, such as strontium-89 and 90, this is not possible. Also, alpha-emitters from the actinides and some of their decay products require radiochemical analyses. The levels of activity at which these radionuclides pose a hazard are low, so that the use of gamma spectrometry is not feasible. In addition, identification and quantification of the various isotopes of the same element, such as uranium, is not possible. The matrices that can be analyzed include air, water, soil, food and other media.

Methods have been published by various societies[5,6,7] in order to "standardize" the procedures being used. This may be for regulatory purposes or other reasons. Federal Government and International Agencies have produced Procedures Manuals for use by these agencies to use which "standardize" the procedure being used throughout their agencies and contractees[8,9,10,11,12,13,14].

The limits of detection that is required for the radionuclides of interest has improved over the years. This is in part due to the more sophisticated instrumentation that is available and the improved methodologies. This paper will discuss the radiochemical methodology available and the limits of detection and errors associated with them. The U.S. Environmental Protection Agency has set these detection limits and errors associated with the analyses, based on its collaborative and inter-comparison studies over the years.

RADIOANALYTICAL CHEMISTRY

Basically, radioanalytical chemistry can be subdivided into three types of analyses. Those gamma and x-ray emitting radionuclides that can be measured with little or no sample preparation. Beta particles and alpha particles must, however, be separated chemically.

Also, the use of neutron activation analysis that has been used in the analysis of specific radionuclides. The latter will not be discussed, due to the necessity of having to have a "reactor" available for this type of analysis.

GAMMA EMITTERS:

In the earlier days, radiochemical separate was necessary even for gamma-emitters. They were normally counted using their beta or alpha particles. They could be detected using their gamma photons, however, the former methods were more sensitive. With the advent of the sodium iodide crystals and the single channel analyzers, the analysis of gamma emitters was made easier. In the very late fifties and early sixties, the use of the solid state multi-channel analyzer and the larger sodium iodide crystals, improved tremendously the analyses of gamma emitters. Some radiochemistry was still needed for the various radionuclides since multiple isotopes and gamma photons of energies limited somewhat the use of gamma analyses by this method. Milk and milk products, however, because of the "discrimination" of the cow made this analysis fairly easy. The use of simultaneous equations made this analysis routine for the following isotopes[7]: iodine-131, barium, lanthanum-140 and cesium-137. Shorter-lived iodine isotopes did cause some interference, however, for other than milk collected near test sites in the early hours of a weapons test, the problem was minimal. The amount of cesium-134 produced didn't interfere as it did later in the Chernobyl Accident. The first germanium (lithium-drifted) detectors and computer assisted multi-channel analyzers made the analysis of gamma-emitters, faster and easier. At the time of the Chernobyl Accident, the intrinsic high-efficiency germanium detectors were available. Many more samples could be processed more accurately and faster. The methods for peak analyses varied somewhat with the systems being used. However, they are all basically similar. The IAEA published a guidebook in 1989 describing this method[14]. It made some specific recommendations for the effective and accurate use of gamma analyses of matrices of interest. These are as follows:

-Sample geometries must be selected for the matrices of interest including air filters, water, vegetation, milk, fresh vegetables and other foods, and fresh water and marine organisms.

-The geometries must be calibrated for the densities of the sample of interest as a function of gamma ray energy. This involves the preparation of calibration curves of gamma ray counting efficiency versus energy.

-In preparing the calibration curves, standard preparation of radionuclides from an organization such as the National Institute of Standards and Technology (USA) or other reliable sources must be used.

-Calibration curves for unit density materials including water and meat can be made by using known amounts of radioisotopes in aqueous solution in the sample containers of interest. Samples of greater or less than unit density should be radiolabelled with the appropriate radionuclide(s), and calibration curves should be prepared on the labelled matrix.

-Radionuclide standards such as ^{137}Cs and ^{60}Co should be counted daily to ensure that the gamma ray spectrometer is operating correctly.

The form in which the sample is presented to the gamma-ray detector depends on the sample type, the available equipment, the radionuclides present and the levels of activity. Some sample containers include nylon planchets, aluminum cans, plastic "cottage cheese" containers and molded Marinelli beakers. Measuring times vary with activity present, sample type, detection limits required, detector efficiency and radionuclides of interest.

RADIOCHEMICAL METHODS

a.) Alpha-Emitters

The EPA lists various alpha-emitting radionuclides in its regulations regarding limits for alpha emitters. They have promulgated new rules, but the present rules for contaminations are radium-226, radium-228 and gross alpha in water is for combined radium-226 and 228 - 5 pCi/L (0.185 Bq/L), gross alphas (including radium-226, but excluding radon and uranium - 15 pCi/L (0.555 Bq/L). The method recommended is either that appearing in the Standard Methods[5] or the EPA Method[11]. For samples containing solids greater than 500 mg/l the Standard Method or the EPA Method[12] co-precipitation method is recommended. Should the gross alpha limit exceed the 5.0 pCi/L limit, then analyses for radium-226 and radium-228 must be performed. The gross alpha is a guide screening method requiring a short period of time and man power. There are a variety of methods available for the determination of the radium isotopes, these have been summarized in the chapter[22] on "Analytical Methodology for Radium in Food and Water" and in "Radon, Radium and Uranium in Drinking Water". These methods are more time consuming. The methods use a barium carrier to separate the radium isotopes from the solution. The radium may be precipitate and counted or, in the case of radium-226, the ingrowth product radon-222 may be collected and determined. A barium-133 tracer may also be used for the latter. Usually if the radium-226 is determined by alpha counting, the ingrowth should be followed.

Two other alpha-emitters of importance are uranium and plutonium. The Standard Methods[5] includes both a method for total uranium and isotopes uranium. The uranium proposed maximum contamination limit is 20 mg/L or 30 pCi/L (1.11 Bq/L). This analysis may be required when the gross alpha concentration exceeds

15 pCi/L (0.555 Bq/L). The total uranium method requires only the alpha counting of the separated uranium. The isotopic uranium method requires electroplating and alpha counting using a solid state detector (normally a silicon detector). Some laboratories are using a rare-earth fluoride co-precipitation method, which may be used, if it can provide adequate resolution when using the alpha spectrometry system.

Currently there are no "standard methods" for plutonium in drinking water or any standard regulation. The proposed rule for the 40CFR Parts 141 and 142[19] proposes a limit of 6.2 E01 pCi/L (2.294 Bq/L). The current ICRP-30 limits the ingestion of plutonium-239 to the Rad worker of an ALI of 5.4 E06 pCi. Per day, for the general population, (1/100) compared with radium-226, it would be three times that allowed for this isotope. The newer ICRP-61 (1990) reduces that to approx 1/2 of the radium-226 allowable concentration. (Table A)

Currently there are several methods for plutonium in water[9,10]. These usually require separation and addition of a tracer for the recovery. Electroplating and detection by alpha spectrometry to determine the isotope content and tracer recovery.

Radon is another alpha-emitting isotope that certainly requires discussion. The present liquid scintillation method has been tested twice by the EPA. The first study was inconclusive, at least at the level that EPA found to be of concern. The second study has not been reported to date. The proposed regulations sets for Radon-222 a limit for the Maximum Concentration Level at 300 pCi/L[19]. There are essentially two methods for determining radon-222 in water[20,21]. These are by liquid scintillation counting and the Lucas Cell. The radon-222 in drinking water is found only in groundwater supplies. Milny and Cathern[22] have reported that if the water concentration of radon is 10,000 pCi/L, an average of 1 pCi/L is contributed to the air, (a factor of 10,000 less). A radon concentration of 1000 pCi/L in water would contribute to indoor air containing the amount roughly equal to the average outdoor concentration which is about 0.1 pCi/L of air.

b.) Beta-Emitters

The EPA proposed drinking water standards for beta's and photon emitters is limited to exposure of 4 mRem ede/yr (ede = effective dose commitment, for a 50 year period, considering 2 Liters/day intake). The 1976 Interim drinking water standard for strontium-90 is 8 pCi/L (0.296 Bq/L), when other sources are not considered. The other, being a long-lived beta emitter, is tritium. Presently, the contamination level is set at 20,000 pCi/L (740 Bq/L).

The strontium-90 and total strontium methods can be found in the official methods books[5,6,7]. The methods essentially separate the radio-strontium using stable strontium as a carrier by nitric acid separation. The radio-strontium may be counted to determine the combined strontium-89 and strontium-90 (if the strontium-89 is suspected to be present). The yttrium-90 is allowed to grow in and separated by solvent extraction and/or precipitation. The yttrium-90 is then counted in a low-background, low-level beta counter. The strontium-89 is determined by calculations. The strontium-90 is calculated from the yttrium-90 content. Other methods[15,16] have been used to directly determine the yttrium-90, knowing that the strontium-89 is not present.

Tritium is determined by liquid scintillation counting. Normally it may be determined directly, with little preparation. It may be concentrated by electrolysis[9] should the need arise for lower concentrations. The proposed EPA rules does not require this concentration.

DETECTION LIMITS

Different conventions with differing terminology and mathematics have been used to estimate the lower limit of detection (LLD) or the minimum detectable activity (MDA)[9,17,18]. To eliminate confusion and the production of noncomparable data, it has been proposed that the Environmental Measurements Laboratory procedure[9] be used exclusively. The basis of this procedure is hypothesis testing. LLD is defined as the smallest quantity of sample radioactivity that will yield a net count for which there is a predetermined level of confidence that radioactivity is present. Two errors may occur: Type I, in which a false conclusion is reached that radioactivity is present, and Type II, with a false conclusion that radioactivity is absent.

The LLD may be approximated as

$$LLD \cong (K_\alpha + K_\beta)S_o$$

where:

K_α = value for the upper percentile of the standardized normal variate corresponding to the preselected risk of concluding falsely that activity is present (α).

K_β = the corresponding value for the predetermined degree of confidence for detecting presence of activity ($1 - \beta$), and

S_o = estimated standard error of the net sample counting rate.

For sample and background counting rates that are similar (as is expected at or near the LLD) and for α and β equal to 0.05, the smallest amount of radioactivity that has a 95% probability of being detected is,

$$LLD_{95} = 4.66S_b$$

where:

S_b = standard deviation of the instrument background counting rate.

The LLD thus calculated is in units of counts per minute; to convert to concentration use the appropriate factors of sample volume, counting efficiency, etc. Note that the approximation $LLD = 4.66\ S_b$ can be used only for determinations where S_b is known so that $S_o = \sqrt{2}\ S_b$ and there are no counting interferences. Examples of appropriate determinations are tritium, gross alpha or beta, or any single nuclide determination.

Where tracers are added to determine yield or more than one radionuclide is counted in a sample, use the general form of the equation above, for which the 95% confidence level would be $LLD \simeq 3.29\ S_o$.

The detection limits for various radionuclides have been determined by the EPA. Also, the Laboratory Precision of these radionuclides have also been determined, through various collaborative studies done by the EPA. These studies have been accepted by the various National Societies in their Standard Methods[5,6,7] Books of the past years. The methods in these Books are a result of these Collaborative Studies that had been done for these Societies. The precision and accuracy of the methods appearing in these Books are a result of these Studies. As early as 1966 this was proposed in an article in Health Laboratory Science[23]. Table B is the result of these studies. The "Activity Level" lists the "one standard deviation" for a single determination. Activities (results) below these numbers are considered "not detectable" on the LLD.

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SUMMARY

The instrumentation used in the determination of radionuclides, especially gamma-emitters has improved over the past decades. The detectors have gone from G-M Tubes to high efficiency intrinsic germanium detectors. Computers now are used to perform peak search, nuclear identification, efficiency calculations, alignment, etc. They are highly efficient and usually user-friendly. Portable systems are now in routine use, for on the spot determinations.

Many radiochemical procedures have been standardized and the instrumentation is now highly sophisticated, usually computer assisted with the necessary user-friendly software.

While the instrumentation has significantly improved, the lower limit of detection has not been lowered by much. This is due primarily to natural background. The standardization and improved instrumentation has improved to some extend the precision and accuracy of methods.

TABLE B. LABORATORY PRECISION: ONE STANDARD DEVIATION VALUES AND CONTROL LIMITS FOR VARIOUS ANALYSES

ANALYSIS	ACTIVITY LEVEL	ONE STANDARD DEVIATION FOR SINGLE DETERMINATION	CONTROL LIMITS AVG. OF 3 DET
Gamma emitters	5 to 100 pCi/liter or kg	5 pCi/liter	$\mu \pm 8.7$ pCi/l
	>100 pCi/liter or kg	%5 of known value	$\mu \pm 0.087\ \mu$
Strontium-89	5 to 100 pCi/liter or kg	5 pCi/liter	$\mu \pm 8.7$ pCi/l
	>100 pCi/liter or kg	5% of known value	$\mu \pm 0.087\ \mu$
Strontium-90	2 to 30 pCi/liter or kg	1.5 pCi/liter	$\mu \pm 2.6$ pCi/l
	>30 pCi/liter or kg	5% of known value	$\mu \pm 0.087\ \mu$
Potassium	≥0.1 g/liter or kg	5% of known value	$\mu \pm 0.087\ \mu$
Gross Alpha	≤20 pCi/liter	5 pCi/liter	$\mu \pm 8.7$ pCi/l
	>20 pCi/liter	25% of known value	$\mu \pm 0.087\ \mu$
Gross Beta	≤100 pCi/liter	5 pCi/liter	$\mu \pm 8.7$ pCi/l
		5% of known value	$\mu \pm 0.087\ \mu$
Tritium	<4,000 pCi/liter	$1s(\text{pCi/liter}) = (170)(\text{known})^{.0933}$	$\mu \pm 294(\mu)^{.0933}$
	≥4,000 pCi/liter	10% of known value	$\mu \pm 0.17\ \mu$
Radium-226, Radium-228	≥0.1 pCi/liter	15% of known value	$\mu \pm 0.26\ \mu$
Plutonium	0.1 pCi/liter gram or sample	10% of known value	$\mu \pm 0.17\ \mu$
Iodine-131	≤55 pCi/liter	6 pCi/liter	$\mu \pm 10.4$ pCi/l
	>55 pCi/liter	10% of known value	$\mu \pm 0.17\ \mu$
Uranium	≤35 pCi/liter	6 pCi/liter	$\mu \pm 10.4$ pCi/l
	>35 pCi/liter	15% of known value	$\mu \pm 0.26\ \mu$

TABLE A

Radiation Protection Guides (RPG) for Transient Rates of Intake of Radionuclides Recommended for the Average of Suitable Samples of the Population.

RADIONUCLIDE	Intake/day (pCi/day)(1) RANGE I	RANGE II	RANGE III
Radium-226	0-2	2-20	20-200

EPA Drinking Water Standards(40 CFR 141.15) = 15 pCi/L

ICRP No. 2 (Basis for FRC Guidelines)

	Frac. of Transfer from G.I. Tract to Blood
Radium-226	0.3
Plutonium-239	0.00003

ICRP No. 30	"Limits of Intake for Rad Workers" ALI-pCi	Per Day (1/100) p/Ci
Radium-226	1.89 E06	51.8
Plutonium-239	5.4 E06	148

ICRP No. 61 (1990)

Radium-226	2.43 E06	66.5
Plutonium-239	1.08 E06	29.6

(1) Range I requires only periodic surveillance; Range II, quantative surveillance and routine control; Range III, evaluation and additional controls.

PROGRESS TOWARD MATURITY OF "DOE METHODS FOR EVALUATING ENVIRONMENTAL AND WASTE MANAGEMENT SAMPLES"

Steven C. Goheen, Senior Research Scientist, Margaret McCulloch, Technical Specialist, Robert G. Riley, Senior Research Scientist, Sandra K. Fadeff, Research Scientist, Berta L. Thomas, Project Manager, Gary M. Mong, Research Scientist, Georgia K. Ruebsamen, Senior Clerk, Wayne C. Cosby, Editor, and Debbie S. Sklarew, Senior Research Scientist, Pacific Northwest Laboratory, P. O. Box 999, Richland, Washington 99352

ABSTRACT

The document *DOE Methods for Evaluating Environmental and Waste Management Samples* (*DOE Methods*) has been in circulation since October 1992. *DOE Methods* is a living document, being updated twice each year. It contains both sampling and analytical methods in support of U. S. Department of Energy/environmental restoration and waste management (DOE/EM) activities. Guidance on how to carry out sampling and analysis activities, focusing on EM needs, is also included in *DOE Methods*. This guidance applies to all aspects of sampling and analysis for EM. Methods from traditional standard methods documents often cannot provide needed characterization data because of radioactivity or complexity of the matrix. The intent of *DOE Methods* is to provide an alternative source of methods to meet this need. Efforts are underway to expand the use of *DOE Methods* throughout all DOE/EM programs.

Copies of *DOE Methods* are available free of charge. The April 1994 update of the document includes 42 methods, of which 13 are new. In October 1994, Revision 2 of *DOE Methods* will be distributed. It will include additional guidance on how to plan sampling and analysis activities and will also include several new methods.

DOE Methods is supported by the Laboratory Management Division of DOE. It is a vehicle for transferring new technology for characterization capability within the environmental restoration (ER) and/or waste management (WM) community. As *DOE Methods* continues to evolve, its use and application will continue to grow.

INTRODUCTION

DOE Methods has been available since October 1992 (1). Since then it has grown in circulation and size to become a standard for DOE and DOE contractor laboratories (history of development to be presented at Spectrum '94 in a paper entitled "A DOE Manual: DOE Methods For Evaluating Environmental and Waste Management Samples"). *DOE Methods* also provides guidance on planning for sampling and analysis activities, and it encourages the use of both sampling and analytical methods for ER and WM, selected either from a variety of standard references (2-5) or from *DOE Methods*.

Two years ago at this conference, the first issue of *DOE Methods* was introduced. Last year the performance approach to method selection and qualification was discussed. This presentation is focused on the progress of the document toward maturity.

Development of *DOE Methods.* Before 1991, all DOE sites independently developed standard operating procedures for sampling and analyzing radioactive environmental and waste matrices. In 1991, DOE decided that it was important to make these sampling and analysis procedures available to all sites (in July 1991, the Laboratory Management Branch of DOE's Office of Environmental Restoration and Waste Management issued a draft "five year plan" for the Analytical Services Program; copies of the final version may be obtained from Daniel Lillian, Mike Carter, or David Bottrell at the Office of Technology and Waste Management, Trevion II, 12800 Middlebrook Road, Germantown, Maryland 20874). This need was to be filled in two ways: 1) a database, containing key information, from which standard operating procedures from all sites could be accessed, and 2) a document similar to EPA's SW-846 (2). The DOE document has evolved into *DOE Methods.* The *DOE Procedures Database* is available through Los Alamos National Laboratory (LANL) staff.

The *DOE Procedures Database* contains many procedures from across the DOE complex whose technical content is duplicated several times. For example, more than one hundred procedures are available from the database for the analysis of uranium. Consolidating the procedures would allow similar approaches to be represented in a single method. Consolidated methods would allow the site chemists to indicate that their methods were shared standard methods used by other laboratories across the DOE complex. This standardization process could be useful in several ways:

- Methods accepted and applied complex-wide would be more easily accepted by regulators.
- Uniformity would help keep results comparable and defensible.
- Guidance would be provided to contractors wanting to do DOE work.

Meeting these needs was the justification for publishing *DOE Methods.*

Needed Technology. *DOE Methods* addresses technology needs for sampling and analyzing DOE/EM samples, particularly as these needs relate to the sampling and analysis of radioactive and mixed waste. Characterization of radioactive and mixed waste is currently being addressed at several DOE sites to help solve immediate problems. As methods are developed to meet these needs, editors of *DOE Methods* are pursuing documented solutions to the problems.

Distributing Information. *DOE Methods* is a tool for distributing technical information to the DOE/EM characterization community. It provides guidance on quality assurance, quality control, sampling, safety, and analysis. It also provides guidance on how to modify existing methods or develop new methods. With each issue, *DOE Methods* encourages comments from everyone on its distribution list. This provides a mechanism for *DOE Methods* to become tailored to the needs of the EM community, thus minimizing concerns that it may be outside the scope of any EM program. *DOE Methods* primarily contains methods that fit the needs of DOE/EM programs.

DOE Methods is part of the DOE Methods Compendium Program, which includes participants from the U.S. Environmental Protection Agency (EPA) and from DOE sites

across the country. These participants work together to create a holistic approach to solving the DOE/EM sampling and analysis problems. *DOE Methods* is one component of this network. Staff at PNL and LANL work closely to consolidate methods. The EPA at the National Air and Radiation Laboratory (NARL) and DOE-HQ are also involved in the consolidation process. Oak Ridge National Laboratory, LANL, Argonne, INEL, and other DOE labs provide methods generated specifically for inclusion in *DOE Methods* (see earlier note on five year plan). Together, components of the DOE Methods Compendium Program aim toward filling technology gaps that respond to EM needs as quickly as possible.

DOE Methods is updated twice a year. Both guidance chapters and methods can undergo revision during this updating cycle. The document is distributed in April and October of each year. This frequent update cycle ensures that input from readers and new information are incorporated quickly. All readers are encouraged to provide methods and/or comments at any time. The publication schedule ensures that reader comments will be addressed and, if appropriate, incorporated in less than 1 year from the time of submission.

The first issue of *DOE Methods* contained chapters on quality control, safety, waste handling, and sampling methods; it also contained four analytical methods and an appendix on method validation and selection. Since the first issue, nearly all chapters have been modified. An index and a second appendix (guidance on a performance-based approach to modified or new methods) have been added. A separate chapter on quality assurance was included, and more than 40 methods are now part of this document. Over the past year, the number of comments and corrections received has diminished dramatically, which appears to indicate widespread acceptance of the contents.

The titles of methods and their distribution by method class are summarized in Table I. Sampling methods include one addressing radioactive tank waste and two addressing vapor samples from drums. Analytical methods include all major classes of analytes (organic, inorganic, radiochemistry). Analytical methods generally include field screening, adapted methods, and new methods. Adapted methods are those that have been modified, usually from SW-846, to meet DOE requirements {e.g., as low as reasonably achievable (ALARA)}. New methods reflect a new approach not described elsewhere. The initial emphasis was on the inclusion of methods that were focused on high-level mixed waste. As these needs are filled, additional needs will be addressed, including lower-level mixed waste and environmental methods.

Sampling and analytical method formats are available (contact Margaret McCulloch at Pacific Northwest Laboratory, P.O. Box 999, MS P8-08, Richland, Washington 99352) to guide authors interested in submitting methods (6). These formats are similar to those of SW-846, with some adjustments made to conform to DOE/EM needs. Methods that are submitted undergo a peer review process. Many methods are distributed as draft methods until they have successfully completed the peer review process, and quality control data meet specifications (7). Once these criteria are met, the method becomes verified.

CONCLUSION

DOE Methods meets a need of EM programs by providing guidance and methods that are unavailable elsewhere and are needed to support the DOE/EM mission. *DOE Methods*

also makes the capabilities of the DOE complex more accessible, increasing the cost effectiveness of characterization in support of EM activities at DOE sites.

DOE Methods contains sampling and analysis guidance as well as methods to address DOE's characterization needs for EM programs.

ACKNOWLEDGMENTS

The DOE Methods Compendium Program is supported by the Laboratory Management Division of the U.S. Department of Energy. The document *DOE Methods for Evaluating Environmental and Waste Management Samples* is produced at Pacific Northwest Laboratory. Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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Environmental and Waste Management Samples. DOE/EM-0089T, Pacific Northwest Laboratory, Richland, Washington, April 1994.

Table I. Methods Included in DOE Methods for Evaluating Environmental and Waste Management Samples

Method Class	Title
Sampling	General Method for Sampling Liquids and Solids in Low-Level Waste Storage Tanks
	Sampling Headspace Gas for Volatile Organic Compounds Within a TRU Waste Drum with a Sampling Manifold
	Sampling Headspace Gas within a TRU Waste Drum with SUMMA™ Canisters for Volatile Organic Compounds
Organic	Total Organic Chlorine in Oil, Field Test Kit Method
	Immunoassay for Polychlorinated Biphenyls (PCBs) in Soils
	A Photoacoustic Infrared Method for the Detection of Selected Chlorinated Volatile Organic Chemicals (VOCs) in Water
	Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds
	Remote Purge and Trap Gas Chromatography of Volatile Organics in High-Level Radioactive Wastes
	Ultrasonic Solvent Extraction for Volatile Organic Analysis of Solid Radioactive Mixed Waste (RMW)
	Purge and Trap in a Glovebox
	PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and Gas Chromatogrpahy-Electron Capture Detection (GC-ECD)
	Reduced-Scale Liquid-Liquid Extraction of Semivolatile Organic Compounds
	Ultrasonic Extraction in a Glovebox or Hot Cell
	Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography (DAI-GC)
	Analysis of PCBs as Aroclors in Solid Radioactive Mixed Wastes

Table I. Contd.

	Direct Analysis of Toxicity Characteristic Leach Procedure (TCLP) Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates using HPLC with UV Absorbance Detection
Inorganic	Immunoassay for Mercury in Soil
	Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes
	Cleanup of Transuranic Liquid Wastes using Extraction Chromatography
	Total CN by Microdistillation
	An Indicator Strip-Based Test for Chromate Ions (CRO_4^{2-}) in Aqueous Samples
	An Indicator Strip-Based Test for Lead in Water
	An Indicator Strip-Based Test for Nitrate in Water and Soil
	An Indicator Strip-Based Test for Nickel (Ni^{2+}) in Aqueous Samples
Radiochemistry	*In situ* Analysis of Gamma-Ray Emitting Radionuclides by Borehole Logging
	Iodine-129 Analysis in Aqueous Solutions
	Nickel-59 and Nickel-63 Determination in Aqueous Samples
	Separation of Niobium for Niobium-94 and Niobium-93m Determination
	Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement
	Determination of Total Radioactive Strontium in High-Level Samples Using Extraction Chromatography
	Determination of Strontium-90 in Dissolved Environmental Samples Using Chelex-100
	Determination of Strontium-90 in soil, Water, and Filter Samples
	Determination of Selenium-79 in Aqueous Samples

Table I. Contd.

	Technetium-99 Analysis Using Extraction Chromatography
	Waste Distillation from Soil and Aqueous Matrices Using a Lachat Mirco-Dist™ System for Tritium Determination
	Laboratory Method for Gross Alpha and Beta Activity Determination
	Rapid Determination of Gross Alpha, Gross Beta, and Gross Tritium in Water Using a Liquid Scintillation Counter
	Gross Gamma Screening for Environmental Matrices
	Gamma-Ray Spectrometry
	Liquid Scintillation Instrumentation Method
	Method for Utilization of Alpha Track Detectors for Characterization of Gross Alpha Emissions from Indoor Surfaces
	Method for Utilization of Electret Ionization Chambers for Characterization of Gross-Alpha Emission from Indoor Surfaces

QC DATA REVIEW FOR GAMMA RAY/LIQUID SCINTILLATION ANALYSIS

Robert Litman, Chemistry Support Supervisor, NAESCO, Seabrook Station
Seabrook , New Hampshire 03874

ABSTRACT

Independent review of laboratory quality control data can provide valuable insight to the accuracy and precision of the analytical data produced, as well as provide important information about laboratory operations. The tools used to review the data are initially statistical, and the acceptance criteria for hese tools are based on laboratory history, or an 'industry' standard. The reviewer should not be satisfied with 'the way it's always been', but instead should attempt to look for the best way to improve laboratory performance. This may mean being innovative or just inquiring, but in either case the objective should be improvement.
This paper presents the QC methodology we use at Seabrook Station for gamma ray and liquid scintillation analysis. Specific cases of the utility of independent review are discussed.

INTRODUCTION

An important protocol for radiochemical laboratories to establish is not only how, but who performs data review for radiochemical measurements. The parameters which effect the measurement system may be as important to trend as the final QC analytical values. These other parameters often may provide clues which can trace a problem to its source. Gamma ray spectrometry and liquid scintillation analysis lend themselves to a myriad of parameters that can be trended. A choice of what to routinely follow is the judgement of the independent reviewer. The frequency of QC checks and data summary should be adjusted based on the sample loading, number of analysts, number of different analyses and laboratory history. The data reviewer should also review laboratory techniques.

DISCUSSION

Gamma Analysis

In our laboratory, we have four germanium detectors, each with 4 geometries. This is a potential for 16 different QC checks. We have our geometry positions fixed relative to each other and, as such, we feel a single QC check for the detector would serve all geometries for one detector.

The source used for QC is a solid, compact ^{152m}Eu source, whose true activity is within about 5% of the activity which is purchased. Since for this QC source we are more interested in the trended activity, the approximation of its absolute activity is satisfactory. The long half life(13.5 a) is advantageous since it will transcend the repair/replacement of many components such as pre-amps, amplifiers, cables , etc. A separate source which is very accurately known is used for detector calibrations. This separate source does not only have different radionuclides from the QC source, but is also purchased from a separate vendor. Figure 1 shows the gamma ray lines of interest that we use for the QC source, which transcends the range of interest for us for gamma ray analysis. Figure 2 shows a plot for the 122 KeV peak; the target value is plotted as a constant, a horizontal line parallel to the X-axis. Our gamma ray analysis QC software decay

corrects the activity to the standard date for the source. If the same data is plotted using the current activitiy of the QC source(i.e., not decay corrected)and compare it to the theoretical decay plot we would have a line with a negative slope for the true value. This method, used by some laboratories puts the analyst at somewhat of a disadvantage because it is difficult to discern any trends in the data at an angle. Feedback to the analyst on their work is important because it can ' short-circuit' problems in the analysis before they affect laboratory performance. Figure 3 shows a plot of our GO/NO GO check for the FWHM of the 964 KeV peak. This provides us with a good indicator of the electronic response of the detector, without a rigorous trend evaluation.

The messages we provide to the analyst for their recorded QC result are shown in Figure 4. Our warning limit is 2 sigma, our control limit is 3 sigma and our outlier limit is 4 sigma(data points wihich are outliers are not used in the data summary for statistical purposes). These messages allow the analylst to participate in the data review process as the data is generated. Other important parameters reported to the analyst are seen in Figure 5. We choose to use FWHM and energy checks as a *Go/No go* value and not as a trend. The background is checked for peaks(other than natural) and for potential contamination. This responsibility lies squarely with the analyst for potential corrective actions. Our current software has an additonal feature which prevents an analyst from analyzing a sampl if the QC check is unsatisfactory. They may take remedial actions and re-count the QC but not a sample.

The X-axis for the data plots should run for 25-50 analyses, at which point a data summary should be performed. A typical data summary is shown in Figure 6. The parameters of skewness and kurtosis are used as tools to help evaluate the data trends, but they have no specific warning messages. Figure 7 lists the statistical data tests that are performed on each data set.

The t-test compares the data set mean with the target, and uses a standard deciation based on the historical data set which contains 100 values.

The F-test compares the variances of the current data set with the variance of the last 100 data points.

The bias mean test compares the data set mean with the target value ± 0.65 sigma.

The Wilk-Shapiro test is performed on the current data set to determin if the data are normally distributed.

A printout of the test results provides the reviewer with the information needed to evaluate the analytical testing in the laboratory. Problem Resolution Reports(PRR) are issued when any of the statistical evaluations fails the null hypothesis, and when an analyst reveives a message 4, 6, or 8(see Figure 4). While the individual data entries are reviewed by the technician and supervisor, the dat summaries are reviewed by an independent analyst, who does not participate in the data generation. Figure 8 is a typical PRR.

The above data analyses are applied to each detector and each of the gamma rays used in the QC analysis.

Liquid Scintillation

Although we only perform tritium analysis in our laboratory, we apply the same statistical tests to the data generated for this analysis. Figure 9 shows how the tests are applied. The QC preparation involves pipetting a standard, and adding an aliquot of the cocktail as would be done for the sample. It should be noted that on a quarterly basis the entire sample treatment (i.e. including distillation) is performed on an interlaboratory cross check sample *as part of the QC process.* Once again the tritium source used to generate the quench curve and the QC are of separate origin.

Preparation of the QC in this manner will detect problems with

*glassware contamination
*cocktail decomposition
*pipetting technique
*loss of pipet calibration
*distillation carryover.

The routine checks performed also include

*total counts for a sealed unquenched standard
*background on the low energy channel
*background on full open energy channel
*comparison of the low energy to the full energy background to within 5%
*statistical tests on background and QC trend graphs

Figures 10 and 11 show two months of QC trend graphs. At the end of the first data set, the mean activity was 1.95E-04 microcuries/ml(the target value for the QC is 1.98E-04). There were some mechanical problems with the instrument for sample numbers 11 through 28. We had also been getting lower than normal values for the low energy channel backgrounds(this seemed to be related to the colder temperature in the count room during the winter months). The sample analyses were still in control , but these problems masked an underlying long term trend in the data which were not obvious to the supervisor or the analysts. When the printout for data set in Figure 11 was reviewed it was clear that a bias existed for the data set; a PRR with the bias mean low message was received after the statistical data evaluation. The bias limit for the data set was 1.92E-04 and the data set mean was 1.89E-04 microcuries/ml.

**An important point to note here was that only two of the data points in the current data set were at or beyond the control limits(i.e. a normal data distribution) and we had just confirmed that our quarterly QC interlaboratory check result was within the NRC acceptance criteria(-7.0%). **

The investigation examined the following items:

a. Accuracy of the pipet calibration
b. Balance accuracy checks(used for the pipet calibration)
c. Repipet delivery volume(used for aliquoting the cocktail)
d. Operation of the instrument

e. Expiration date of the cocktail
f. Contamination of the tritium standard with water(i.e. inadvertant dilution). This was achieved through review of our source control log sheets.
g. The quench curve and the original data for it.
h. The previous data set.

In the end it was items f, g, and h which solved the concern. The examination of the source log sheets and the instrument quench curve showed that a new quench curve had been generated on January 12(see data point 8 on Figure 10). Initially a low bias appeared to be in the works, but then the sporadic instrument and low background concerns detracted from the significance of the initaial drop in activity. The specific problem with the new quench curve was that the analyst who prepared it forgot to decay correct the tritium to the present time, giving an apparent higher activity for an equivalent count rate. In the QC procedure the decay correction is part of the software program, so it appeared that the QC activity was *low*. When the decay for the tritium was accounted for in the quench curve, the interlaboratory QC was within 1% of the stated value.

In this review process two important side issues were uncovered.

1. The quench curve procedure was missing a step to decay correct the standard
2. The source log sheets for the quench curve standard and the QC had both been labelled "QC". This was of significance since the QC had been used to generate the quench curve.

SUMMARY

The routine evaluation of QC data printouts as described herein takes approximately 15 minutes. Often PRR's which accompany these ae easily resolved or the corrective actions verified during that 15 minute review. Typically the analyst has performed the corrective actions and the reviewer ensures that it was appropriate for the error message received. These actions include gain adjustment, geometry adjustment, cleaning of the cocktail vial, low cryostat level, wrong year or month used for decay correction. In the particular case discussed here for tritium, approximately 5 hours were spent on the investigation; some of this time included interviews with the analysts. Approximately three hours were needed to correct the problems.

The analyst and the supervisor are often 'too close' to minor QC problems to see them. It is advantageous to have an independent resource examine the data and evaluate potential long term trend problems. In our case the statistical treatment of our data provided the trigger to investigate- the independent reviewer was able to look at the process without worrying about sample schedules.

FIGURE 1

^{152m}Eu $t_{1/2} = 13.5$ a

Gamma 1 = 121.8 KeV
Gamma 2 = 964.1 KeV
Gamma 3 = 1408 KeV

QA filename : CAS$DISK:[SNS.QAF]ADC1_DCAL.QAF;22
Parameter Name : NLACTVTY-121 (DECAY CORRECTED ACTIVITY @121KEV)
Start/End Dates : 10-FEB-1994 16:11:26 through 10-MAR-1994 00:00:00
Mean +- Std Dev : 1.54000 +- 3.922500E-02 (2.55 %) <USER>

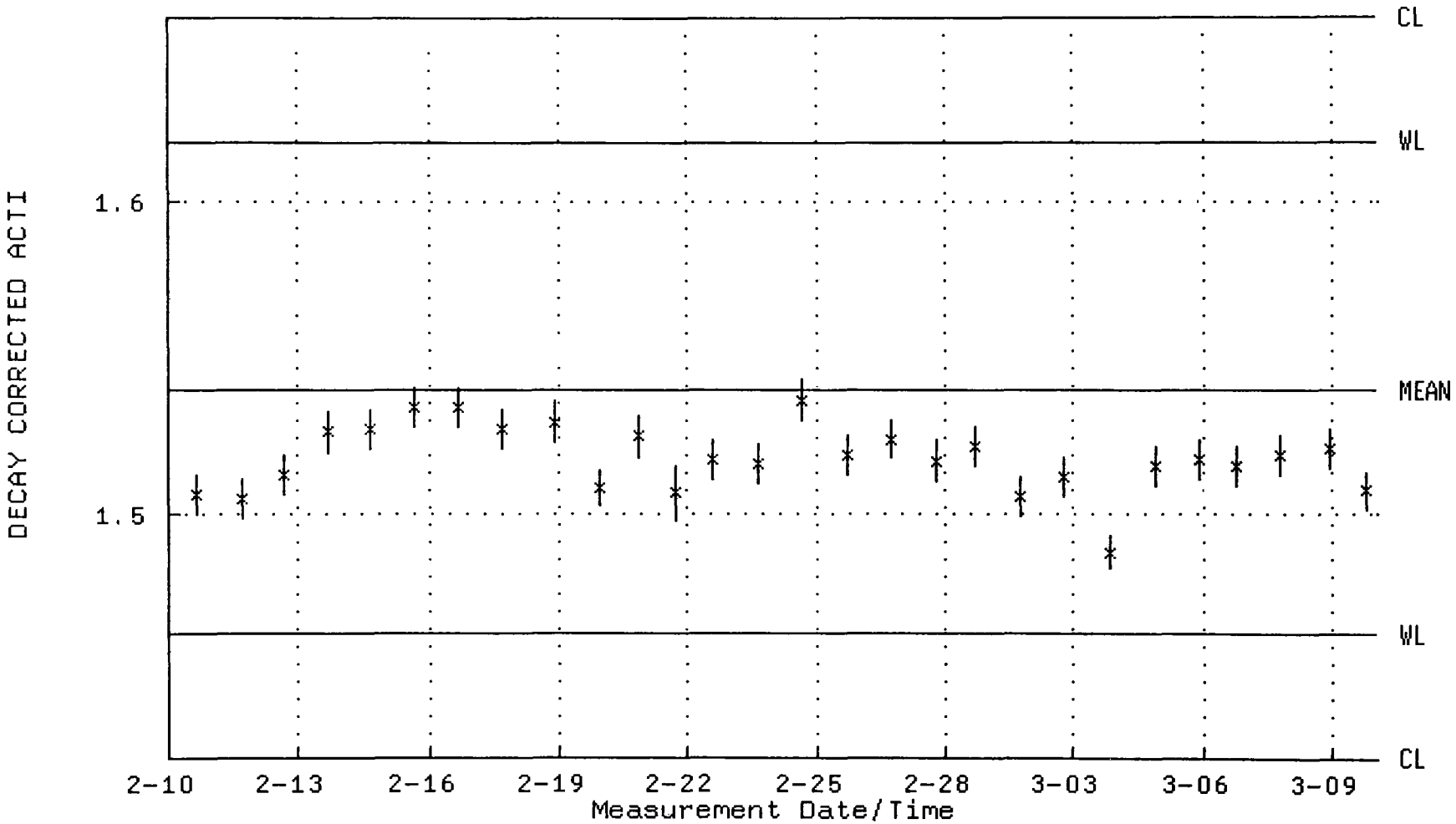


FIGURE 2

QA filename : CAS$DISK:[SNS.QAF]ADC1_DCAL.QAF;22
Parameter Name : PSFWHM-1407 (PEAK FWHM - 1407)
Start/End Dates : 10-FEB-1994 16:11:26 through 10-MAR-1994 00:00:00
Lower/Upper Lmts: 1.50000 through 2.50000

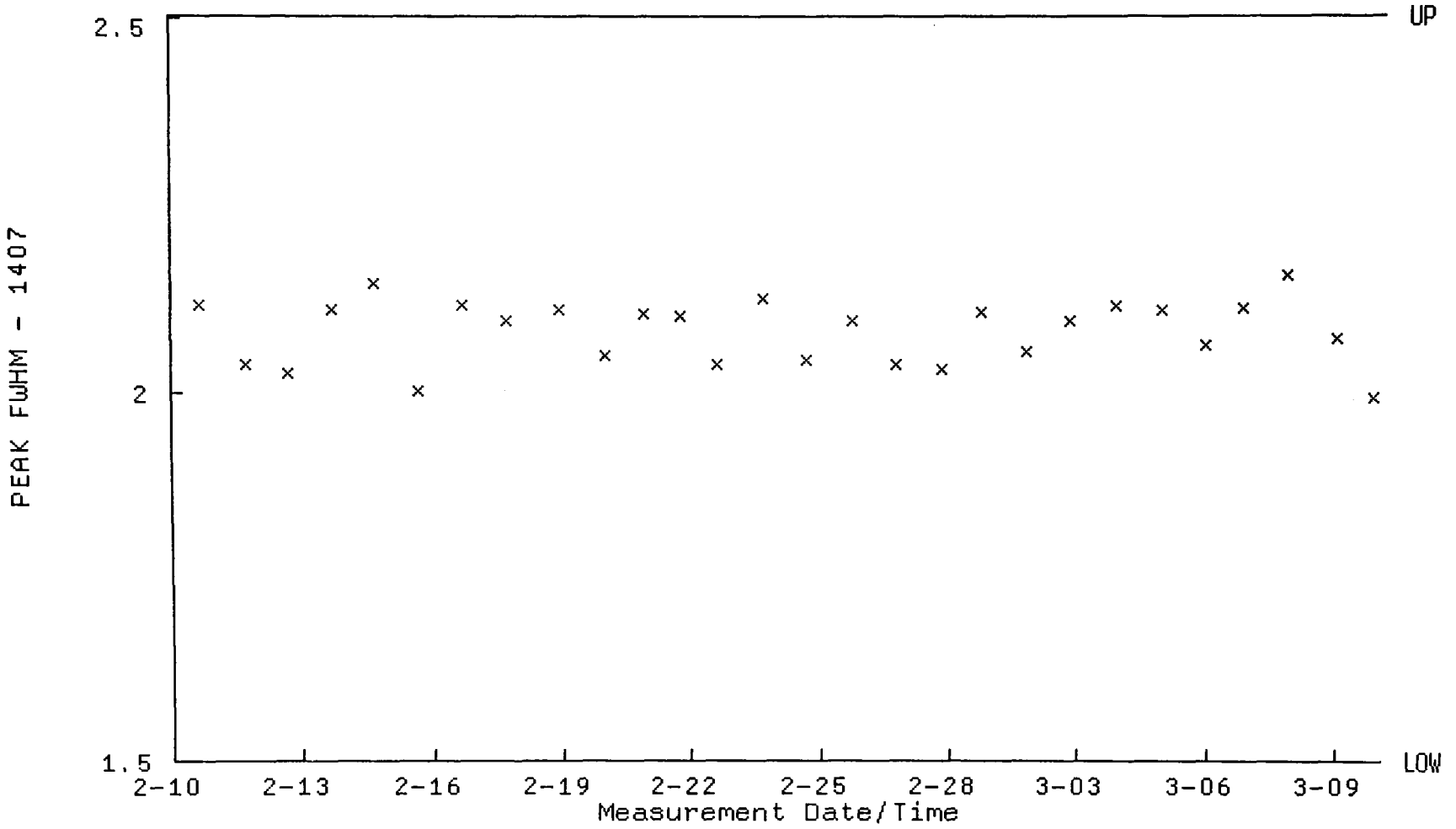


FIGURE 3

FIGURE 4

Messages to Analyst After QC Data Input

1. Data point is within one sigma of target
2. Data point is within warning limit
3. Data point is within control limit
4. Data point is fourth consecutive one beyond warning limit
5. Data point is beyond control limit
6. Second consecutive data point beyond control limit. **STOP** analysis
7. Data point is beyond outlier limit
8. Data point is seventh consecutive point beyond the bias limit

FIGURE 5

Other Parameters Checked As *go/no go* Values

FWHM	$\leq$2.3 KeV @1408 and $\leq$1.3 KeV @ 122 KeV
Energy	$E_{target} \pm 0.7$ KeV
Background	Trended like QC activity(daily short count)

Countroom Quality Control Charts
CH-L-722
DETECTOR 664 QC DATA
13-JAN-93 to 09-FEB-93

	Date	Time	Tech	121 FWHM	121 Flag	Centroid Channel	1299 FWHM	1299 Flag	Centroid Channel	Energy Drift	Drift Flag	121 Kev Activty	121 Flag	964 Kev Activity	964 Flag	1408 Activity	1408 Flag	BKGD cnts	BKGD Flag
1	13-JAN-93	20:54:00	JAT	1.1	ok	243.91	1.7	ok	2615.17	0.10	ok	0.107	1	0.106	1	0.101	1	780	1
2	14-JAN-93	19:42:00	AAG	1.1	ok	243.94	1.7	ok	2615.84	0.42	ok	0.108	1	0.104	1	0.107	1	809	1
3	15-JAN-93	18:35:00	SDA	1.1	ok	243.95	1.5	ok	2615.27	0.25	ok	0.107	1	0.105	1	0.109	1	820	1
4	16-JAN-93	12:31:00	SDA	1.2	ok	242.52	1.8	ok	2595.62	-0.26	ok	0.107	1	0.106	1	0.107	1	865	1
5	17-JAN-93	17:30:00	SDA	1.2	ok	242.63	1.7	ok	2596.66	0.43	ok	0.106	1	0.104	1	0.105	1	773	1
6	18-JAN-93	19:32:00	SDA	1.2	ok	242.61	2.1	ok	2597.18	0.56	ok	0.106	1	0.103	2	0.106	1	813	1
7	19-JAN-93	19:51:00	SDA	1.2	ok	242.60	2.1	ok	2596.56	0.36	ok	0.106	1	0.109	2	0.107	1	813	1
8	20-JAN-93	20:36:00	SDA	1.2	ok	242.63	2.0	ok	2596.59	0.41	ok	0.107	1	0.105	1	0.108	1	818	1
9	21-JAN-93	17:15:00	MAG	1.2	ok	242.61	2.1	ok	2596.52	0.44	ok	0.107	1	0.103	2	0.104	1	810	1
10	22-JAN-93	17:40:00	MAG	1.2	ok	242.64	2.1	ok	2596.43	0.35	ok	0.106	1	0.106	1	0.110	1	836	1
11	23-JAN-93	18:00:00	MAG	1.2	ok	242.67	1.9	ok	2596.90	0.60	ok	0.108	1	0.104	1	0.108	1	816	1
12	24-JAN-93	17:00:00	MAG	1.2	ok	242.72	1.9	ok	2596.95	0.54	ok	0.106	1	0.108	2	0.107	1	823	1
13	25-JAN-93	21:25:00	MAG	1.2	ok	242.67	2.0	ok	2597.47	0.91	FAIL	0.106	1	0.105	1	0.109	1	793	1
14	25-JAN-93	22:35:00	MAG	1.2	ok	242.66	2.3	ok	2597.54	0.09	ok	0.108	1	0.106	1	0.109	1	793	1
15	1 26-JAN-93	08:53:28	DAR								ok								
16	30-JAN-93	13:08:00	JDB	1.1	ok	242.77	2.0	ok	2598.65	-0.17	ok	0.107	1	0.107	1	0.105	1	808	1
17	31-JAN-93	13:29:00	JDB	1.1	ok	242.89	2.0	ok	2598.56	-0.21	ok	0.107	1	0.106	1	0.106	1	840	1
18	01-FEB-93	21:17:00	JDB	1.1	ok	242.86	2.0	ok	2598.70	-0.14	ok	0.105	1	0.103	2	0.105	1	849	1
19	03-FEB-93	01:01:00	JDB	1.1	ok	242.89	1.7	ok	2599.11	0.22	ok	0.106	1	0.104	1	0.104	1	799	1
20	03-FEB-93	22:39:00	JDB	1.1	ok	242.85	2.1	ok	2598.84	0.08	ok	0.105	1	0.105	1	0.103	1	801	1
21	04-FEB-93	21:05:00	MJP	1.1	ok	242.87	2.0	ok	2599.20	0.12	ok	0.106	1	0.104	1	0.106	1	808	1
22	05-FEB-93	22:26:38	MJP	1.1	ok	242.89	1.9	ok	2598.93	0.18	ok	0.108	1	0.104	1	0.108	1	811	1
23	06-FEB-93	17:08:00	MJP	1.1	ok	242.97	2.3	ok	2599.61	0.44	ok	0.107	1	0.105	1	0.107	1	775	1
24	07-FEB-93	22:11:00	AAG	1.1	ok	242.97	2.2	ok	2599.57	0.36	ok	0.107	1	0.103	2	0.105	1	768	1

Flag messages:

1 = Result is inside the bias limits.
2 = Result is inside the warning limits.
3 = Result is inside the control limits.
4 = Possible trend outside warning limit developing. Problem/Resolution Report is required.
5 = Result is at or exceeds the control limits, a second control check is required.
6 = Second control check failure, Problem/Resolution Report is required.
7 = Result is at or exceeds the outlier limit.

Supervisor [signature] Date 2-12-93
Chemist [signature] Date 2/16/93

① Detector OOS for calibration 1-27-93 → 1-29-93

FIGURE 7

Statistical Evaluations

t-test
F-test
Bias Mean Test
Wilk-Shapiro Test of Normality

Chemistry Department Problem/Resolution Report Form
CH-L89

I. Tech: System Generated Date: 23-APR-94 19:58:55

Instrument: LS 1800 Analyte: Activity Check

Target Value: 1.980e-04 uCi/m Result: 1.912e-04 uCi/ml

Upper Limit = 2.040e-04 uCi/m Lower Limit = 1.920e-04 uCi/m

ote : The mean for the Activity Check data set is less than the 'BIAS' limits of 1.920e-04 uCi/ml for this analysis. Please initiate a Problem/Resolution Report as required by JS0999.001.

I. Supervisor:_____

A. Corrective action(s) recommended:_____

_____

_____

_____

B. Are any procedural changes required? YES NO
If YES describe the revisions and list the date submitted.

_____

_____

_____

C. Review ALL data since the last satisfactory QC check on this analysis. SAT UNSAT If UNSAT describe actions taken and date.

_____

_____

_____

FIGURE 9

Liquid Scintillation

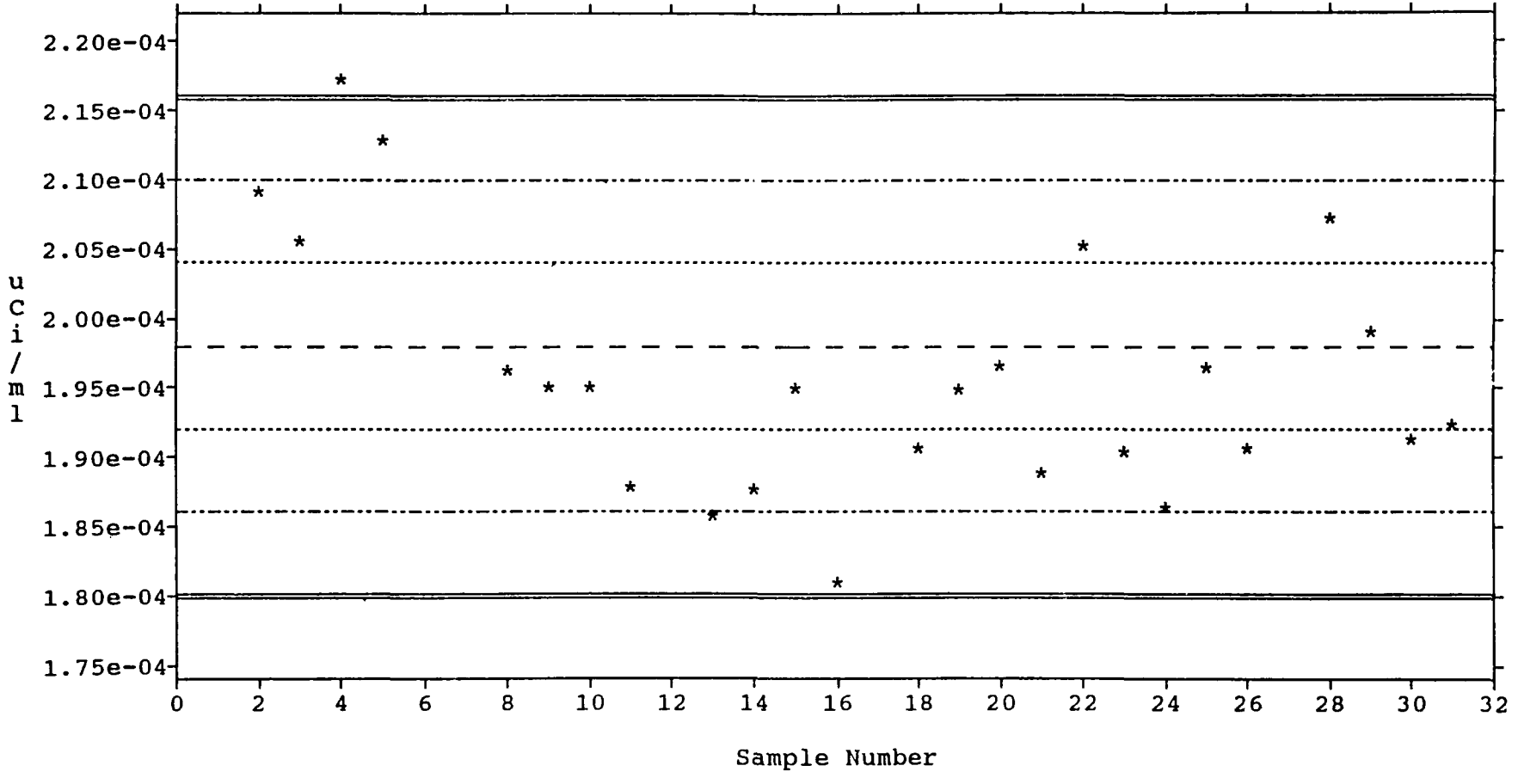
Low Energy Window Background

Full Energy Window Background

Sealed Source Counts(go/no go)

Preparation of Daily QC as a Sample

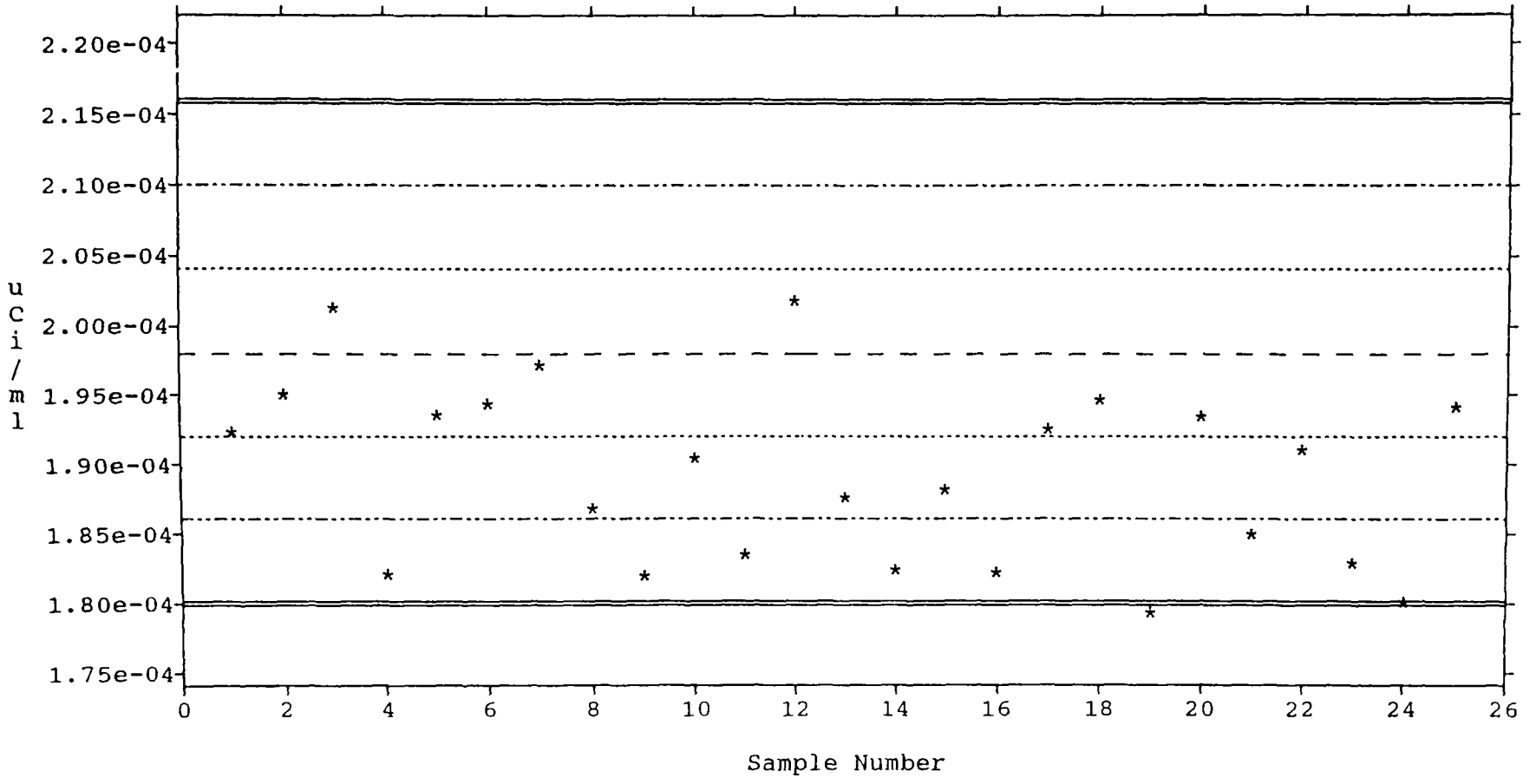
FIGURE 10
Countroom Quality Control Charts
CH-L-725
LS 1800 Activity Check Results
07-JAN-94 to 12-FEB-94



* Activity Check Results
— — — TARGET VALUE = 1.980e-04
····· BIAS HIGH = 2.040e-04
····· BIAS LOW = 1.920e-04
—·—·— WARNING LOW = 1.860e-04
—·—·— WARNING HIGH = 2.100e-04
═══ CONTROL LOW = 1.800e-04
═══ CONTROL HIGH = 2.160e-04

FIGURE 11

Countroom Quality Control Charts
CH-L-725
LS 1800 Activity Check Results
12-FEB-94 to 07-MAR-94



* Activity Check Results
— — — TARGET VALUE = 1.980e-04
····· BIAS HIGH = 2.040e-04
····· BIAS LOW = 1.920e-04
—·—·— WARNING LOW = 1.860e-04
·—·—· WARNING HIGH = 2.100e-04
═══ CONTROL LOW = 1.800e-04
═══ CONTROL HIGH = 2.160e-04

NATIONAL INSTITUTE of STANDARDS and TECHNOLOGY's MEASUREMENT QUALITY ASSURANCE PROGRAMS for IONIZING RADIATION

Kenneth G.W. Inn, Jimmy Humphreys and Jileen Shobe, National Institute of Standards and Technology, Ionizing Radiation Division, Building 245, Room C229, Gaithersburg, MD 20899.

ABSTRACT

The Ionizing Radiation Division of the National Institute of Standards and Technology (NIST) has implemented a number of quality assurance programs to provide a consistent basis for national and international ionizing radiation measurement credibility and comparability. The programs cuts across a variety of sectors that include: 1) personnel protection; 2) survey instrument calibration; 3) medical diagnostics; 4) medical therapy; 5) radiopharmaceuticals; 6) nuclear power plant radiochemistry; 7) regulatory agencies; 8) environmental; and 9) radiobioassay. The four basic elements of the MQA programs are: 1) conformance to fundamental consensus operational criteria; 2) documented in-house quality assurance and control practices; 3) periodic performance evaluations using appropriate testing materials and instruments; and 4) periodic on-site assessments by technical experts. The periodic performance evaluations are particularly important for the demonstration of measurement traceability to the national and international physical standards. Traceability alone, however, must be augmented by the other elements to provide the strongest rational for measurement assurance.

DEVELOPMENT OF A MIXED-ANALYTE PERFORMANCE EVALUATION PROGRAM FOR THE ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT OFFICE OF THE UNITED STATES DEPARTMENT OF ENERGY

Dr. Stan Morton
Senior Scientist
United States Department of Energy
Radiological and Environmental Sciences Laboratory
850 Energy Drive
Idaho Falls, Idaho 83402

Telephone 208/526-2186
FAX 208/526-2548

The United States Department of Energy (DOE) has established the Office of Environmental Restoration and Waste Management (EM) to oversee the program activities within the complex. The Laboratory Management Division (EM-563) in the Office of Technology Development is charged with assuring adequate analytical capabilities, quality assurance, and sample management for the EM programs. To address these issues, EM-563 has developed an Analytical Services Program consisting of: Analytical Support, Resource Planning, and Quality Assurance. The Quality Assurance function includes the development, coordination and management of quality assurance guidance documents, performance evaluation programs, and field and laboratory assessment programs.

Increasing regulatory requirements demand that analyses performed by DOE quantify nonradioactive compounds or elements in addition to the radioactive isotopes of interest. Adequate quality assurance requires quality control maticos representative of the routine sample. None of the major performance evaluation programs currently in use are designed to address radioactive and nonradioactive constituents in a single sample matrix.

At the request of EM-563, a new performance evaluation program was developed by the Radiological and Environmental Sciences Laboratory (RESL) that combines radioactive and nonradioactive analytes into one analytical sample. The establishment of this program creates a new category of performance evaluation called mixed-waste or more aptly the mixed-analyte performance evaluation program (MAPEP). Participation requires analysis of only those constituents that are a component of the facility's routine analytical work load. At the completion of each round, a published report will present the participant's results using a scoring system rather than a ranking system.

The program will distribute samples on a semiannually basis. The samples, in various matrices, will contain types and concentrations of analytes that are typical of those found in the complex. The radioactive constituents will contain gamma, beta and alpha emitting isotopes at concentrations ranging from one to 1000 Bq/l or Bq/kg. The nonradioactive constituents will consist of some or all of the metals listed in 40 CFR part 261, Appendix III. The concentration of those metals listed in part 261.24, Table 1, will not exceed the regulatory levels as defined therein.

The program is designed to provide information on the quality of radiological and nonradiological analytical techniques used by all laboratories on which DOE is relying for EM sample analyses. The MAPEP will be a major part of the Integrated Performance Evaluation Program being developed by EM.

IMPLEMENTATION OF A FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER FOR THE DETERMINATION OF VOC'S IN WASTE DRUM HEAD SPACE

W.F. Bauer and M.J. Connolly, Idaho National Engineering Laboratory, EG&G Idaho Inc., Idaho Falls Idaho 83415, *D. Gravel and A. Rilling*, Bomem (Hartman & Braun Inc.), Quebec, Quebec, Canada G2E5S5, and *F. Baudais*, Applied Automation (Hartman & Braun Inc.), Willowbrook Illinois 60521

ABSTRACT

The Conditional No-Migration Determination (NMD) for the Waste Isolation Pilot Plant (WIPP) requires that a representative waste drum head space sample be collected for analysis. The NMD also requires that the head space of all layers of confinement within the drum be sampled. This level of sampling will be required until it can be demonstrated that existing process knowledge is adequate for waste drum characterization. The Idaho National Engineering Laboratory has been involved in the development and evaluation of methods for the analysis of RCRA (Resource Conservation and Recovery Act) constituents in the gaseous head space of the waste drums. Currently this analysis is performed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) of samples collected in SUMMA canisters. The ability to do "at-line" analysis would significantly reduce the necessary sample handling and therefore the cost of each VOC analysis. Fourier transform infrared spectroscopy (FTIR) was selected as a GC/MS replacement for the analysis of volatile organic compounds (VOC's) since FTIR instrumentation is relatively simple, durable and can easily be operated "at-line" A two phase study to assess the feasibility of using FTIR for VOC analysis in waste drum head space was initiated. In the first phase it was determined that FTIR could be used to identify and quantitate at least 25 gaseous analytes simultaneously with detection limits for most analytes being within the 1-10 ppmv-m range. The results from this first phase were used to develop the requirements for the second phase of the study. This second phase of the study is currently under way and involves the evaluation of a "turn-key" FTIR gas analysis system installed at a waste drum characterization facility.

The "turn-key" FTIR system was intended for use by technicians and as such is designed to operate with minimal input from the technician. This FTIR system is directly interfaced to a preexisting automated gas sampling system (GSS) used to collect SUMMA canister samples for laboratory analyses. When sample volume permits, an additional aliquot of the gas sample is pulled into the FTIR for analysis and the results compared to the GC-MS analysis results when they become available. A single pass 20 cm cell is used in the FTIR system to accommodate the wide range of concentrations expected in the waste drum head space while maintaining adequate detection limits. The "turn-key" system is able to identify and quantitate 29 target VOC's and the C_1-C_3 hydrocarbons.

INTRODUCTION

The Idaho National Engineering Laboratory (INEL) is currently participating in the Waste Isolation Pilot Plant (WIPP) Experimental Test Program (WETP). The goal of this program is to collect data in support of a disposal decision for the WIPP In addition to the data required for

WETP, the Environmental Protection Agency (EPA) has issued a Conditional No-Migration Determination (NMD)[1] for the WIPP which requires that a representative drum head space sample be collected and that all layers of confinement be sampled until it can be demonstrated not to be necessary. The uses of the data generated from these activities include verification of process knowledge, further waste characterization, verification of gas generation and transport models, and determining the suitability for transport to and acceptance in the WIPP.

The majority of the gas samples collected at the INEL will come from either the Drum Vent Facility (DVF) or the Waste Characterization Area (WCA). At the DVF, waste drums will pass through and gas samples collected at a rate of 1 every 5-8 minutes. At the WCA, only 2-3 waste drums will be examined per week, however, multiple samples will be collected for each drum in order to sample the drum head space and the head space of all the inner layers of confinement within the drum.

The constituents of the waste drum head space are normally identified and quantitated by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). The analysis of the 29 organic target compounds[2] typically costs on the order of $1000+ per sample and has a relatively poor turn around time, typically at least 2 days. The analysis takes a minimum of ~4 hours. This time includes sampling into a SUMMA canister, transport of the sample to the analytical laboratory, initial dilution of the sample, and the first GC analysis. The initial dilution and analysis may need to be followed by an additional dilution and analysis, depending upon the results of the initial analysis. For the routine analysis of drum head space on the thousands of existing waste drums, the layers of confinement within the drum, and long-term monitoring of these drums, the time and cost limitations of these GC methods are obvious and clearly prohibitive. An alternative analysis technique that is rapid, reliable and easily operated "at-line" is needed. Fourier transform infrared (FTIR) spectroscopy is a technique that can potentially answer this need.

With FTIR, relatively high resolution (0.5-2 cm^{-1}) spectra can be collected in times as short as seconds. Even with scan averaging to reduce the signal-to-noise ratio, spectra can be collected and processed within minutes of sample collection. Qualitative identification is made from the IR spectrum "fingerprint" of the compound and quantitation is performed using the Beer-Lambert law:

$$a(\nu) = \alpha(\nu)\, c\, b$$

where $a(\nu)$ is the absorbance of the sample at frequency ν, $\alpha(\nu)$ is the molecular absorption coefficient, c is the analyte concentration and b is the path length of the sample cell. The values of $\alpha(\nu)$ are typically determined from a series of standards at known concentrations. When multiple analytes are absorb at a given frequency, the total absorbance is a simple sum of the contributions from each analyte.

Even though it is relatively easy to identify molecules by their infrared spectra, quantitation at the part-per-million (ppmv) to part-per-billion (ppbv) level is difficult because the absorptivity coefficients are typically quite low in the infrared region. In the gas phase, the poor detection limits due to low absorptivities can be easily overcome by using longer path length cells. Quantitation difficulties can be amplified when more than one analyte is present. Statistical analysis tools such as classical least squares (CLS)[3] and partial least squares (PLS)[4] can be used to

separate and quantitate the components of the spectrum. The target list of 29 organic analytes, as well as some additional inorganic analytes, appear to be well suited to determination by FTIR spectroscopy. Analysis times on the order of minutes instead of hours should be easily achieved.

This study was originated and designed to assess the feasibility of utilizing FTIR spectroscopy to determine the volatile components in the head space of waste drums containing transuranic waste (TRU). The FTIR laboratory demonstration represented Phase I of a two phase feasibility study aimed at demonstrating the applicability of FTIR in performing near real-time, at-line analysis of drum head space volatile organic compounds (VOCs). Phase II consists of drum and inner layer of confinement head space analysis by FTIR by a "turn-key" system installed "at-line" at the WCA with subsequent comparison to results from SUMMA canister collection followed by GC/MS analysis. The objective of the two phase feasibility study is to demonstrate to the U.S. EPA that FTIR can be used to perform drum head space VOC analysis and yields comparable results to SUMMA canister collection followed by GC/MS or meets established WIPP program requiments.

EXPERIMENTAL

Instrumentation: Bomem furnished the FTIR based VOC system as specified by EG&G Idaho, Inc. Because the "turn-key" FTIR system is located in a "suspect radiation contamination zone" near where the waste drums are handled and mounted into the waste characterization hot cell at the WCA, the hardware is enclosed in a NEMA 12 enclosure (48" tall x 36" wide x16" deep) for protection from damage and from contamination by radiation. Figure 1 is a schematic of the components comprising the FTIR based VOC analysis system. A Bomem MB 100 series FTIR is vertically mounted and equipped with a specially designed top plate. The optical bench is purged with hydrocarbon and CO_2 free dry air which is vented into the NEMA 12 enclosure to help maintain a slight positive pressure within the enclosure. A 20 cm gas cell with zinc selenide windows coated with an anti reflection coating to reduce the refractive index and a DTGS detector are mounted on the top plate. All sample transfer lines and the sample cell are maintained at 110°C. Transducers are mounted in the cell to record the temperature and pressure of each sample. Because of the heat load supplied by the instrumentation and the other heated components, the NEMA 12 enclosure needed to be cooled and is maintained at ~28°C with a closed cycle air conditioner. Operation of the valves and the FTIR are controlled via RS232 and RS422, respectively from a 486 based PC located >60 feet away at the WCA control center.

Sampling and analyses is initiated when the start signal is received from the GSS computer. At this point the three way valve (V1) rotates toward the sample line and the cell and lines are evacuated to <5 Torr by opening V4. The cell and lines are backfilled to ~625 Torr with HC/CO_2 free dry air by closing V4 and opening V3. The cell and lines are reevacuated by closing V3 and opening V4. Once evacuated to < 5 Torr, V4 is closed and the "ready evacuated" signal is sent to the GSS computer which then opens V0 and the lines and cell begin to fill with the sample. When the pressure has stabilized, V1 is rotated to isolate the cell and spectral acquisition is initiated. Each spectrum is the result of 10 coadded scans.

Generation of library spectra: Because quantitative IR spectra of several of the VOC's of interest were not available at all or not available at the conditions at which the sample spectra were to be recorded, it was decided to record the quantitative spectra at the sampling conditions, i.e. at

110°C with a nominal pressure of 640 Torr (near ambient pressure in eastern Idaho). A second manifold which included a cold finger was constructed and connected to a second MB 100 series spectrometer with an identical top plate. After inserting the sample of the neat analyte into the cold finger and attaching it to the manifold, the sample was frozen with liquid nitrogen. The space over the frozen sample in the cold finger, the manifold and heated gas cell were evacuated using a mechanical and a turbo pump in series. Once a stable vacuum was reached, the cold finger containing the sample was isolated by closing the valve, the liquid nitrogen was removed and the sample heated to room temperature. The valve to the sample was then opened and the sample allowed to "evaporate" into the evacuated manifold and cell until the desired partial pressure of the analyte was reached (usually ~0.64 Torr). The total pressure was then brought to 640 Torr with nitrogen and the spectrum was acquired with 50 coadded scans at 1 cm^{-1} resolution. Many of the more polar and less volatile VOC's presented problems that were likely due to adsorption of the analyte onto the walls of the cell and manifold. The addition of nitrogen to the sample to bring it to 640 Torr seemed to enhance the instability of the analyte partial pressure. For these cases additional nitrogen was not added to bring the total pressure to 640 Torr. There were no apparent differences in the spectral features of the analyte spectra recorded at low and high pressure. Linearity of the samples created in this manifold system was verified by using carbon tetrachloride to construct a calibration curve from 0 to 1000 ppmv.

Computer simulated spectra and CLS analysis: It would be extremely difficult and extremely labor intensive to make and test in the laboratory enough gaseous samples containing the 29 analytes for a full evaluation of the potential and limitations of the FTIR technique. For this reason, it was decided that computer simulated spectra would provide an alternative way of looking at as many potential combinations of components as possible. Table I lists the 29 volatile organic target compounds of interest. The maximum concentrations and the occurrence frequency represent the results from ~93 vented drum and inner bag head space samples as determined by GC and GC/MS analyses. The frequency and concentration ranges found in the table were used as inputs for the generation of the unknown spectra used in the study. Also listed in Table I are the upper concentrations noted in samples from 210 unvented as analyzed by gas phase mass spectrometry[5].

During the first phase of the study, simulated spectra were calculated from known spectra obtained from the MDA spectral library (MDA Scientific, Inc., Lincolnshire, IL, 1991). In the second phase, the new spectra that were acquired as described above were used. All calculations were performed using Gauss - 386i Version 3.0 (Aptech Systems, Inc., Maple Valley, WA), a matrix oriented statistical programming language. Spectra were linearly combined by randomly selecting the components for the new spectrum at the occurrence frequencies found in Table I. The concentrations for the components were also randomly determined within the range extending from 0 ppmv to the maximum found in Table I for the first phase. In the second phase, all concentrations were assumed to range from 0-2000 ppmv with the exceptions being ethane at 1000 ppmv and propane at 500 ppmv. Water was added to each spectrum in concentrations ranging from dry to saturated. Carbon dioxide was also added to each spectrum in concentrations ranging from 0 to 10000 ppmv. Since there is some potential for NO_x, NO_2 was also added to 10% of the spectra in the range of 0-500 ppmv. Random noise of $\pm 10^{-3}$ absorbance units (AU) was added to each spectrum. Randomly fluctuating backgrounds consisting of a simple offset, a sloping line with an offset, or a curved line (defined by $x \cdot \log(x)$ where $0<x<1$) with an offset could also be

added as desired in either a positive or negative direction. Concentrations of the components in the new spectrum were then determined using the CLS approach. For each set of conditions, 1000 spectra were generated and quantitated.

As already stated, the concentrations of the newly generated unknown spectra were determined by CLS. This activity was performed in the both the "fingerprint region" of the spectrum using all data between 671 and 1400 cm^{-1} and the "CH" stretching region extending from 2750 to 3225 cm^{-1} Water, CO_2, NO_2, methane, ethane, propane, cyclohexane, an offset line and a sloping line were included in the calibration set as interferences in the 671-1400 cm^{-1} region. With the interferences, a total of 37 components were in the calibration set for the 671-1400 cm^{-1} region. The primary analytes in the 2750-3225 cm^{-1} region were cyclohexane, methane, ethane and propane, however, 32 components were in the calibration set to accommodate potential interferences including offset and sloping baselines. In both cases, the calibration sets were made from the pure component spectra of the newly acquired library. Prior to forming the actual calibration matrices for each region, each library spectrum was carefully examined and appropriate baseline corrections applied using the baseline correction functions found in Spectra Calc (Galactic Industries).

The predicted concentrations of the computer simulated spectra were evaluated using the standard error of the estimate (SEE):

$$SEE = \sqrt{\frac{\sum_{i=1}^{n} (c_{predict} - c_{true})^2}{n}}$$

where $c_{predict}$ and c_{true} are the predicted and true concentration values for a component in the n computer generated spectra. The SEE value is generated for each component and can be viewed as the standard deviation of the predictions for each component given. Assuming this is a true reflection of the standard deviation for the frequency of occurrence and concentration ranges for the analytes, detection limits can be estimated as 3 x SEE. The detection limits calculated in this fashion are likely to be most appropriate for the occurrence frequencies and concentration limits used to calculate them. High SEE values for a given analyte indicate that the absorptivity for that component is low and/or that there is a significant spectral interferences that limits the detectability of that analyte.

PLS methods: PLS methods were generated using Galactic Industries PLSplus add-on package to Lab Calc. Because of software limitations and the cumbersome calibration sets required for a single method that would quantitate all 29 target VOC's and the C_1-C_3 hydrocarbons, individual PLS methods were used for each analyte in a selected region of the spectrum. Calibration sets consisted of duplicate spectra of each analyte and potential interference (n=70). Wavelength regions for each analyte were selected after evaluating the correlation spectra for that component. Optimum numbers of factor for each analyte method were selected from the evaluation of the predicted residual error sum of squares (PRESS) values determined using the diagnostic routines provided in the PLSplus software. Evaluation of an unknown spectrum for the 32 analytes using the 32 separate methods takes only ~10 seconds. These PLS analysis methods are integrated into the operating software of the FTIR system installed at the WCA. Complete analysis and reports are provided within 5-6 minutes of sample introduction to the system

RESULTS AND DISCUSSION

During phase I of the study, evaluation of FTIR spectroscopy for the determination of VOC's in waste drum head space was performed using both computer simulated spectra with up to 25 components and actual spectra of 5 component mixed gas standards. The CLS methods used to evaluate the computer generated spectra appeared to be quite adequate since the SEE values were reasonably low and, therefore, the detection limits for most components were estimated at 1-10 ppmv-m. At this detection level, it was determined that reasonable detection limits could be achieved in a somewhat shorter cell. Using a shorter sample cell would also maximize the working range, a positive factor considering the very wide range of concentration noted in Table I for many of the analytes.

The goal of phase II is to demonstrate that FTIR spectroscopy is a reliable tool for the analysis of waste drum head space and can be operated "at-line" by facility technicians. The "turn-key" FTIR system for the analysis of VOCs described above has been installed at the WCA and is currently in operation. The use of the 20 cm path length cell in this system allows sufficient light throughput so that a DTGS detector can be used instead of a liquid nitrogen cooled MCT detector. Since the system is mounted in a radiation contamination area, the use of the DTGS detector eliminates the need to transport dewars of liquid nitrogen in and out of this area. Operation of the system is quite simple. After collecting a reference spectrum, no additional input is required by the operator. The signal to start the sampling sequence comes from the GSS computer, spectral filenames are assigned by date and time, and the PLS analysis results are sent to the printer. Total analysis times, including a second spectrum of the diluted sample, are on the order of 5-6 minutes. So far this system has proven to be reliable and the major efforts are now focused on collecting sufficient data to evaluate FTIR spectroscopy for VOC analysis. Included in this effort is refining and optimizing the quantitation algorithms.

Comparison of spectral analysis methods by evaluation of detection limits. Direct comparison of the spectral analysis methods used in this work with those used elsewhere is difficult because of the number and kinds of components. However, the detection limit values estimated in these studies can be crudely compared to other previously published values. Detection limits for the CLS methods were calculated from the SEE values of 1000 computer generated spectra with 7.5×10^{-4} noise and randomly selected backgrounds applied over the spectral range from 500-3300 cm^{-1} These conditions were selected after viewing the spectra obtained from the functioning system installed at the WCA. Detection limits for the PLS methods were determined from 30 blank spectra collected on the system used to generate the new calibration spectra. Table II compares the detection limits estimated in this work with those extrapolated from the published in reference 6.

Overall, the detection limits for the CLS and PLS methods used in this work compare quite favorably with those extrapolated from previously published values[6] The detection limits in this work are somewhat higher than the extrapolated values, but this is to be expected because of the large numbers of components in the methods. Using CLS on the first derivative spectra obtained by applying a 5 point derivative smooth[7] is quite efficient in eliminating the various background components and identifying the analytes actually present, however, it also has a tendency to

dampen broad spectral features and therefore the method typically has poorer detection limits for analytes with broad spectral features.

Detection limits for the PLS and CLS methods are essentially the same for most components considering the differences in how they were determined. Some compounds do appear have somewhat higher detection limits using the PLS methods. This can likely be attributed to a combination of several factors including the fact that only two of the 70 spectra in the calibration set actually contained the analyte of interest and that only narrow spectral ranges (≤ 50 cm^{-1}) were used in the methods. The high detection limit for ethylbenzene using the PLS method is likely attributable to its poor absorptivity coefficients, spectral interferences from carbon dioxide and as many as 9 other VOC's in the window from 690-710 cm^{-1} Thirteen factors were required to describe ethylbenzene in its PLS method. The CLS detection limit for ethylbenzene is also among highest for that calculation method. In general, higher detection limits can be noted in the PLS methods for analytes requiring a larger number of factors to describe a relatively narrow spectral range (e.g. 25 cm^{-1}).

Evaluation of FTIR based VOC analysis system installed at the WCA. Long term evaluation of the FTIR methodologies for determining VOC's in waste drum head space will be the result of two major tests. Repeated analysis of a routine reference standard will be used to evaluate long term reproducibility and accuracy. FTIR analysis results of actual waste drum head space gases will be directly compared to replicate samples collected in SUMMA canisters and analyzed by the normal GC and GC/MS methods. Currently, no direct comparisons of the results from the GC methods to the FTIR results have been made because the GC analysis is still pending. Several analyses of the routine reference standard and of other standard mixtures have been made with the FTIR system.

Table III is a summary of the results from the repeated analysis of the routine reference standard over a period of several months. Precision is very good as relative standard deviations (RSDs) range from 2-16%. The PLS and CLS methods produce comparable results with the possible exception being for dichloromethane where the recovery is somewhat lower and the RSD is higher for the PLS method. There appears to be a significant bias as most of the compounds are recovered only in the 80-90% range. Methanol, however is only recovered at ~35% and methane is recovered at 93-95%. This reference gas mixture is a dry gas in a dry cylinder and must be transported through ~25 feet of tubing before it reaches any heated lines on the GSS. We believe that methanol is adsorbed onto polar sites on the walls of the tubing and manifold and that once adsorbed, it can help to reduce some of the remaining VOC's as well. Methane is very volatile and not likely to be affected by this recovery problem. SUMMA canister samples are often stabilized with water vapor to prevent this problem from occurring[8] In order to test this concept, the routine reference standard cylinder was replaced with a 6 L SUMMA canister pressurized to ~25 psig with a mix of 5 polar VOC's, including methanol, at ~100 ppmv. Water was added to this standard at up to 10000 ppmv. In this case methanol was recovered at 95-98% indicating that either the addition of water to the reference gas standard will be required or the additional transfer line from the reference gas cylinder to the GSS will need to be heated.

Examination of the data in Table I demonstrates that very rarely are there likely to be more than four or five VOC's in a waste drum sample. Analysis of FTIR spectra with such a small number

of analytes is done quite readily. If, however, a drum containing all or most of the potential analytes each at a relatively low concentration but totaling to a significant total VOC concentration, could the FTIR technique identify this situation. To answer this question, a mixture containing 28 of the 29 VOC's was prepared in a 6 L SUMMA with up to 10000 ppmv water. Concentrations ranged from 25-50 ppmv and were verified via the standard GC and GC/MS methods. The 6 L SUMMA was then connected to the GSS in place of the routine reference standard.

The FTIR analysis results of this mixture are presented in Table IV These results are quite encouraging since both PLS and CLS identified most of the compounds present. The PLS methods were able to identify ~80% of the compounds it should have detected. The CLS method identified ~90% of the compounds it should have seen. In this particular instance, the big difference between the CLS and PLS results is that many of the VOC concentrations were slightly closer to the detection limits for the PLS methods and may have caused some identification and/or quantitation problems for some of those analytes. For example, 1-butanol should have been present at ~54 ppmv and the PLS detection limits were slightly less than 53 ppmv, however poor recovery was also noted in the CLS method.

The results in Table IV also point out that some PLS methods may require additional method refinements. In particular, there appears to be a spectral artifact that the PLS methods for ethane and propane interpret as the analyte at significant concentrations. Spectral residuals are also high for these methods. Dichloromethane was not identified at nearly twice the detection limit and 2-butanone which uses a spectral region with significant interference from water is not detected at relatively low concentrations even though it is readily picked up by the CLS method. 2-Butanone is noted often in the spectra at concentration of 15-25 ppmv and is believed to be the result of some contamination of the GSS that occurred when sampling of the ambient air was being performed while some epoxy based paint was being applied at the WCA.

Also to be noted from Table IV is that methanol was recovered from this "wet" sample at >94%. Recovery of other polar VOC's is also good except for 1-butanol and 4-methyl-2-pentanone. These two compounds were also not recovered very well in the sample containing the five polar VOC's. For 4-methyl-2-pentanone, it appears that using the absorption bands in the 2750-3225 cm^{-1} as the primary quantitation region for this compound using CLS since the recovery is >90%. Similar improvements were not noted for 1-butanol possibly indicating that a transport problem still exists.

CONCLUSIONS

Even with the limited test data currently available, it appears that FTIR spectroscopy is a suitable and cost effective method with which to analyze TRU waste drum head space at-line at both the WCA and, in the near future, the DVF. Sampling and analysis can be completed within 5-6 minutes and the analysis results are immediately available. The PLS and CLS spectral analysis methods are very comparable although some refinement of both methodologies is still required. This The most significant errors in the analyses performed so far appear to be related to sample transport and not the analytical technique.

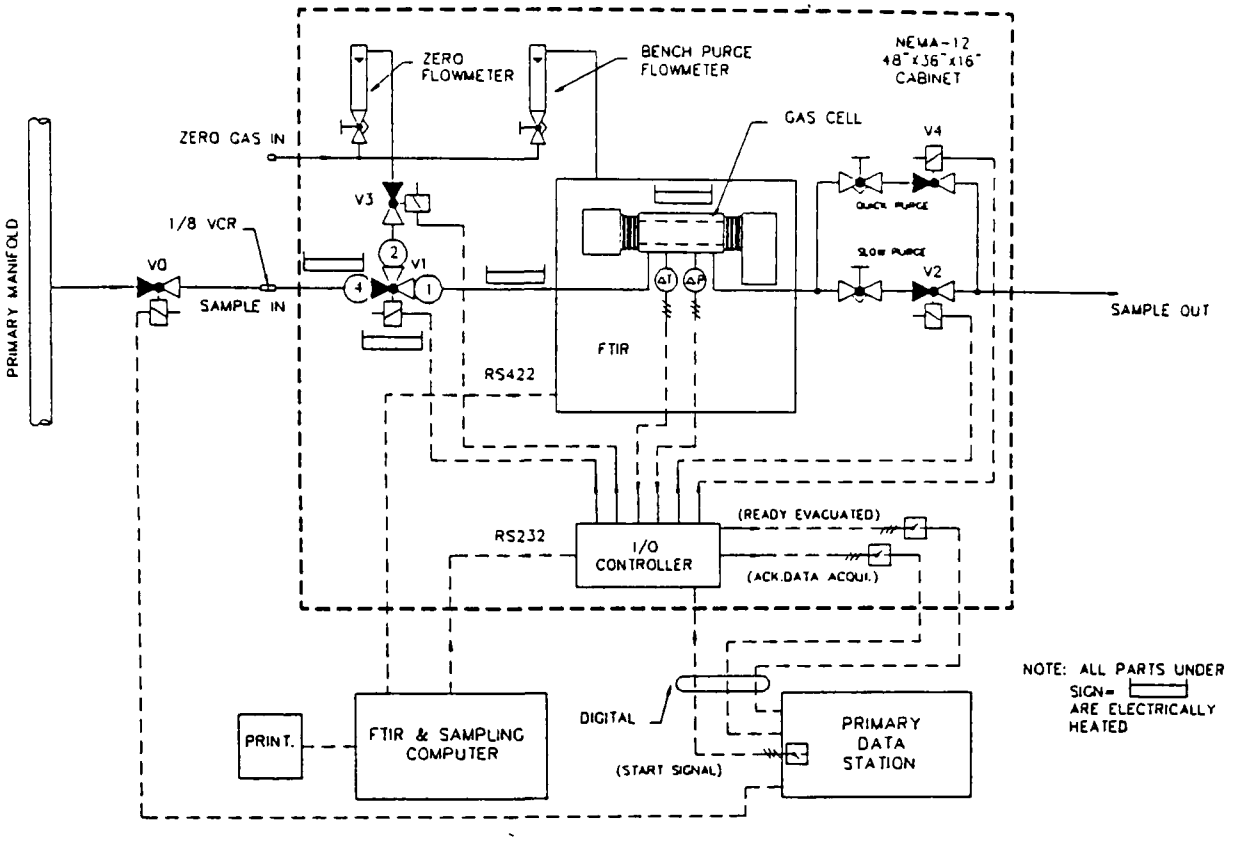


Figure 1. Schematic of FTIR based VOC analysis system.

Table I. Summary of data from previously sampled waste drums.

Compound	Occurrence Frequency %[a]	Maximum ppmv Vented Drum[a]	Maximum ppmv Unvented Drum[b]
1,1,1-Trichloroethane	87	1400	74800
Toluene	76	110	
Dichloromethane	59	72	7100
1,1-Dichloroethene	36	13	3000
Trichloroethene	29	540	1700
Methanol	17	670	
1,1-Dichloroethane	22	33	
Cyclohexane	<5	900	1700
Benzene	<10	2.6	
1,2-Dichloroethane	<10	10	
Freon 113	<10	900	104000
m-Xylene	<5	4.4	
p-Xylene	<5	4.4	
Carbon Tetrachloride	<10	6100	40900
1,3,5-Trimethylbenzene	<5	2.7	
Acetone	<15	460	
Bromoform	<5		
1-Butanol	<5		
2-Butanone	<10	7	
Chlorobenzene	<5		
Chloroform	<5	80	
cis-1,2-Dichloroethene	<5	10	
Ethyl Benzene	<5	1.9	
(di)Ethyl Ether	<5		
4-Methyl-2-Pentanone	<5	2.6	
1,1,2,2-Tetrachloroethane	<5		
Tetrachloroethene	<5	160	
1,2,4-Trimethylbenzene	<5	1.1	
o-Xylene	<5	1.9	
Interferences/additional compounds to consider and quantitate			
Water	100		
Carbon Dioxide	100	6430	273000
Methane	<65[b]		<68000
Ethane	<65[b]		<68000
Propane	<65[b]		<68000
Nitrogen Dioxide	<20[b]		264000

[a]Data acquired from ~93 previously vented drum and inner layers of confinement.
[b]Data from the head space of 210 sealed drums.

Table II. FTIR detection limits for VOC's in a 20 cm cell at a total pressure of 640 Torr.

Compound	Detection Limits at 20 cm (ppmv)			
	Hanst[a]	CLS-1[b]	CLS-2[c]	PLS[d]
Acetone	15.0	5.8	26.2	10.0
Benzene	2.3	4.2	3.5	3.4
Bromoform	7.5	4.9	6.5	9.2
1-Butanol		25.5	62.2	62.7
2-Butanone	11.3	20.2	76.8	4.0
Carbon Tetrachloride	0.8	1.7	2.3	1.6
Chlorobenzene	3.0	12.9	26.1	30.6
Chloroform	1.9	2.1	3.5	7.4
Cyclohexane	1.9	2.3	3.7	2.7
cis-12-Dichloroethene	2.3	5.0	10.1	7.9
11-Dichloroethene		5.4	9.9	8.1
11-Dichloroethane	11.3	6.9	20.3	19.0
12-Dichloroethane	7.5	10.1	20.7	90.8
Diethyl Ether	3.8	4.5	7.6	9.4
Ethane	5.6	91.8	122.9	35.4
Ethylbenzene	15.0	47.3	66.7	114.4
Freon-113	2.3	1.5	4.1	5.9
Methane	7.5	9.8	13.0	11.8
Methanol	5.6	6.5	11.2	10.8
Dichloromethane	4.9	6.0	19.1	27.9
4-Methyl-2-Pentanone		15.4	44.5	22.4
Propane	3.8	16.3	25.7	26.5
1122-Tetrachloroethane		14.0	26.9	51.2
Tetrachloroethene	2.6	2.2	4.1	20.6
Toluene	7.5	12.5	18.2	10.4
111-Trichloroethane	1.9	3.4	6.7	10.5
Trichloroethene	5.3	3.3	11.6	6.2
124-Trimethylbenzene		24.3	35.2	15.3
135-Trimethylbenzene		16.8	23.8	15.9
m-Xylene	7.5	18.3	27.3	21.2
o-Xylene	3.8	9.8	17.6	20.4
p-Xylene	7.5	30.3	35.2	23.8

[a]Extrapolated from data presented in reference 6 for a 100 m path length with 10^{-4} noise.
[b]Calculated from the errors produced by the application of CLS to 1000 simulated spectra with 7.5×10^{-4} noise and random backgrounds.
[c]Calculated from the errors produced by the application of CLS to the first derivatives of 1000 simulated spectra with 7.5×10^{-4} noise and random backgrounds.
[d]Determined from the standard deviation resulting from the application of the PLS methods to 20 actual blank spectra.

Table III. Analysis results from the repeated determination over a 2 month period of a reference standard containing 9 VOC's and methane at ~100 ppmv. Dry gas was transferred through ~25 feet of unheated tubing.

	Concentrations (ppmv)		
Compound	True	PLS (n=9)	CLS (n=16)
Carbon Tetrachloride	96.3	81.6 ± 4.0	85.0 ± 3.0
11-Dichloroethene	98.9	85.3 ± 3.0	88.4 ± 4.8
11-Dichloroethane	96.9	90.9 ± 4.6	93.1 ± 8.3
Freon-113	95.5	84.9 ± 1.8	80.8 ± 1.8
Methane	99.5	93.2 ± 2.8	92.2 ± 2.5
Methanol	96.2	36.2 ± 9.0	38 ± 15
Dichloromethane	97.6	73.4 ± 9.1	84.6 ± 3.4
Toluene	96.7	70 ± 11	85 ± 12
111-Trichloroethane	97.3	89.3 ± 4.4	88.9 ± 3.4
Trichloroethene	100.3	80.7 ± 6.4	80.1 ± 6.7

Table IV. Analysis results from the determination of a prepared sample containing 28 VOC's. Sampled from SUMMA canister which also contained ~10000 ppmv water.

	Concentrations (ppmv)				
Compound	GC	PLS-Run 1	PLS-Run 2	CLS-Run 1	CLS-Run 2
Acetone	41.6	28.4	32.6	39.3	42.7
Benzene	35.0	42.0	33.5	35.5	35.4
Bromoform	43.0[a]	43.0	44.5	40.3	37.2
1-Butanol	53.9	< 52.6	< 52.7	22.1	32.0
2-Butanone	39.7	< 3.4[b]	< 3.4[b]	64.7[c]	63.2[c]
Carbon Tetrachloride	31.0	29.3	29.9	31.4	31.9
Chlorobenzene	37.0	< 25.7	< 25.8	55.7	50.7
Chloroform	35.0	33.7	36.0	33.8	34.9
Cyclohexane	30.0	25.5	27.4	26.2	26.4
cis-12-Dichloroethene	45.0	44.3	50.9	36.7	36.7
11-Dichloroethene	32.0	27.8	29.2	26.3	25.6
11-Dichloroethane	39.0	33.5	40.4	45.5	41.0
12-Dichloroethane	45.0	110.1	< 76.6	39.2	37.6
Diethyl Ether	35.0	26.1	24.3	33.2	34.7
Ethane		657.5[b]	727.9[b]	< 77.1	< 77.4
Ethylbenzene	34.0	< 96.0	< 96.4	< 39.7	< 39.9
Freon-113	27.0	26.2	27.3	26.4	26.9
Methane		< 9.9	< 9.9	< 8.2	< 8.3
Methanol	77.1	72.4	74.0	72.7	74.7
Dichloromethane	50.0	< 23.4	< 23.5	47.2	48.0
4-Methyl-2-Pentanone	28.2	< 18.8	< 26.6	< 12.9	< 13.0
Propane		397.6[b]	427.3[b]	< 13.7	< 13.7
1122-Tetrachloroethane	32.0	72.8	63.9	41.8	36.6
Tetrachloroethene	32.0	34.0	34.9	32.5	32.3
Toluene	36.0	48.3	52.6	53.4	43.1
111-Trichloroethane	34.0	28.8	30.1	33.7	35.6
Trichloroethene	40.0	43.1	49.3	40.0	39.1
124-Trimethylbenzene	32.0	< 12.8	< 12.9	24.2	< 20.5
135-Trimethylbenzene	28.0	46.0	42.4	42.0	34.2
m-Xylene	36.0	40.4	38.9	45.4	35.4
o-Xylene	37.0	58.8	54.1	21.8	21.8
p-Xylene		< 20.0	< 20.1	< 25.4	< 25.5

[a]Potential problems with the GC analysis may have resulted in a low number.
[b]High spectral residuals were noted.
[c]2-Butanone is often noted at low concentrations and is either due to an unknown spectral component or to residues remaining from prior painting activities in the area that may have contaminated the system.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Waste Management, under DOE Idaho Operations Contract DE-AC07-76ID01570.

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HANFORD ENVIRONMENTAL RESTORATION DATA VALIDATION PROCESS

M.R. Adams, Manager, Environmental Restoration Engineering, R. A. Bechtold, Principal Scientist, Westinghouse Hanford Company, Richland, Washington : K. M. Angelos, Senior Environmental Scientist, Golder Associates Inc., Redmond, Washington.

ABSTRACT

Detailed procedures for validation of chemical and radiochemical data are used to assure consistent application of validation principles and support a uniform database of quality environmental data. During application of these procedures it was determined that laboratory data packages were frequently missing certain types of documentation causing delays in meeting critical milestones in the completion of validation activities. A quality improvement team was assembled to address the problems caused by missing documentation and streamline the entire process. The result was the development of a separate data package verification procedure and revisions to the data validation procedures. This has resulted in a system whereby deficient data packages are immediately identified and corrected prior to validation and revised validation procedures which more closely match the common analytical reporting practices of laboratory service vendors.

INTRODUCTION

The Westinghouse Hanford Company (WHC) Environmental Restoration Engineering (ERE) data validation process is applied to laboratory analyses of environmental samples for Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) related cleanup activities. WHC is the U.S. Department of Energy's (DOE) Operations and Engineering Contractor for the Hanford Site. Under the Hanford Federal Facility Agreement and Consent Order, the U.S. Environmental Protection Agency (EPA), the Washington Department of Ecology, and DOE committed to comply with CERCLA, as well as the Resource Conservation and Recovery Act, and the State of Washington's Hazardous Waste Management Act. The ERE function of WHC is conducting CERCLA hazardous substance response investigations under this agreement which require that low-level and mixed waste samples (up to 100 mrem/h) data be received from laboratories within 75 days of collection (as annual average but not to exceed 90 days), validated within 21 days after receipt, and forwarded to the regulatory agencies within an additional 15 days. The tasks of managing sample collection and shipment to the laboratories, obtaining acceptable laboratory deliverables, and providing validated analytical results for decision making within prescribed time frames have been complex and challenging. To support informed decision making and proper expenditure of funds for environmental

cleanup, it is essential that data of known quantity and quality are obtained on a timely basis. Delays in any step can have a cascading effect on ERE programs, resulting in delays in meeting regulatory-imposed milestones for site restoration.

DATA VERIFICATION AND DATA PACKAGE COMPLETENESS

Traditionally, data package completeness checks and the verification of proper laboratory reporting have been conducted by data validation personnel. During prior application of data package completeness checks, the frequency of occurrence of missing pieces of documentation was holding up the completion of validation activities. To understand the reasons behind the missing data package items, a Pareto analysis was conducted of over 50 data package submittals that contained missing documentation (as identified by the validation procedures). Table I shows the results of a survey of volatile organic data packages. As shown in Table I, the highest number of incidences of missing documentation occurred with items that had been determined to be not essential for completion of key validation processes. Requests for these missing documentation items caused unnecessary delays in the completion of validation reports.

A quality improvement team was established with key members from ERE management, data managers at Hanford, data validators, and the analytical laboratories' personnel to address the problems caused by missing documentation and to streamline the entire process. As a result, a separate data package verification procedure was developed and implemented with the consensus of laboratories' personnel, data managers, and validation personnel on the technical content of data packages and the team provided a recommended approach. A diagram of the current verification-validation process being followed for environmental samples at the Hanford Site is shown in Fig. 1. Application of this new process has resulted in significant improvements in the delivery of complete data packages. The data verification process is finding significantly fewer deliverable omissions (a reduction of approximately 50%) resulting in an overall improvement in the timely completion of data validation activities.

Technical verification is the act of reviewing, inspecting, and checking analytical laboratory data packages by a page-by-page review to determine and document whether their contents conform to the specified package constituents required for data validation.

Personnel currently performing verification are required to be trained with a 40-hour technical training course. This course covers the identification of specific deliverables from the individual laboratories as well as the use of the verification forms and the processes for obtaining any missing information from that laboratory.

Individualized chemistry checklists were prepared for metals, semivolatiles, volatiles, pesticides/PCB, herbicides, and general/wet chemistry. Development of a "standardized" checklist for general chemistry parameters (Fig. 2) proved to be the most challenging due to the number and types of analytical methods used by the laboratories. The resulting solution was a subdivision by types of analytical techniques. The categories used currently are ion chromatography, colorimetric, gravimetric, ion selective electrode, titrimetric, infrared spectroscopy, and other. Checklists for radiochemistry were also prepared by subdivision according to the analytical technique. Individualized checklists were prepared for gas proportional counting, alpha spectroscopy, gamma spectroscopy, alpha-emitting isotopes by scintillation counting, radium-226 by radon emanation, liquid scintillation counting, uranium by fluorometry, uranium by kinetic phosphorimetry, and radioisotopes by inductively coupled plasma/mass spectroscopy (ICP/MS).

During technical verification, the verifier completes checklists for every type of analyte with each data package. Upon completion, the verifier prepares a daily verification summary and missing information report (Fig. 3) for both chemical and radiochemical data packages. This information is then compiled to track performance of the improved verification process.

DATA VALIDATION PROCESS

Data validation is a formal process of reviewing a body of analytical data against predefined criteria to assure the data are applicable for their intended use. The process of data validation consists of the following steps:

- Editing and correcting of reported results.
- Verifying compliance with quality assurance (QA) requirements.
- Checking quality control (QC) values against defined limits.
- Applying qualifiers to analytical results for the purpose of defining the limitations in the use of the reviewed data.

WHC ERE has developed detailed validation procedures for radiochemical (1) and chemical (2) analytical data validation, which are in use by all personnel validating data produced as a result of Hanford site CERCLA response and cleanup activities. These procedures have been developed based on EPA functional guidelines and standard laboratory reference methods. The chemical data validation procedures generally follow the EPA Contract Laboratory Program (CLP) protocols (3,4) and SW-846 (5) methodologies.

For the Hanford Environmental Cleanup Program, data validation is conducted using the WHC validation procedures in conjunction with the applicable project-specific work plans, QA project plans, analytical method references, and contractor laboratory statements of work. The final products consist of narrative reports, checklists, summary reports, and electronic data deliverables. A flow diagram of the data validation process used at the Hanford Site is given in Fig. 4.

As described under Data Verification and Data Package Completeness, in addition to the improvement of data package completeness, a new and streamlined radiochemical data validation procedure was prepared to improve the consistent application of validation principles to nonstandard radioanalytical data. The radiochemical procedures follow the EPA reference analytical methods and procedures developed at other DOE contractor operated sites (6). The procedure addresses the common requirements from radiochemical analyses, as well as those that are specific for validation of data from the radioanalytical methods for gross alpha/beta, strontium-90, alpha spectrometry, gamma spectroscopy, tritium, radium-226 by radon emanation, fluorometric uranium, phosphorimetric uranium and ICP/MS.

The key aspects of this procedure are summarized in Table II. For consistency, general validation control limits were established for key data quality indicators such that variations in analytical procedure between laboratories would not result in rejection of data sets as long as key QA requirements have been met. This procedure also addresses requirements for the transmittal of electronic data in a format that is compatible with the Hanford Environmental Information System (HEIS) database.

DATA VALIDATION DOCUMENTATION AND REPORTS

To provide a useful presentation of validation results without requiring the completion of complex forms and checklists and the preparation of extensive technical reports, a simple validation documentation and reporting format was developed. Simple checklists are filled out at the completion of validation of a single data package which may contain multiple analyses. These checklists are general enough to allow the combining of several types of analyses into one checklist for documentation purposes. Fig. 5 provides an example cover page for radiochemical analyses.

A simple reporting procedure is required in the latest revisions to the validation procedures. The reporting format requires the summary by the validator of the following key elements in a simple technical memorandum format:

- Introduction - identifying data package tracking number, samples, matrices and analyses validated and the laboratory performing the analysis.

- Summary of Data Quality - summarizing the results of precision, accuracy, result verification, detection limit compliance and completeness in terms of the percentage of valid measurements versus expected measurements

- Summary of Major Deficiencies - an itemized listing of the major QA/QC deficiencies identified during validation, which resulted in the rejection of sample data.

- Summary of Minor Deficiencies - an itemized listing of the minor QA/QC deficiencies identified during validation which resulted in qualification of sample data, which, though qualified may still be considered usable for decision making purposes.

ELECTRONIC DATA REPORTING

The HEIS database is accessible to various parties involved with environmental restoration at the Hanford Site, including state and federal (EPA) regulators. Recent improvements in the availability of electronic data summary software in use by laboratories and subsequent upgrades of the HEIS utility programs have enabled the easy transmittal of validated results and update of result qualifier flags within the HEIS database. A standardized format for reporting validated data in electronic format has been developed. This format known as the UPQUAL format enables the transmittal of changed or qualified data only into the HEIS database resulting in faster updating of results with fewer errors or omissions of necessary data. Table III provides the structure of the UPQUAL format. Validation personnel can be provided with the laboratory data in electronic format and can select only those results which require correction and qualification for inclusion in the UPQUAL file, which is then transmitted to the HEIS data managers for loading and verification. Future improvements to the system will include the automation of certain aspects of technical verification and data validation to further improve the timeliness, completeness and consistency of data validation activities.

SUMMARY

Providing quality, timely, and valid environmental data for informed decision making is essential for the successful completion of environmental restoration efforts at Hanford. This paper presents the iterative processes involved in analytical data package deliverable verification, the refinement of validation procedure requirements, and the development of detailed and standard yet consistent, streamlined approaches to the technical performance, documentation and reporting of these processes. As a

result, a significant improvement in the completion schedule for delivery of validated analytical data to site managers and regulatory authorities has been achieved.

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Figure 1. Data Validation Process Flow Diagram

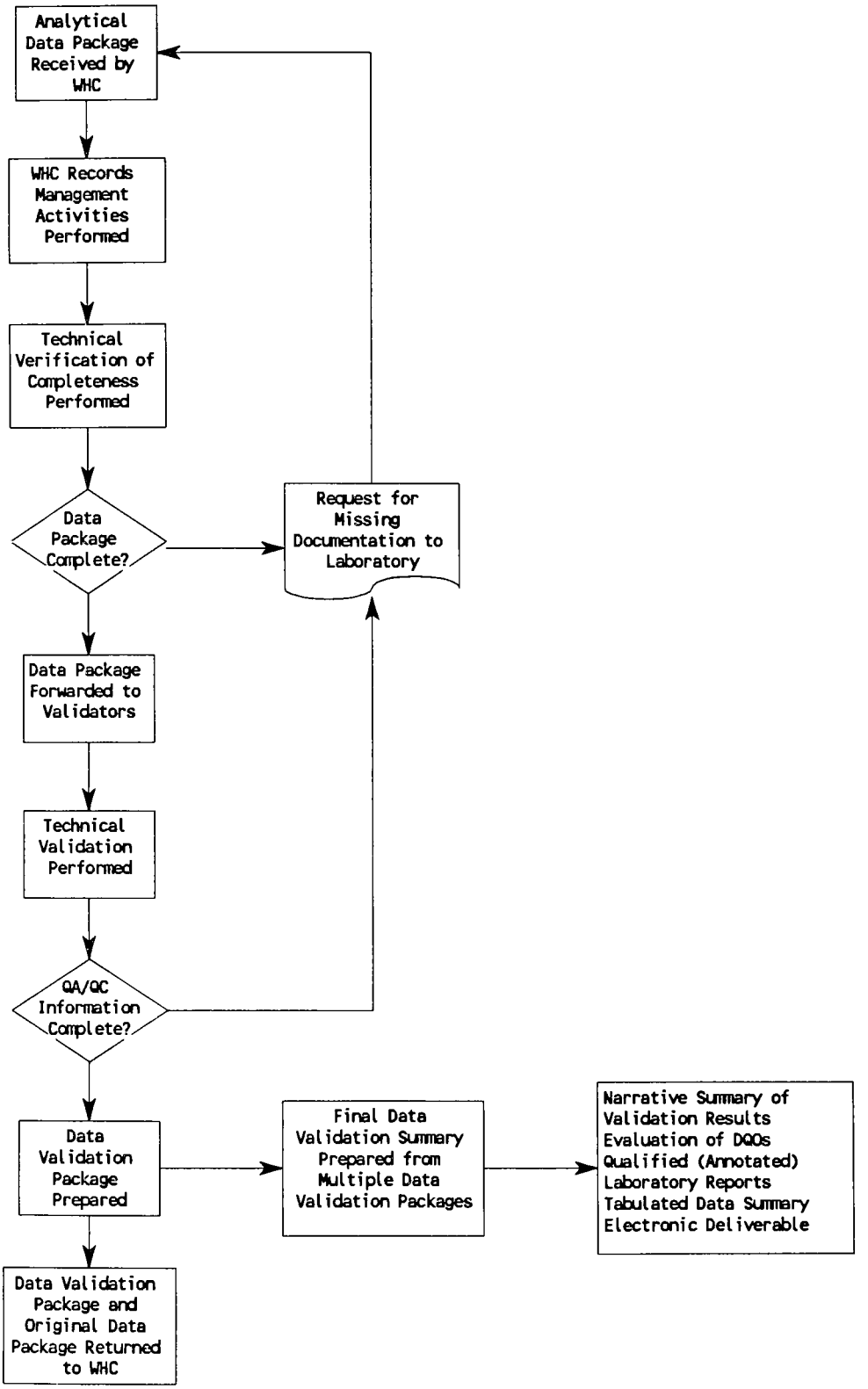


Figure 2. General Chemistry Data Verification Checklist.

Package ID:_____

GENERAL CHEMISTRY DATA VERIFICATION CHECKLIST - FORM A-7

Review the data package for completeness and check off the items below. If any data review elements are missing, contact the laboratory for submittal of the omitted data.

Data Package Item	Present?	Yes	No	N/A
☐ Anions by Ion Chromatography (Method 300.0)				
Sample Results		____	____	
Initial Calibration Data		____	____	
Continuing Calibration Verification		____	____	
Calibration Standard Concentrations		____	____	
Blank Analysis Data or Summary Report Forms		____	____	
Duplicate Sample Analysis Report Forms		____	____	
Spike Sample Recovery Data		____	____	
Laboratory Sample Control Data		____	____	____
Raw Data		____	____	
Analytical Sequence		____	____	
Ion Chromatograms		____	____	
Quantitation Report		____	____	
Additional Data				
Moisture/% Solids Data Sheets		____	____	____
Sample Preparation Sheets (Soils, Other only)		____	____	____
Colormetric (Note: Identify by Name, Analyte and EPA Method)_____				
_____				
_____				
☐ Sample Results		____	____	
Initial Calibration Data		____	____	
Continuing Calibration Verification		____	____	
Calibration Standard Concentrations		____	____	
Blank Analysis Data or Summary Report Forms		____	____	
Duplicate Sample Analysis Report Forms		____	____	
Spike Sample Recovery Data		____	____	
Laboratory Sample Control Data		____	____	____
Raw Data		____	____	
Analytical Sequence		____	____	
Laboratory Bench Sheets		____	____	
Chart Recorder Printouts		____	____	____
Additional Data				
Moisture/% Solids Data Sheets		____	____	____
Sample Preparation Sheets		____	____	____

GENNM092593-C

Figure 3. Daily Verification Summary and Missing Information Report.

Form-DVS-MIR-R
Revision 0, 1/18/93

Daily Verification Summary and Missing Information Report: Radchem (DVS-MIR-R) [a]

1 Verification BOA _____

Verifier _____

Date _____

2 Project(s) _____ or (OU) _____

Cognizant Engineer _____

3 Data packages verified this date (list by number or other identifier) | Analytical types contained in data packages (shade -in)

	Gas Count	Alpha-s	Gamma-s	Alpha-scint	Ra-226	LSC	Fluor. U	Laser U	ICP/MS
1 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
2 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
3 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
4 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
5 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
6 - _____	☐	☐	☐	☐	☐	☐	☐	☐	☐
Total _____	—	—	—	—	—	—	—	—	—

4 Data packages and analytical groups with missing information. (circle above)

Total _____ — — — — — — —

5 % Data packages and analytical groups with missing information $\left(\frac{\text{Total 4} \times 100}{\text{Total 3}}\right)$

% _____ — — — — — — —

6 Confirmation: Every data package item shaded in item 3 has checklist attached.

Verifiers initials _____

7 Confirmation: Every checklist for data package items circled above has been faxed to lab for 24 hour return of missing information to verifier.

Verifiers initials _____

8 _____
Verifier Signature

9 WHC Distribution, Per Current Distribution List

[a] Notes:
Do not file daily report on days you do not complete any verification.

MRA/M012193-A

Figure 4. Data Validation Flow Diagram

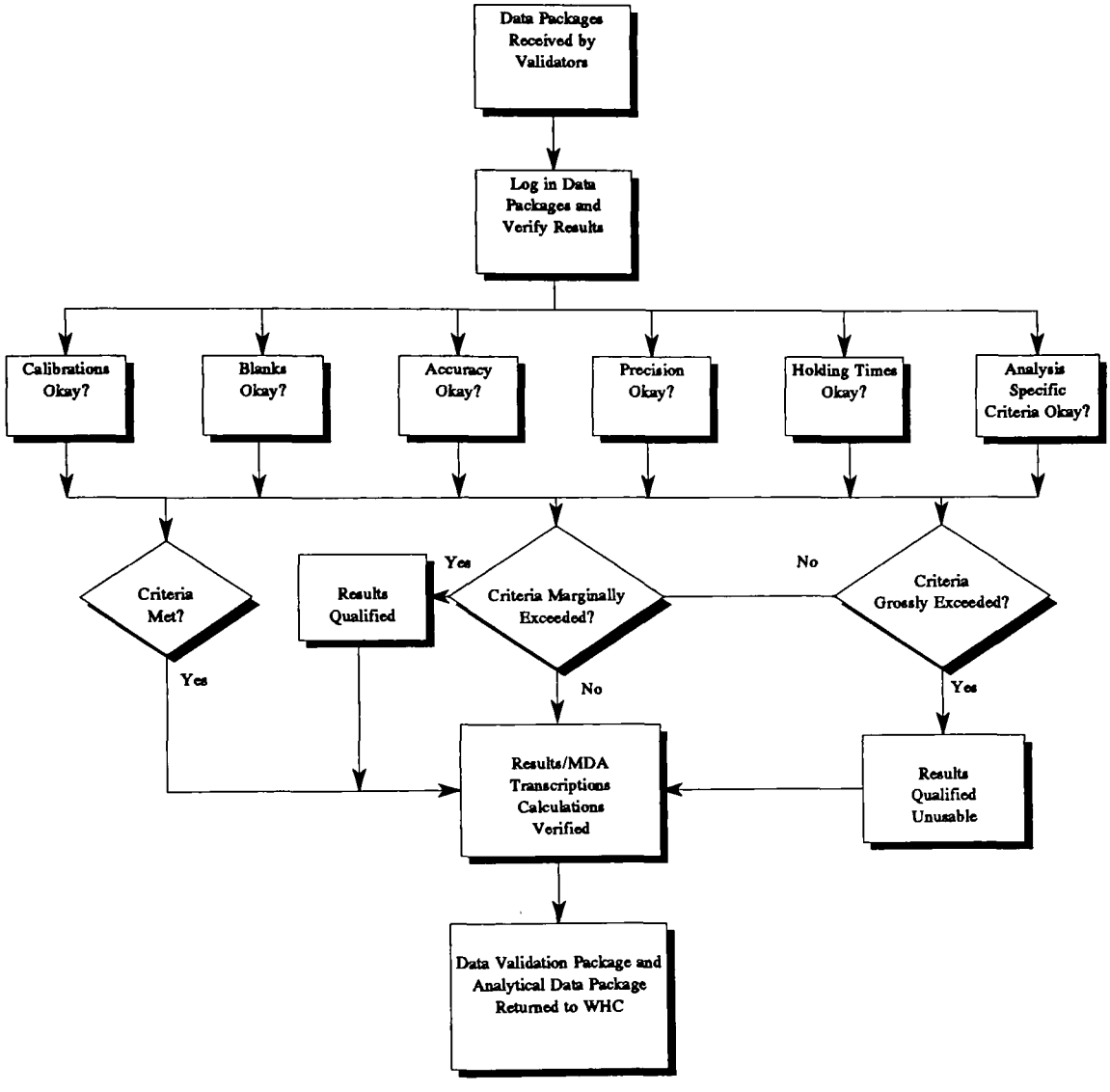


Figure 5. Radiochemical Data Validation Checklist.

Radiochemical Data Validation Checklist

(cover page)

VALIDATION LEVEL: A B C D E			
PROJECT:		DATA PACKAGE:	
VALIDATOR:		LAB:	DATE:
CASE:		SDG:	
ANALYSES PERFORMED			
☐ Gross Alpha/Beta	☐ Strontium-90	☐ Technetium-99	☐ Alpha Spectroscopy
☐ Gamma Spectroscopy	☐ Total Uranium	☐ Radium-226	☐ Tritium
☐	☐	☐	☐
SAMPLES/MATRIX			

1. Completeness ..... ☐ N/A

Technical verification forms present? ..... Yes No N/A

Comments: _____

2. Initial Calibration ..... ☐ N/A

Instruments/detectors calibrated within one year of sample analysis? ..... Yes No N/A

Initial calibration acceptable? ..... Yes No N/A

Standards NIST traceable? ..... Yes No N/A

Standards expired? ..... Yes No N/A

Comments: _____

GENM092593-B

Table I. Summary of Missing Volatile Organic Data Package Items*

Data Package Item	Number of Times Found Missing	Comments
Chemist Logbook Pages	48	Not essential
Reduction Formulae	47	Not essential
Instrument Time Logs	45	Not essential
Sample Preparation Sheets	15	Required Item
MS/MSD Report	13	Required Item
MS/MSD Forms	9	Required Item
Data Summary	9	Required Item
RIC and Quantitation Reports for MS/MSD	6	Required Item
Calculation data for TIC	5	Required Item
Moisture/Percent Solids Sheets	5	Required Item (matrix-dependent)
Internal Chain-of-Custody Forms	2	Not essential
Other Data	1	- - -

* A total of 50 data packages were evaluated.
MS/MSD = matrix spike/matrix spike duplicate.
RIC = reconstructed ion chromatogram.
TIC = tentatively identified compounds.

Table II. Summary of Radiochemical Data Validation Requirements.

Data Validation Item	Required Frequency of Performance by Laboratory	Validation Criteria
Initial demonstration of instrument calibration	Once for each project and at least annually. Documentation required on a periodic basis or whenever calibration is updated on an instrument specific basis.	Calibration must meet minimum performance criteria that are method specific. If criteria are not met or documentation is unavailable, all associated data must be rejected.
Calibration Checks	Each sample batch or weekly (for long count analyses)	The most recent calibration check must be within the laboratory-generated control limits or ± 3 standard deviations from the mean check value.
Background Checks	Each sample batch or weekly (for long count analyses)	The most recent background check must be within the laboratory-generated control limits or ± 3 standard deviations from the mean background value.
Method Blanks	One in 20 samples or each sample batch, whichever is more frequent	The method blank must contain less than the minimum detectable activities (MDA) of any target analyte. Sample results that are less than 10x the blank results must be qualified as undetected.
Laboratory Control Standards (LCS) or Blank Spikes	One in 20 samples or each sample batch, whichever is more frequent	LCS or blank spike results must be within the control limits of 50% to 150%. If exceeded, associated results must be rejected.
Chemical Recovery or Tracers or Matrix Spikes	Each sample, blank, LCS, blank spike, matrix spike and duplicate as applicable to the method of analysis	Recovery of chemical carrier or radioactive tracer must be within the control limits of 20 to 100% (115% for tracers). If exceeded, associated undetected results are rejected.
Laboratory Duplicates	One in 20 samples or each sample batch, whichever is more frequent	Relative percent difference between duplicate results or MDA values (if analyte undetected) must be ≤20% for water samples and ≤35% for solid samples.
Holding Times	Not applicable	All analytes with the exception of short half-life parameters must be analyzed within 180 days of collection. Short half-life parameters must be analyzed within five half-lives.
Sample Result Calculations	Not applicable, calculation formulae must be provided at least one time during project startup and when revision is made to analytical procedure	If calculation is required based on the specified level of data validation.
MDA	MDA must be reported for each sample and analyte	Sample aliquots must be at least large enough to meet the required detection limit or the MDA concentration must be less than or equal to the required detection limit.

Table III. UPQUAL Input File Format

Field Name	Column	Valid Values
Sample Number	1-12	HEIS Sample Number
Form Type	13-16	CLP - Contract Laboratory Program LAS - Laboratory Analysis System NCLP - Non-CLP
Form Number	17-19	1A, 1B, 1C, 1D, 1E, 1F, I, R, NA
Lab Code	20-25	Abbreviated Lab Code (assigned by WHC)
Constituent ID	26-35	Element Symbol, CAS Number, Element Symbol and Isotope Number
Media	36-38	BI = biota GW = groundwater SS = surface soil GS = geologic soil SW = surface water
Value Reported	39-48	constituent concentration
Qualifier	49-54	validated result qualifier
Counting Error	55-64	radionuclide result counting error
Analysis Units	65-72	reporting units for constituent (i.e. μg/L, μg/Kg, mg/L, mg/Kg, %, ppm, ppb, μmhos/cm^3, pCi/L, pCi/g)

GENERAL

CORROSITEX®, a New Solution for Determining Corrosivity of Products and Waste.

Virginia C. Gordon, Soheila Mirhashemi, and Rosalind Wei. InVitro International, 16632 Millikan Avenue, Irvine, CA 92714

ABSTRACT

A new *in vitro* method, CORROSITEX®, has been developed to determine the corrosive potential of chemicals, formulations and waste. This *in vitro* method assigns corrosive materials into United Nation(UN)Packing Groups I, II or III which is required by the U.S. Department of Transportation (DOT) as of October 1993.

Corrosivity has been defined in a variety of manners. The DOT, previous to issuing an administrative exemption for use of CORROSITEX (DOT E - 10904), defined corrosivity by the time it took for a substance cause tissue destruction on the backs of six albino rabbits (49 CFR 173 Appendix A)[1]. Consistent with UN Guidelines, Packing Groups were determined by the following time criteria:

Packing Group I:	Skin tissue destroyed after a 3 minute exposure
Packing Group II:	Skin tissue destroyed after a 60 minute exposure
Packing Group III:	Skin tissue destroyed after a 240 minute exposure
Noncorrosive:	No skin tissue destruction within 240 minutes

The Office of Solid Wastes, a part of the Environmental Protection Agency (EPA), currently defines corrosivity as a substance which has a pH of below 2.0 or above 12.50 (40 CFR §261.22)[2]. Substances with a pH above 2.0 or below 12.50 are considered to be noncorrosive under these guidelines.

Several limitations are inherent in both the DOT and EPA definitions. Specifically, *in vivo* rabbit tests show a significant variability from test to test. Reproducibility is a challenge and is caused by such factors as variable hair growth, age of the animal and lab-to-lab technique. The use of pH, on the other hand, is limited to aqueous solutions and cannot be used for solids. In addition, a study of *in vivo* corrosivity results and corresponding pH demonstrates very limited correlation in determining corrosive versus noncorrosive substances.

CORROSITEX, as an alternative to either methodology, is a precise test that determines not only corrosivity, but assigns UN Packing Groups as well. This *in vitro* assay consists of two compartments -- a Dermal Biobarrier and a Chemical Detection System (CDS). Test samples are placed on the Dermal Biobarrier. When the sample destroys or penetrates the Biobarrier, the sample is detected by the CDS which produces a simple color or other physical change. The time required to observe a color change is recorded and used to assign the Packing Group.

In a study of 85 commercially-available chemicals listed on the DOT Hazardous Materials Table (49 CFR 172.101), CORROSITEX assigned 80 to the same or safer Packing Group designated by the table. Additionally, inter-laboratory studies were also conducted using a number of these chemicals and resulted in a lab-to-lab reproducibility of about 95%. More than 4,000 substances have now been tested by CORROSITEX throughout a variety of industries including hazardous waste. These industries have found the new methodology to be accurate, easy-to-use and cost effective for determining corrosivity and the degree of corrosivity for both liquid (including non-aqueous) and solid test materials.

CORROSITEX is accepted by both the United States Department of Transportation and the Occupational Health and Safety Administration, as well as Canada, Germany and Switzerland, for defining biological corrosivity.

INTRODUCTION

In Vivo Corrosivity Testing

The Department of Transportation (DOT) uses an *in vivo* rabbit dermal test to evaluate the dermal corrosivity of substances. Corrosion is considered to have occurred if the substance in contact with the rabbit skin causes destruction or irreversible alteration of the tissue on at least two of six rabbits tested[1]. Tissue destruction is defined, at any of the readings, as ulceration or necrosis of the skin. Tissue destruction does not include merely sloughing of the epidermis, erythema, edema, or fissuring.

Assignment of Packing Groups for corrosive chemicals and formulations is based on the United Nations printed special recommendations for Class 8 or corrosive chemicals[3]. The distinctions among chemicals in Packing Groups I, II and III are as follows:

Packing Group I:	Skin tissue destroyed after a 3 minute exposure
Packing Group II:	Skin tissue destroyed after a 60 minute exposure
Packing Group III:	Skin tissue destroyed after a 240 minute exposure
Noncorrosive:	No skin tissue destruction within 240 minutes

This *in vivo* test method has inherent limitations which are reflected in the test protocol of requiring only two out of six rabbits to be positive in order to assign corrosivity. It is difficult to achieve reproducible results with this test. Such factors as variable hair growth, age of the animal, the time of year the test is run, and variations in lab-to-lab techniques, all add to the variability in test results. In addition tissue ulceration and necrosis are subjective measures.

Utilization of pH

EPA regulations (40 C.F.R. §261.22) define a substance to be corrosive if it " is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.50". One of the most important limitations of this definition is that there are many substances that have a pH greater than 2 or less than 12.5 that have been proven to be corrosive by *in vivo* testing. Figure 1 gives the pH value and the Packing Group assignment for 147 substances, as determined either by *in vivo* testing or as assigned by the Hazardous Materials Table found in 49 C.F.R. §172.10. Sixty-nine percent of the substances whose pH was greater than 2 or less than 12.5 were found to be corrosive. These would have been identified as noncorrosive using the EPA definition of corrosivity thereby creating a substantial risk to transporters, workers and the environment due to their misclassification. In addition, ten percent of the substances that did fall into a corrosive category, according to the EPA definition, were shown by *in vivo* experiments to be noncorrosive. This would mean that these substances would be treated as corrosives, even though they are not, thereby incurring additional paperwork and expenses that would not be required under a more accurate classification method. .

Not only do pH values not accurately predict whether a substance is corrosive or not, it is impossible to assign a Packing Group (PG) using a pH value. This would mean that severe, extremely harmful, corrosives would not be differentiated from mild, less harmful, substances. For fifty-two substances that had a pH of less than or equal to 2.0, four were assigned to PG I, thirty-five to PG II, eight to PG III, and five were found to be noncorrosive. The same was also true for the thirty substances whose pH was great than or equal to pH 12.5; two were assigned to PG I, fifteen to PG II, three to PG III and ten were found to be noncorrosive. Narrowing a pH range down does not help in the assignment of Packing Groups. In the pH range of 0 to 0.9, for each sample, substances were assigned to all three Packing Groups and two were even found to be noncorrosive. Clearly, pH cannot be used to distinguish between severely harmful, and less harmful substances.

Figure 1. Relationship Between pH and Packing Groups

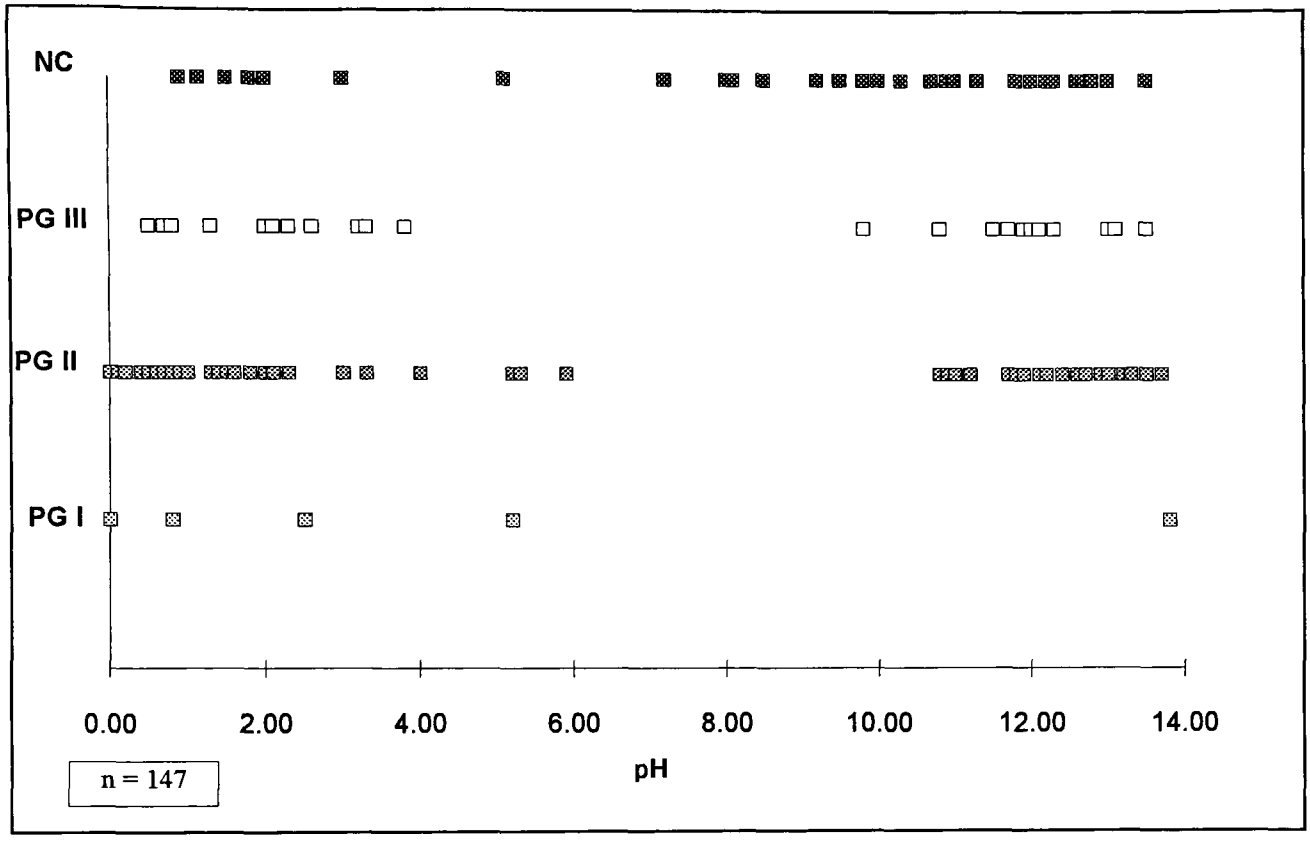


Table 1. Relationship between pH and Packing Group Assignment

#	Chemical	pH o 10 % Solution	Pkg Group DOT/In vivo
1	Fluorosulfonic acid	0.00	I
2	Nitric acid	0.00	I
3	Selenic acid	0.00	I
4	Trifluoroacetic acid	0.75	I
5	Benzyl chloroformate	2.54	I
6	Sulfur monochloride	5.20	I
7	COR 003	13.54	I
8	COR 001	13.56	I
9	Bromoacetyl bromide	0.00	II
10	Dichlorophenylphosphine	0.00	II
11	Phenyl trichlorosilane	0.00	II
12	Phosphorous pentachloride	0.00	II
13	Phosphorous tribromide	0.00	II
14	Sulfuric acid	0.00	II
15	Fumaryl chloride	0.05	II
16	Octyltrichlorosilane	0.10	II
17	Antimony trichloride	0.30	II
18	Hydrogen bromide (hydrobromic acid)	0.30	II
19	Mercaptoacetic acid	0.30	II
20	Octadecyltrichlorosilane	0.30	II
21	Antimony tribromide	0.35	II
22	Boron trifluoride-dihydrate	0.41	II
23	Valeryl chloride	0.45	II
24	Dichloroacetyl chloride	0.46	II
25	Dodecyl trichlorosilane	0.50	II
26	Hydrobenzene sulfonic acid	0.55	II
27	Dichloroacetic acid	0.64	II
28	Anisoyl chloride, ortho-	0.72	II
29	COR 014	0.72	II
30	Trichloroacetic acid	0.74	II
31	Iodine monochloride	0.75	II
32	Ammonium hydrogen sulfate	0.78	II
33	Potassium hydrogen sulfate	0.85	II
34	Phenylacetyl chloride	0.92	II
35	Boron trifluoride-acetic acid complex	0.95	II
36	Aluminum bromide, anhydrous	1.22	II
37	Fluoboric acid	1.30	II
38	Bromoacetic acid	1.41	II
39	Chloroacetic acid	1.44	II
40	Formic Acid	1.55	II
41	Sulfurous acid	1.78	II
42	Acetic anhydride	1.99	II
43	Acetyl bromide	2.00	II
44	Ferrous chloride tetrahydrate	2.05	II
45	Acrylic acid	2.07	II
46	Acetic acid, glacial	2.30	II
47	Dimethylcarbamyl chloride	2.31	II
48	Aluminum chloride	2.92	II
49	Trichlorotoluene	3.32	II
50	Chromium (III) fluoride	3.90	II
51	Sodium hydrogen fluoride	5.16	II
52	Ammonium hydrogen difluoride	5.22	II
53	Thiophosphoryl chloride	5.81	II

54	Dimethylbenzylamine, N,N-	10.70	II
55	COR 008	10.81	II
56	COR 036	11.00	II
57	COR 010	11.17	II
58	Dimethylcyclohexylamine 2,3-	11.79	II
59	Lithium hydroxide, monohydrate	11.80	II
60	Triethylenetetramine	11.91	II
61	Diethylenetriamine	12.01	II
62	Ethylenediamine	12.13	II
63	COR 037	12.20	II
64	Cyclohexylamine	12.34	II
65	COR 034	12.50	II
66	COR 033	12.60	II
67	COR 019	12.80	II
68	COR 011	12.85	II
69	COR 009	12.99	II
70	COR 007	13.19	II
71	COR 016	13.29	II
72	COR 002	13.34	II
73	COR 005	13.35	II
74	Tetramethylammonium hydroxide pentahydrate	13.61	II
75	COR 015	13.64	II
76	Sodium hydroxide, solid	13.81	II
77	Sodium hydroxide	13.81	II
78	COR 017	13.85	II
79	Potassium hydroxide	14.00	II
80	Cleaner 1	0.51	III
81	Sulfamic acid	0.65	III
82	Sodium hydrogen sulfate	0.75	III
83	Phosphoric acid	0.85	III
84	Maleic anhydride	1.05	III
85	Maleic acid	1.30	III
86	Cyanuric chloride	1.72	III
87	Benzene sulfonyl chloride	1.80	III
88	Butyric acid	2.15	III
89	Crotonic acid	2.30	III
90	Propionic acid	2.68	III
91	Copper (II) chloride	2.99	III
92	Ferric Chloride	3.00	III
93	Hexanoic acid	3.00	III
94	Butyric anhydride	3.08	III
95	Hydroxylamine sulfate	3.58	III
96	Dicyclohexylamine	9.57	III
97	Tributylamine	10.70	III
98	Aminoethoxy) ethanol, 2-(2-	11.30	III
99	Sodium hypochlorite w/ 5% chlorine	11.65	III
100	Piperazine, 1(2-AE)	11.78	III
101	Ethanolamine	11.82	III
102	Tetraethylenepentamine	11.85	III
103	Ethylhexylamine, 2-	11.98	III
104	Diaminopropane, 1,2-	12.06	III
105	Diethylaminopropylamine, 3-	12.17	III
106	COR 031	12.40	III
107	Cleaner 2	12.83	III
108	COR 020	12.90	III
109	COR 013	13.34	III
110	Oxalic acid, 10% (in 50% EtOH)	0.81	NC
111	Dichloroacetic acid, 3.1%	0.98	NC
112	Maleic acid, 3.8%	1.25	NC
113	Formic acid, 7%	1.70	NC
114	Citric acid, 14.6%	1.73	NC
115	COR 039	2.80	NC

116	Adamquat BZ 80	5.06	NC
117	COR 012	7.25	NC
118	J 0087	7.89	NC
119	J 0074	7.96	NC
120	J 0077	8.17	NC
121	J 0537	8.65	NC
122	Bowl cleaner, blue	9.07	NC
123	Bowl cleaner, green	9.16	NC
124	Diethylamine-3-propionitrile	9.40	NC
125	Heptanoic acid	9.80	NC
126	Triethanolamine, 100%	10.07	NC
127	Laundry detergent	10.48	NC
128	J 0097	10.51	NC
129	Window Cleaner 1	10.76	NC
130	Window Cleaner 2	10.79	NC
131	Dishwashing soap	10.87	NC
132	COR 018	11.16	NC
133	Butylamine, 7% (in EtOH/EG, 1:1)	11.80	NC
134	Diethylamine, 6%	12.01	NC
135	Cleaner 3	12.18	NC
136	COR 006	12.23	NC
137	Cleaner 4	12.26	NC
138	COR 032	12.50	NC
139	Pyrrolidine, 5.30%	12.53	NC
140	Calcium carbonate	12.56	NC
141	Cleaner 5	12.64	NC
142	Cleaner 6	12.67	NC
143	Cleaner 7	12.70	NC
144	Sodium hydroxide, 0.36%	12.74	NC
145	Cleaner 8	12.97	NC
146	COR 004	13.01	NC
147	Triethanolamine, 80%	13.35	NC

In Vitro Testing

Compared to *in vivo* methods, *in vitro* methods are quantitative and reproducible, overcoming two major scientific limitations of the *in vivo* methods. *In vitro* methods can screen multiple samples and concentrations quantitatively making them useful in all stages of the manufacturing and formulating process. These tools evaluate the safety of a product from its raw materials, through production and final safety evaluation. Therefore, *in vitro* methods are now the foundation of broader safety evaluation programs in many major industries. Today, some companies actually perform many more tests utilizing *in vitro* methods than prior to 1988 when they used *in vivo* methods.

CORROSITEX is a new, reliable, reproducible and cost-effective *in vitro* test method that accurately determines the corrosive potential of chemical formulations and waste.

MATERIALS AND METHODS

The CORROSITEX system consists of a pre-qualification test, a screening test, and a corrosivity classification assay. The steps used to develop a tiered CORROSITEX *in vitro* approach are straight forward (see Figure 3).

Figure 2. The CORROSITEX Test Method.

1. Evaluate test sample for compatibility with a prequalification test.
2. If the test sample is nonqualified in this *in vitro* method, test as described in 49 CFR 173.136.
3. If test sample is qualified, perform the Screening Test and assign Categories for test samples.
4. Evaluate test sample with CORROSITEX and assign Packing Group I, II, or III or Noncorrosive, based on test sample screening and time in CORROSITEX test.

Prequalification Test

Prior to performing the CORROSITEX test, the sample is pre-qualified to assure that the substance being tested is compatible with CORROSITEX. The sample is placed directly in a small amount of CDS fluid. If any detectable change occurs in the CDS, the sample is qualified and can be run in CORROSITEX.

Screening Test

After running in excess of 4,000 mixtures, pure chemicals and waste in CORROSITEX, it has been determined that behavioral differences exist between substances that are strong acids or bases and those that are weak acids or bases. Therefore, a screening test has been developed to distinguish between these categories.

Using this test, samples are classified into categories. Packing Groups are assigned according to category and the results from the CORROSITEX assay. Test samples are classified according to changes produced in two well-defined classification tests -- one designed to test for acids and another designed to test bases. The four different categories are defined as follows: (see Figure 3).

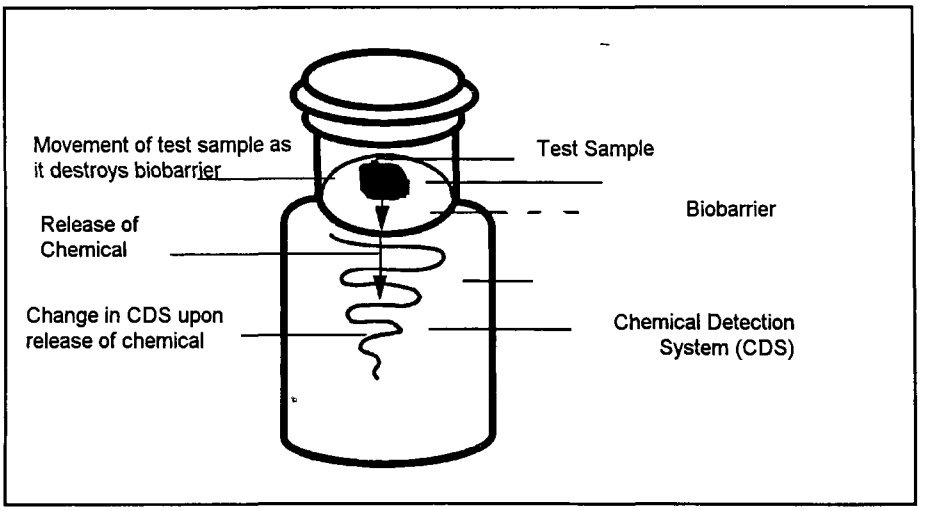
Figure 3. Categorization of Test Samples in Screening Test

- Category A_1 substances produce a distinct color change when they are added to the acid test.
- Category B_1 substances produce a distinct color change when they are added to the base test.
- Category A_2 substances produce little or no color changes when added to the acid test
- Category B_2 substances produce little or no color changes when added to the base test.

CORROSITEX Assay

CORROSITEX consists of two compartments — a Dermal Biobarrier and a Chemical Detection System (CDS). The dermal biobarrier has been developed using relevant target macromolecules. Test chemicals and formulations, including solids and liquids, are applied directly to the dermal biobarrier. (See Figure 4.) When the chemical destroys the full thickness of this biobarrier, it is detected by the CDS which produces a simple color change. This color change is visually observed and the time required for the color change to occur is recorded in order to assign a Packing Group. If no color change occurs, the chemical may be noncorrosive.

Figure 4. Biobarrier and Chemical Detection System of CORROSITEX



1. Dermal Biobarrier

The Dermal Biobarrier has been developed using specifically formulated solubilized proteins. This biobarrier is prepared by coating a support with a mixture of diluent and solubilized protein. The macromolecules are gelled onto a cellulose support within a circular disc delivery system. The biobarrier is then and stored at 4°C. The shelf life of the biobarrier is two weeks under these storage conditions. Prior to mixing with the diluent, the shelf life of the materials is two years. Mixing may take place in a laboratory setting or in the field.

2. Chemical Detection System

The Chemical Detection System (CDS) consists of multiple chemical detectors including specific ions, indicators and other detectors which have demonstrated responsiveness with numerous classes of chemicals. Examples of some of the Chemical and Product Classes identified by the CDS are given in Table 2. A simple, visually detectable color change of the CDS occurs when the biobarrier is altered or destroyed due to the chemical exposure. If no color change occurs, the sample is not compatible with the CORROSITEX assay.

Table 2. Chemical and Product Classes Identified by CORROSITEX Chemical Detection System.

primary alkyl amines	quaternary salts
secondary alkyl amines	polymers
tertiary alkylamines	biocides
alkylamine salts	insect powders
ethoxylates	pesticide classes
n-oxides	fertilizer classes
organic chemicals	propellants
oxidizing agents	metal working fluids
reducing agents	organophosphates
metal salts	fuel additives
halides	heavy duty cleaners
acids	window cleaners
bases	strippers
acid salts	light duty cleaners
acid esters	powdered cleaners
anhydrides	anionic surfactants
halogen derivatives	cationic surfactants
silanes	nonionic surfactants
organic solvents	amphoteric surfactants
formulated amines	surfactant blends
acrylates	mercaptans
sterols	hydrocarbons

3. Packing Group Assignments.

In the CORROSITEX system Packing Group assignments are made by taking into account the category that is assigned to a sample by the Screening test, and by the time it takes to detect a color change in the CDS.

Packing Group I, II or III are assigned to test samples from Category A_1 and B_1 which produce a detectable color change in the CDS between zero and three minutes, greater than 3 minutes to 60 minutes, or greater than 60 minutes to 240 minutes, respectively. If no color change occurs in 240 minutes, the chemical is classified as Noncorrosive (see Table 3).

Table 3. CORROSITEX Assignment of Corrosive Packing Groups for Category A_1 and B_1 Samples

Time (h:mm:ss)	Abbreviation	Classification
0:00:00 - 0:03:00	I	Corrosive Packing Group I
>0:03:00 - 1:00:00	II	Corrosive Packing Group II
>1:00:00 - 4:00:00	III	Corrosive Packing Group III
>4:00:00	NC	Noncorrosive

Packing Group I, II, or III is assigned to test samples from A_2 and B_2 which produce a detectable color change in the CDS between zero and three minutes, greater than 3 minutes to 30 minutes, or greater than 30 minutes to 45 minutes, respectively. If no color change occurs in 45 minutes, the chemical is classified as noncorrosive (see Table 4).

Table 4. CORROSITEX Assignment of Corrosive Packing Groups for Class A_2 and B_2 Samples

Time (h:mm:ss)	Abbreviation	Classification
0:00:00 - 0:03:00	I	Corrosive Packing Group I
>0:03:00 - 0:30:00	II	Corrosive Packing Group II
>0:30:00 - 0:45:00	III	Corrosive Packing Group III
>0:45:00	NC	Noncorrosive

RESULTS

In order to assure that CORROSITEX would give the same Packing Groups assignment to pure chemicals as the DOT Table 172.101, all commercially available corrosive chemicals listed on that table were tested in CORROSITEX. A summary of the results is presented in Table 5 and the details are given in Table 6. Corrosive classifications were assigned for the chemicals based on Tables 3 and 4. *In vivo* Packing Groups were obtained from industrial laboratories or the DOT Hazardous Materials Table 172.101 of CFR 49. When actual *in vivo* data was available, it was the preferential data used for comparison. Using the pre-screen test, CORROSITEX correctly distinguished 100% of the chemicals to be corrosive or noncorrosive and also assigned correct Packing Groups with 84% concordance, having 9 overestimates and 5 underestimates.

Table 5. Summary of the 85 DOT Corrosive Chemicals Study using New Categorization Test

	Number of Chemicals	New Study With Screening Test	Original Study Without Screening Test
Total Tested	85		
Correct Corrosive/Noncorrosive Classification (concordance)	85	100%	97.7%
Correct Packing Group assignment (concordance)	71	84%	79%
Higher Packing Group Assignment (overestimates)	9	10%	16%
Lower Packing Group Assignment (underestimates)	5	6%	5%

Table 6. Corrosive Chemicals of Hazardous Material Table (CFR 49. 172.101 U.S. Department of Transportation).

	71	84%
Overestimates	9	10%
Underestimates	5	6%

	Chemical	U.N. #	Chemical Class	Conc.	pH of 10%	CORROSITEX Time Mean	CORROSITEX Time Std	Cate-gory	Packing Group	DOT Table	*In Vivo* Group	Concordance
1	Benzyl Chloroformate	1739	acid ester	95%	2.54	> 4 hours		A_1	NC	I	NC	1
2	Fluorosulfonic Acid	1777	acid	Pure	0	0:00:13	0:00:02	A_1	I	I		1
3	Nitric Acid	2031	acid	90%	0	0:00:34	0:00:05	A_1	I	I		1
4	Selenic Acid	1905	acid	95%	0	0:01:41	0:00:07	A_1	I	I	I	1
5	Sulfur Monochloride	1828	halogen derivative	98%	5.2	0:05:54	0:00:28	A_1	II	I	I	under
6	Trifluoroacetic Acid	2699	acid	99%	0.75	0:04:30	0:00:12	A_1	II	I		under
7	Acetic Acid, Glacial	2789	acid	99+%	2.3	0:29:31	0:02:58	A_1	II	II		1
8	Acetic Anhydride	1715	anhydride	Pure	1.99	0:47:00	0:02:29	A_1	II	II		1
9	Acetyl Bromide	1716	halogen derivative	99%	~2.0	0:00:42	0:00:27	A_1	I	II		over
10	Acrylic Acid	2218	acid	99%	2.07	0:29:00	0:00:13	A_1	II	II		1
11	Aluminum Bromide, anhydrous	1725	metal salt	98+%	1.22	0:10:30	0:00:10	A_1	II	II		1
12	Aluminum Chloride	1726	metal salt	Pure	2.92	0:16:30	0:01:53	A_1	II	II		1
13	Ammonium Hydrogen Fluoride	1727	halogen derivative	98%	5.22	0:26:30	0:00:03	A_1	II	II		1
14	Ammonium Hydrogen Sulfate	2506	acid	neat	0.78	0:13:00	0:02:28	A_1	II	II		1
15	Anisoyl Chloride, ortho-	1729	halogen derivative	97%	0.72	0:10:20	0:00:19	A_1	II	II		1
16	Antimony Tribromide	NA 1549	metal halide	99%	0 35	0:22:00	0:00:07	A_1	II	II		1
17	Antimony Trichloride	1733	metal halide	100%	0.3	0:04:15	0:00:00	A_1	II	II		1
18	Boron Fluoride-dihydrate	2851	reducing agent	96%	0.41	0:01:15	0:00:07	A_1	I	II	I	1
19	Boron Trifluoride-acetic acid complex	1742	reducing agent	98%	0.95	0:03:34	0:00:13	A_1	II	II	II	1
20	Bromoacetic acid	1938	acid	99+%	1.41	0:09:30	0:00:31	A_1	II	II		1
21	Bromoacetyl bromide	2513	halogen derivative	98+%	0	0:02:05	0:00:08	A_1	I	II		over
22	Chloroacetic acid	1751	acid	99+%	1.44	0:04:30	0:01:49	A_1	II	II		1
23	Chromium (III) Fluoride	1756	metal salt	97%	3.9	3:00:00	0:15:00	A_2	NC	II	NC	1
24	Cyclohexylamine	2357	amine	99%	12.34	0:31:00	0:12:04	B_1	II	II	II	1
25	Dichloroacetic acid	1764	acid	99+%	0.64	0:08:00	0:01:12	A_1	II	II		1
26	Dichloroacetyl Chloride	1765	halogen derivative	99+%	0.46	0:05:00	0:01:01	A_1	II	II		1
27	Dichlorophenylphosphine	2798	acid	97%	0	0:02:00	0:00:04	A_1	I	II		over

	Chemical	U.N. #	Chemical Class	Conc.	pH of 10%	CORROSITEX Time Mean	CORROSITEX Time Std	Cate-gory	Packing Group	DOT Table	*In Vivo* Group	Concordance
28	Diethylene triamine	2079	amine	99%	12.01	0:34:00	0:00:22	B_1	II	II		1
29	Dimethylbenzylamine	2619	amine	99+%	10.7	1:27:00	0:00:00	B_2	NC	II	III	under
30	Dimethylcarbamyl Chloride	2262	halogen derivative	98%	2.31	0:17:00	0:00:18	A_2	II	II		1
31	Dimethylcyclohexylamine 2,3-	2264	amine	99+%	11.79	1:25:00	0:02:00	B_1	III	II	II	under
32	Dodecyl trichlorosilane	1771	silane	98%	0.5	0:11:35	0:00:09	A_1	II	II		1
33	Ethylenediamine	1604	amine	neat	12.13	0:19:00	0:00:30	B_1	II	II		1
34	Ferrous Chloride Tetrahydrate	NA 1759	metal salt	pure	2.05	0:35:00	0:10:00	A_2	III	II	III	1
35	Fluoboric Acid	1775	acid	48w+%	1.3	0:02:24	0:00:10	A_1	I	II	III	over
36	Formic Acid	1779	acid	96%	1.55	0:06:30	0:00:36	A_1	II	II		1
37	Fumaryl Chloride	1780	halogen derivative	95%	0.05	0:18:50	0:00:12	A_1	II	II		1
38	Hydrobenzene Sulfonic Acid	1803	acid	65w+%	0.55	0:13:00	0:00:35	A_1	II	II		1
39	Hydrogen Bromide	1788	acid	48%	0.3	0:02:39	0:00:18	A_1	I	II		over
40	Iodine Monochloride	1792	halogen derivative	98%	0.75	0:03:12	0:00:03	A_1	II	II		1
41	Lithium Hydroxide, Monohydrate	2680	base	98%	11.8	0:20:00	0:00:24	B_1	II	II		1
42	Mercaptoacetic Acid	1940	acid	97%	0.3	0:11:37	0:02:27	A_1	II	II		1
43	Octadecyltrichlorosilane	1800	silane	95%	0.3	0:17:00	0:00:18	A_1	II	II		1
44	Octyltrichlorosilane	1801	silane	97%	0.1	0:07:30	0:00:40	A_1	II	II		1
45	Phenyl acetyl chloride	2577	halogen derivative	98%	0.92	0:13:20	0:00:31	A_1	II	II		1
46	Phenyl trichlorosilane	1804	halogen derivative	98%	0	0:07:00	0:00:18	A_1	II	II		1
47	Phosphorus pentachloride	1806	halogen derivative	98%	0	0:00:18	0:00:01	A_1	I	II	I	1
48	Phosphorus tribromide	1808	halogen derivative	97%	0	0:01:00	0:00:11	A_1	I	II	I	1
49	Potassium Hydrogen Sulfate	2509	salt	35-37%	0.85	0:21:00	0:00:16	A_1	II	II		1
50	Potassium Hydroxide	1813	base	Pellets	14	0:06:50	0:00:05	B_1	II	II		1
51	Sodium Hydrogen Fluoride	2439	halogen derivative	99%	5.16	1:36:00	0:00:00	A_2	NC	II	NC	1
52	Sodium Hydroxide, solid	1823	base	Pellets	13.81	0:12:00	0:02:00	B_1	II	II		1
53	Sulfuric Acid	1830	acid	100%	0	0:01:30	0:00:04	A_1	I	II	I	1
54	Sulfurous Acid	1833	acid	neat	1.78	0:18:00	0:03:24	A_1	II	II		1
55	Tetramethylammonium hydroxide pentahydrate	1835	base	99%	13.61	0:11:30	0:00:45	B_1	II	II		1
56	Thiophosphoryl Chloride	1837	halogen derivative	98%	5.81	0:10:08	0:00:23	A_1	II	II		1
57	Trichloroacetic acid	1839	acid	99+%	0.74	0:11:00	0:00:21	A_1	II	II		1
58	Trichlorotoluene	2226	solvent	99%	3.32	> 4 hours		A_2	NC	II	NC	1
59	Triethylene Tetramine	2259	amine	60%	11.91	0:49:00	0:01:19	B_1	II	II	II	1
60	Valeryl Chloride	2502	halogen derivative	98%	0.45	0:10:40	0:00:09	A_1	II	II		1
61	1(2-AE)piperazine	2815		99%	11.78	0:44:15	0:05:11	B_1	II	III	II	1

	Chemical	U.N. #	Chemical Class	Conc.	pH of 10%	CORROSITEX Time Mean	CORROSITEX Time Std	Cate-gory	Packing Group	DOT Table	*In Vivo* Group	Concordance
62	2,2-Amino ethoxyethanol	3055		98%	11.3	0:31:00	0:04:09	B_1	II	III	II	1
63	Benzene sulfonyl chloride	2225	halogen derivative	neat	1.8	3:30:00	0:14:22	A_1	III	III		1
64	Butyric Acid	2820	acid	99%	2.15	0:55:40	0:04:20	A_1	II	III	II	1
65	Butyric Anhydride	2739	anhydride	99.2%	3.08	2:30:00	0:02:35	A_1	III	III		1
66	Copper(II) Chloride	2802	metal salt	97%	2.99	0:42:41	0:06:20	A_1	III	III		1
67	Crotonic Acid	2823	acid	99+%	2.3	1:22:25	0:00:00	A_1	III	III		1
68	Cyanuric Chloride	2670	halogen derivative	99%	1.72	3:40:00	0:04:05	A_1	III	III		1
69	Diaminopropane	2258	solvent	99+%	12.06	0:21:36	0:00:14	B_1	II	III	I	under
70	Dicyclohexylamine	2565	amine	99%	9.57	3:30:00	0:02:17	B_1	III	III		1
71	Diethylaminopropylamine	2684	amine	99+%	12.17	0:61:00	0:00:40	B_1	III	III		1
72	Ethanolamine	2491	amine	99+%	11.82	0:21:41	0:00:00	B_1	II	III	II	1
73	Ethylhexylamine	2276	amine	98%	11.98	2:45:00	0:14:21	B_1	III	III		1
74	Ferric Chloride	1773	metal salt	98%	3	0:21:18	0:00:59	A_1	II	III	II	1
75	Hexanoic Acid	2829	acid	99.5%	3	2:29:00	0:15:00	A_1	III	III		1
76	Hydroxylamine Sulfate	2865	salt	97+%	3.58	3:30:00	0:00:00	A_1	III	III		1
77	Maleic Acid	NA 2215	acid	99%	1.3	0:15:33	0:00:00	A_1	II	III		over
78	Maleic Anhydride	2215	anhydride	99%	1.05	0:34:34	0:02:19	A_1	II	III		over
79	Phosphoric Acid	1805	acid	85%	0.85	0:15:00	0:00:57	A_1	II	III	II	1
80	Propionic Acid	1848	acid	99+%	2.68	0:41:00	0:05:15	A_1	II	III	II	1
81	Sodium Hydrogen Sulfate	1821	acid salt	pure	0.75	0:14:04	0:01:06	A_1	II	III		over
82	Sodium Hypochlorite w / 5% available chlorine	1791	oxidizer	5% Cl	11.65	> 4 hours		B_2	NC	III	NC	1
83	Sulfamic Acid	2967	acid	99+%	0.65	0:20:55	0:01:14	A_1	II	III		over
84	Tetraethylenepentamine	2320	amine	neat	11.85	1:01:00	0:00:00	B_1	III	III		1
85	Tributylamine	2542	amine	99+%	10.7	> 4 hours		B_2	NC	III	NC	1

In the studies indicated below, addition, 776 samples were analyzed in the CORROSITEX system. A summary of the data is presented in Table 7. The samples include dilutions of pure chemicals, petrochemicals, surfactants, industrial cleaners, waste, etc. Excellent concordance to *in vivo* data was observed.

Table 7. Summary of CORROSITEX Results with 776 Test Materials

	Study	Number of Samples	No. of Qualified Samples with In Vivo Data	Concordance to In Vivo	% Under	% Over
1	General Industrial	104	58	88%	3%	9%
2	Pure Surfactants	63	34	97%	3%	0%
3	Mixtures and Dilutions	395	207	78%	6%	16%
4	ECVAM Prevalidation/ CL	50	50	87%	13%	0%
5	ECVAM Prevalidation/ IVI	50	35	83%	17%	0%
6	A French Industry	45	19	89%	11%	0%
7	A Swiss Industry	19	16	94%	0%	6%
8	European Union Reference Chemicals	50	47	89%	2%	8%

CONCLUSION

Traditional *in vivo* corrosivity testing has demonstrated a number of limitations. The *in vivo* rabbit test, previously prescribed by the DOT, lacks in accuracy, repeatability and humaneness. It is costly and time consuming to industry overall. These limitations, among others, prompted the DOT to issue an administrative exemption (DOT E-10904) for the use of CORROSITEX as an alternative to the rabbit test for assigning UN Packing Groups to corrosive materials. OSHA subsequently followed the DOT's lead and is now accepting CORROSITEX results for workplace safety.

In vitro methods, such as CORROSITEX, can be used for a wide variety of applications in a diverse number of industries. Large companies, such as Chemron, Aldrich, Westinghouse, Texas Instruments, and General Electric, are among more than 200 organizations using this new *in vitro* assay for products, formulations and/or hazardous waste characterization. The accuracy of the test has shown to be far greater for determining the corrosivity of substances compared to using either the *in vivo* or pH methodologies.

CORROSITEX is accepted by both the United States Department of Transportation and the Occupational Health and Safety Administration, as well as Canada, Germany and Switzerland, for defining biological corrosivity. InVitro International is currently in the process of working with other governmental agencies to gain acceptance for CORROSITEX as well as seeking an expansion of the current DOT exemption. These steps and acceptances will provide companies and others worldwide with the ability to more quickly, cost effectively, and humanely ensure public safety.

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REACTIVITY CHARACTERIZATION BY DIFFERENTIAL SCANNING CALORIMETRY

Marcela L. Siao, Chemist, Laboratory Services Division, and Joe H. Lowry, Senior Science Advisor, Laboratory Services Division, National Enforcement Investigations Center, US Environmental Protection Agency, Denver, CO 80225

ABSTRACT

Differential scanning calorimetry (DSC) was evaluated for the characterization of materials for RCRA reactivity. Substances with National Fire Protection Association (NFPA) reactivity ratings and actual waste specimens were analyzed for exothermic decomposition energy under a number of DSC experimental conditions. The results indicate that the exothermic decomposition energy observed with DSC using high pressure capsules and scanning to 400 °C is plausible as a regulatory method when combined with a threshold of 1000 Joules/gram of exothermic energy. The above conditions can discern some substances with NFPA reactivity ratings of 3 and 4.

INTRODUCTION

The evaluation of the thermal reaction hazard of wastes is of interest to the Agency. Presently, the Agency's hazardous waste regulations provide for the identification of RCRA reactivity characteristic wastes by addressing the thermal reaction hazard, but the regulations do not provide analytical methods or thresholds. Differential thermal analysis and differential scanning calorimetry are used in the chemical industry in quantitating heats of reaction and studying reaction kinetics as an important aspect of the safety of manufacturing, transporting, storing and processing chemicals. Standardization of thermoanalytical practices and methodology has been undertaken (1-7). Such standardization is a desirable for regulatory test methods. Adaptation of such methodology could fill the Agency's regulatory gap. To this end, Science Applications International Corporation in cooperation with Perkin Elmer produced a DSC method for use in reactivity characterization for the USEPA in 1992 (8). This method used 60 microliter stainless steel Vitron™ O-ring sealed capsules that withstand an internal pressure of 150 psi, collected the thermogram from 20 to 250 °C, and recommended a reactivity threshold limit of 1000 Joules/gram of exothermic energy.

The wording of the RCRA reactivity characteristic in the regulations is quite similar to that in the National Fire Protection Association (NFPA) code for reactivity (9). Given the RCRA ties to NFPA, a desirable characteristic of a method and a respective threshold for identifying wastes as thermal hazards, would be consistency with the NFPA reactivity rating. Moreover the method should provide quantitative data and be simple to conduct. The DSC method described below addresses these criteria and is a realistic option for regulatory testing for the RCRA characteristic of reactivity.

EXPERIMENTAL

Differential scanning calorimetry was performed on a Perkin Elmer DSC 7 thermal analysis system. The software supplied by the manufacturer was used for the analysis of DSC thermograms. Commercial samples of indium, tin and lead (99.999% purity) were used as calibration standards. The melting transitions of indium, tin and lead at 156.6, 231.9 and 327.4 °C have enthalpies of 28.4, 59.6 and 23.2 Joules/gram, respectively. Nitrogen was flushed through the DSC cell at the rate of about 80 mL/min. The heating block was cooled constantly with an ice bath. Stainless steel, Vitron™ O-Ring sealed capsules with a volume of 60 microliters that can withstand an internal pressure of 350 psi (24 atmospheres) were used for the preliminary studies where thermograms were scanned to 300 °C. Stainless steel, copper sealed capsules with a volume of 30 microliters that can withstand an internal pressure of 2175 psi (150 atmospheres) were used for experiments where thermograms were scanned to 400 °C. Evaluation of the two capsules is part of the study and is discussed below. Heating rates of 10 or 20 °C/min were employed.

RESULTS AND DISCUSSION

Sample Holders

The stainless steel, Vitron™ O-ring sealed capsules; stainless steel, copper sealed capsules; and glass capillaries have can withstand maximum temperatures of 300, 400, and 500 °C; pressures of 24, 150, and greater than 204 atmospheres; and have maximum volumes of 60, 30, and 4 microliters, respectively. The glass capillary system is reported to be able withstand greater than 204 atmospheres and possibly as high 680 atmospheres (10). In consideration of the volumes and pressure limitations of the capsules, and assuming all water molecules are in the gas phase, the maximum water volumes were calculated for each capsule at different temperatures and are given in Table 1.

Table 1 Sample Holder Water Capacity

Sample Holder	Holder Vol, uL	P, atms	Temp, °C	Water Vol, uL
SS Vitron O-ring	60	24	250	0.605
			300	0.551
SS Copper ring	30	150	250	1.89
			400	1.47
Glass Capillary	4	204	250	0.342
			400	0.266
			500	0.232
		680	250	1.14
			400	0.887
			500	0.772

As indicated by the calculated water sample size, all sample capsules have very limited sample capacity. The nominal sample size is about one milligram regardless of the capsule type. This very small sample size seems inadequate when considering the heterogeneity observed in most hazardous waste materials. However, it has been our experience, that most wastes encountered that are reactive are usually fairly pure substances or simple

mixtures and formulations. Thus limited sample size should not restrict this test with respect to ensuring a representative subsample.

The stainless steel, Vitron™ O-ring sealed capsules were found to be inadequate because of the temperature and pressure limitations. The thermal reaction energy produced by nitrocellulose could not be contained consistently, even at quite small sample sizes. Furthermore, the maximum temperature of 300 °C is not high enough to observe the thermal reaction energy of many compounds (11).

The glass capillary is capable of higher temperature and pressure, but has drawbacks, such as the smaller sample size compared to the stainless steel, copper sealed capsule. Moreover, two matched silver capillary sample holders must be fabricated and a minitorch with a liquid nitrogen cold finger must be assembled for sealing the glass capillaries. Furthermore, placement of the sample inside the tiny capillary may be tedious. The glass capillaries are, however, more suitable for handling volatile substances and are more inert than the stainless steel capsules. Corrosion by acids on the stainless steel may present a problem.

Of the two sample holders employed, the stainless steel, copper sealed capsules were the most rugged. They can be cleaned for repeated use while the Vitron™ O-ring capsules can not. Furthermore, they contained the most thermally reactive compounds tested even at sample weights as high five milligrams.

Inorganic Compounds

Table 2 presents DSC results and provides NFPA codings for some common inorganic chemicals. The decomposition energy of a functional group is not systematic (11). For example, ammonium nitrate and nickel nitrate had large exothermic decomposition energies while sodium nitrate and potassium nitrate did not. Some inorganic chemicals recognized as oxidizers show an exothermic decomposition, e.g. hypochlorites, chlorates, peroxides, perchlorates, and persulfates. Large exothermic decomposition energies are observed for salts of ammonium with oxygen containing acids, e.g. ammonium nitrate and ammonium perchlorate.

Table 2 DSC Thermal Reaction Energy for Some Inorganic Compounds

Substance	NFPA Code	Energy J/g	Substance	NFPA Code	Energy J/g
Perchloric Acid	3	-5660	Potassium Hydroxide	1	234
Hydroxylamine	3	-1030	Sodium Hydroxide	1	217
Ammonium Perchlorate	4	-3570	Ammonium Persulfate		-295
Potassium Perchlorate	1	-236	Potassium Persulfate		-352
Hydrogen Peroxide	3	-291	Ammonium Nitrate	3	-1590
Sodium Peroxide	1	-289	Nickel Nitrate		-1550
Calcium Hypochlorite	2	-419	Sodium Nitrate		167
Potassium Chlorate	1	-74	Potassium Nitrate		62

Ideally, a DSC based reactivity method and threshold should be able to discern zero coded compounds as non-reactive. With respect to the NFPA coding and basing reactivity characterization simply on the observation of exothermic decomposition energy, false positive identification would be obtained for ammonium persulfate, potassium persulfate, and nickel nitrate. False negatives would be obtained for potassium hydroxide and sodium hydroxide. In summary five of the sixteen inorganic compounds tested would be misclassified with respect to the NFPA coding system. A threshold limit of 1000 Joules/gram of exothermic energy would classify nickel nitrate as reactive and only four of the eleven reactive compounds would be classified correctly.

Organic Compounds

A large number of organic compounds are capable of exothermic decomposition. The DSC decomposition energies of 32 organic compounds or substances and their respective NFPA codings are given in Table 3. The relationship between functional group and exothermic decomposition is more systematic than for inorganic compounds (11). Relatively low energies were observed for some common "non-reactive" carbon, hydrogen and oxygen containing compounds, e.g. cellulose, cornstarch, glacactose, glucose, and pyruvic acid. Large energies were observed for many peroxides and nitro- containing compounds.

Table 3 DSC Thermal Reaction Energy for Some Organic Compounds

Substance	NFPA Code	Energy J/g	Substance	NFPA Code	Energy J/g
Cornstarch		-306	Nitroethane	3	-23
Cellulose		-166	Nitromethane	3	399
Galactose		-495	Propyl Nitrate	3	-495
Glucose		-406	Nitrocellulose	3	-1730
Pyruvic Acid		-535	p-Nitroaniline	3	-1850
Sucrose		298	2,4-Dinitroaniline	3	-912
Urea		252	3,4-Dinitroaniline	3	-1710
			2,4-Dinitrotoluene	3	-844
p-Nitrotoluene	0	188	o-Nitrotoluene	4	-1360
			m-Nitrotoluene	4	268
Ally Bromide	1	-710	Trinitrotoluene	4	-2540
Maleic Anhydride	1	-54	o-Dinitrobenzene	4	136
Benzyl Chloride	1	-148	1-Chloro-2,4-Dinitrobenzene	4	-56
Acetic Anhydride	1	-167	o-Nitrophenol	4	-3515
			p-Nitrophenol	4	-1834
Acrylic Acid	2	243	Dibenzoyl Peroxide	4	-1480
			t-Butyl Hydroperoxide	4	-800
			Cumene Hydroperoxide	4	-1040
			t-Butyl Peroxybenzoate	4	-1590

The wide range of energies observed for compounds with NFPA codings of greater than zero, precludes identification of all the compounds as reactive through these test results. Use of a threshold limit of 1000 Joules/gram of exothermic energy would classify only ten

of the twenty four "reactive" compounds properly, but no "non-reactives" would be misclassified.

It should be noted that the weighing of nitroethane, nitromethane, and propyl nitrate was quite difficult due to the volatility of these compounds and the energies are suspect.

Waste Specimens

Table 2 presents DSC results for five waste materials that had been determined to be reactive previously through constituent identification using variety of analytical instrumental techniques. Use of a threshold limit of 1000 Joules/gram of exothermic energy would classify these solid wastes as reactivity characteristic wastes. PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylenetrinitramine), and TNT (trinitrotoluene), "noninitiating" explosives, are interestingly considered relatively insensitive to heat (12). The rocket propellant was a mixture of potassium perchlorate with butyl rubber.

Table 2 DSC Thermal Reaction Energy for Some Wastes

Substance	Energy J/g
PETN	-1690
RDX	-3750
TNT	-2540
Rocket Propellant	-1300
Gunpowder	-3690

CONCLUSIONS

Many substances with NFPA codings greater than zero are not discernible from zero coded or uncoded substances by DSC thermal reaction energy. Some substances with NFPA reactivity codings of 3 or 4 have DSC thermal reaction energies greater than 1000 Joules/gram of exothermic energy. The exothermic decomposition energy observed with DSC using high pressure capsules and scanning to 400 °C is plausible as a regulatory method when combined with a threshold of 1000 Joules/gram of exothermic energy. This regulatory testing scheme would only identify some of the substances classified as thermal reaction hazards by the NFPA.

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Overview of NIST SRM Activities for Inorganic Environmental Studies

Jean S. Kane

Standard Reference Materials (SRMs) are used to assess the validity of analytical methods for environmental studies. This use assures that decisions regarding environmental contamination and hazards are based on data of demonstrable accuracy. The National Institute of Standards and Technology first began issuing environmental reference materials almost twenty years ago. Both the number of environmental SRMs available, and the number of units per year sold, have been continuously increasing ever since. This paper will review inorganic environmental SRM certifications completed in the last two years, and will also present those now in process, which should be completed in the near future.

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